Notes on statistical mechanics

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Contents

Preface . . . iii

1 Mechanics, probability, diffusion, chaos 1

1.1 Classical mechanics . . . 1
- 1.1.1 Generalised coordinates: Lagrange's equations . . . 2
- 1.1.2 The principle of least action . . . 3
- 1.1.3 Hamilton's equations . . . 4
- 1.1.4 Canonical transformations . . . 5
- 1.1.5 Perturbation theory . . . 6

1.2 Probability . . . 8
1.3 Fluid mechanics . . . 11
1.4 Brownian motion . . . 16
- 1.4.1 The Langevin equation . . . 17
- 1.4.2 Random walks . . . 18

1.5 Chaos . . . 19
- 1.5.1 Maps . . . 20
- 1.5.2 Circle maps . . . 23

1.6 Notes and references . . . 26
Exercises . . . 26

2 Stochastic processes 32

2.1 The Chapman–Kolmogorov equation . . . 32
2.2 The master equation . . . 34
2.3 The Fokker–Planck equation . . . 35
2.4 Stochastic differential equations . . . 36
- 2.4.1 Liouville's equation . . . 37
- 2.4.2 Ornstein–Uhlenbeck process . . . 38
- 2.4.3 The Itô–Stratonovich dilemma . . . 38

2.5 Notes and references . . . 38
Exercises . . . 38

3 Statistical mechanics 39

3.1 The Liouville equation . . . 39
- 3.1.1 The ergodic hypothesis . . . 41

3.2 The Boltzmann equation . . . 43
- 3.2.1 The collision integral . . . 45

- 3.2.2 Conservation laws . . . 51
- 3.2.3 Boltzmann's H–theorem . . . 54
- 3.2.4 The Chapman-Enskog method . . . 58
- 3.2.5 Viscosity and thermal conductivity . . . 64
- 3.2.6 The Maxwell slip boundary condition . . . 68
- 3.2.7 Dense gases . . . 68

3.3 Entropy and free energy . . . 68

3.4 Thermodynamic relations . . . 70

3.5 Classical statistical mechanics . . . 72
- 3.5.1 Chemical potential . . . 78
- 3.5.2 Ideal solutions . . . 81
- 3.5.3 Chemical reactions . . . 82
- 3.5.4 Osmotic pressure . . . 84
- 3.5.5 Polymer solution theory . . . 86

3.6 Phase change . . . 89
- 3.6.1 The virial expansion . . . 90
- 3.6.2 Condensation . . . 95
- 3.6.3 Surface energy . . . 101
- 3.6.4 The Clapeyron equation . . . 102
- 3.6.5 Alloys . . . 103
- 3.6.6 Nucleation and crystal growth . . . 104

3.7 Notes and references . . . 113
- 3.7.1 Boltzmann equation . . . 114
- 3.7.2 Chapman–Enskog method . . . 114
- 3.7.3 Chemical reaction rates . . . 115
- 3.7.4 Flory–Huggins theory . . . 115
- 3.7.5 Phase change . . . 115
- Exercises . . . 116

References **139**

Preface

These notes accompany the section C course on statistical mechanics, C5.3. The notes have been revised and updated since those used in 2016 (which in any case are longer visible on the re-vamped course web page). Some sections are incomplete, particularly chapter 2 whose material is only included for reference. Comments and reports of errors would be very welcome.

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Chapter 1

Mechanics, probability, diffusion, chaos

1.1 Classical mechanics

We consider a family of point particles of mass m (all the same, though this is not necessary). Particle position is denoted by $\mathbf{r}$, particle velocity is $\mathbf{v} = \dot{\mathbf{r}}$, momentum is $\mathbf{p} = m\mathbf{v}$, and then Newton's second law for an individual particle is

$$\dot{\mathbf{p}} = \mathbf{F}, \tag{1.1}$$

where $\mathbf{F}$ is the force acting on the particle.

Now suppose we have a finite number of particles, indexed by a suffix i. It is often the case in mechanical systems that additional forces $\mathbf{f}_i$, known as forces of constraint, exist in order to restrict the motion in some way: thus the corresponding form of Newton's law is

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{f}_i, \tag{1.2}$$

where $\mathbf{F}_i$ is the external force on particle i. An example of such restricted motion is the simple pendulum, in which the bob of the pendulum is constrained to move on the arc of a circle (or the surface of a sphere) by means of a tension exerted along the string or rod connected to the bob. In the absence of friction, it is notable that this tension does no work, and this observation leads us to the consideration of systems in which the constraint forces do no work, which, as we will see, allows us to formulate the equations of motion in terms of *generalised coordinates* which automatically accommodate the constraints.

D'Alembert's principle follows from the assumption that the 'constraining' forces $\mathbf{f}_i$ allow no work under a *virtual* displacement $\delta\mathbf{r}_i$, meaning that

$$\sum_i \mathbf{f}_i . \delta\mathbf{r}_i = 0. \tag{1.3}$$

A virtual displacement is distinguished from an actual displacement which might occur under the action of Newton's law, as it represents an externally imposed displacement. It is as if the particles are represented in their positions by flags on a map, and the virtual displacement occurs when the flags are moved by the observer. Specifically, $\delta\mathbf{r}_i \neq \mathbf{v}_i\,\delta t$.

The assumption of zero virtual work by the constraint forces leads to D'Alembert's principle:

$$\sum_i (\dot{\mathbf{p}}_i - \mathbf{F}_i).\delta\mathbf{r}_i = 0. \tag{1.4}$$

Note that although this is a consequence of Newton's second law, it is essentially equivalent to it, since it applies for *any* virtual displacement.

1.1.1 Generalised coordinates: Lagrange's equations

Most generally, cartesian coordinates may not be the most natural set of coordinates to use. For example, a simple pendulum swinging in three dimensions is most naturally described by spherical polar angle coordinates θ and ϕ, with the polar radius r being fixed; use of cartesian coordinates is possible but unwieldy. This observation leads to the idea of *generalised coordinates*, which we will denote as $\mathbf{q}$, and generally we will have $\mathbf{r} = \mathbf{r}(\mathbf{q}, t)$.

Now we wish to derive the form of Newton's equations in generalised coordinates, and to do this we repeatedly use the chain rule. Thus we have

$$\mathbf{v}_i = \frac{\partial\mathbf{r}_i}{\partial t} + \sum_k \dot{q}_k \frac{\partial\mathbf{r}_i}{\partial q_k} \tag{1.5}$$

(note that now $\mathbf{v} = \mathbf{v}(\mathbf{q}, \dot{\mathbf{q}}, t)$), and

$$\sum_i \mathbf{F}_i.\delta\mathbf{r}_i = \sum_k Q_k\,\delta q_k, \quad Q_k = \sum_i \mathbf{F}_i.\frac{\partial\mathbf{r}_i}{\partial q_k}, \tag{1.6}$$

and also (allowing for different mass of particles)

$$\sum_i \dot{\mathbf{p}}_i.\delta\mathbf{r}_i = \sum_{i,k} m_i\ddot{\mathbf{r}}_i.\frac{\partial\mathbf{r}_i}{\partial q_k}\delta q_k. \tag{1.7}$$

Taking the q_j and $\dot{q}_j$ derivatives of (1.5) and noting that $\dfrac{\partial\dot{q}_k}{\partial q_j} = \dfrac{\partial^2 q_k}{\partial q_j \partial t} = \dfrac{\partial}{\partial t}\delta_{jk} = 0$, we have

$$\begin{aligned} \frac{\partial\mathbf{v}_i}{\partial q_j} = \frac{\partial^2\mathbf{r}_i}{\partial q_j\partial t} + \frac{\partial}{\partial q_j}\sum_k \dot{q}_k\frac{\partial\mathbf{r}_i}{\partial q_k} = \frac{\partial^2\mathbf{r}_i}{\partial q_j\partial t} + \sum_k \dot{q}_k\frac{\partial^2\mathbf{r}_i}{\partial q_j\partial q_k} &= \frac{d}{dt}\left(\frac{\partial\mathbf{r}_i}{\partial q_j}\right), \\ \frac{\partial\mathbf{v}_i}{\partial\dot{q}_j} &= \frac{\partial\mathbf{r}_i}{\partial q_j}, \end{aligned} \tag{1.8}$$

and thus

$$\begin{aligned}\sum_i \dot{\mathbf{p}}_i.\delta\mathbf{r}_i &= \sum_{i,k} m_i\ddot{\mathbf{r}}_i.\frac{\partial\mathbf{r}_i}{\partial q_k}\delta q_k \\ &= \sum_{i,k}\left[\frac{d}{dt}\left(m_i\dot{\mathbf{r}}_i.\frac{\partial\mathbf{r}_i}{\partial q_k}\right) - m_i\dot{\mathbf{r}}_i.\frac{d}{dt}\left(\frac{\partial\mathbf{r}_i}{\partial q_k}\right)\right]\delta q_k \\ &= \sum_{i,k}\left[\frac{d}{dt}\left(m_i\mathbf{v}_i.\frac{\partial\mathbf{v}_i}{\partial\dot{q}_k}\right) - m_i\mathbf{v}_i.\frac{\partial\mathbf{v}_i}{\partial q_k}\right]\delta q_k \\ &= \sum_k\left[\frac{d}{dt}\left(\frac{\partial T}{\partial\dot{q}_k}\right) - \frac{\partial T}{\partial q_k}\right]\delta q_k, \qquad (1.9)\end{aligned}$$

where the kinetic energy T is defined as

$$T = \sum_i \tfrac{1}{2}m_i v_i^2. \qquad (1.10)$$

Comparing this with (1.6), we see that D'Alembert's principle implies that Newton's equation generalises to the form (since the generalised coordinates q_j are independent)

$$\frac{d}{dt}\left(\frac{\partial T}{\partial\dot{q}_j}\right) - \frac{\partial T}{\partial q_j} = Q_j. \qquad (1.11)$$

For the particular common case where the external force field is derived from a potential $V(\mathbf{r},t)$, which we may also consider to be a function of the generalised coordinates, $V = V(\mathbf{q},t)$, that is,

$$\mathbf{F}_i = -\boldsymbol{\nabla}_i V, \qquad (1.12)$$

where we write $\boldsymbol{\nabla}_i \equiv \boldsymbol{\nabla}_{\mathbf{r}_i}$, then also

$$Q_j = -\frac{\partial V}{\partial q_j}, \qquad (1.13)$$

and we obtain *Lagrange's equations*:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0, \qquad (1.14)$$

where we have defined the *Lagrangian*

$$L = T - V. \qquad (1.15)$$

1.1.2 The principle of least action

A variational principle, sometimes called the principle of least action, also forms the basis for Lagrange's equations. Define the *action*

$$I = \int_{t_1}^{t_2} L\,dt, \qquad (1.16)$$

and suppose that $\mathbf{q}$ ($= \mathbf{q}_1$ and $\mathbf{q}_2$) is specifed at the two endpoints. Hamilton's principle states that the trajectory which the generalised coordinates take in moving from ($\mathbf{q}_1$ to $\mathbf{q}_2$) is that which causes I to be stationary (and in fact a minimum).

To see this, we form the first variation

$$\delta I = \int_{t_1}^{t_2} \delta L \, dt = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) dt, \tag{1.17}$$

and after integrating by parts and using the boundary conditions, we find that a stationary value, $\delta I = 0$, is only obtained if (1.14) applies.

Hamilton's principle does not carry any useful physical meaning, in particular as it involves specification of boundary conditions in time, whereas in reality initial conditions are appropriate.

1.1.3 Hamilton's equations

A further very useful variant follows from defining, in an obvious way, the generalised momenta[1]

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \tag{1.18}$$

from which it follows that

$$\dot{p}_i = \frac{\partial L}{\partial q_i}. \tag{1.19}$$

Effectively we change the coordinates from q_i, $\dot{q}_i$ to q_i, p_i, and consider the *Hamiltonian*

$$H = \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i, t); \tag{1.20}$$

we think of H as a function of q_i, p_i and t. Under a virtual displacement, the incremental change of H is

$$dH = \sum_i \frac{\partial H}{\partial q_i} dq_i + \sum_i \frac{\partial H}{\partial p_i} dp_i + \frac{\partial H}{\partial t} dt; \tag{1.21}$$

equally, we have from (1.20), using (1.18),

$$dH = \sum_i \dot{q}_i \, dp_i - \sum_i \dot{p}_i \, dq_i - \frac{\partial L}{\partial t} dt; \tag{1.22}$$

consequently we obtain *Hamilton's equations*:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{1.23}$$

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[1] A confusion may arise here, as we have used two sets of subscripts, i for particle number, and k for component of $\mathbf{q}$, but we are going to use the single subscript i to cover both sets. That is, the i in (1.18) ranges over both particle number and vector components. Sometimes, we can avoid the ambiguity by writing, for example, $\mathbf{p}_i = \dfrac{\partial L}{\partial \dot{\mathbf{q}}_i}$, but we shall not be too fussy about this.

as well as

$$\frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}. \tag{1.24}$$

Note further that if $T(\dot{q}_i, q_i)$ is quadratic in $\dot{q}_i$ (the usual case) and V is independent of $\dot{q}_i$, then

$$H = T + V \tag{1.25}$$

is simply the energy of the system. In particular, the energy is conserved for autonomous systems, for which $\dfrac{\partial H}{\partial t} = 0$, so that trajectories reside on constant energy surfaces in the $(\mathbf{q}, \mathbf{p})$ phase space. Typically these surfaces are diffeomorphic to spherical surfaces.[2]

1.1.4 Canonical transformations

The type example of a Hamiltonian system is a (nonlinear) oscillator such as the equation

$$\ddot{x} + V'(x) = 0, \tag{1.26}$$

where V is the potential. The energy integral

$$E = \tfrac{1}{2}\dot{x}^2 + V(x) \tag{1.27}$$

suggests the definition of the Hamiltonian as

$$H = \tfrac{1}{2}p^2 + V(q), \tag{1.28}$$

and we can identify $x = q$, $\dot{x} = p$. The equation (1.26) is trivially solvable, since the first integral (1.27) enables the solution as a quadrature

$$t = \pm\frac{1}{\sqrt{2}}\int^x \frac{d\xi}{[E - V(\xi)]^{1/2}}, \tag{1.29}$$

but this is not very useful: which square root should we select, for example?

When V is convex ($V'' > 0$), the solutions oscillate, and a more natural set of coordinates other than q and p would be θ and I, which are more or less polar coordinates, and in which θ represents the angle of rotation and I the amplitude, typically some function of E. This idea underlies the concept of the canonical transformation, which seeks to find a change of coordinates from q and p to θ and I, such that the new Hamiltonian $H(\theta, I)$ retains the Hamiltonian structure, thus

$$\dot{\theta} = \frac{\partial H}{\partial I}, \quad \dot{I} = -\frac{\partial H}{\partial \theta}, \tag{1.30}$$

but such that in fact $H = H(I)$. In that case, $\dot{\theta} = \omega = H'(I)$ and I is constant, so that in a bounded system, we can interpret θ as an angle, and trajectories are circles. More generally, if $\mathbf{q}$ and $\mathbf{p}$ are n-dimensional, the same principle applies, but

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[2] For example, if T is quadratic and positive definite, and V is convex.

the solutions are the cartesian product of n circles, or n-tori. If the transformation to a Hamiltonian $K(\mathbf{I})$ can be made, then the system is said to be integrable.

How does one find a canonical transformation that preserves the Hamiltonian structure? First note that Hamilton's equations are equivalent to the variational principle in (1.17), and in view of (1.20), this is equivalent to

$$\delta\left\{\int_{t_1}^{t_2} p_i\,dq_i - H\,dt\right\} = 0. \tag{1.31}$$

Now let us define new generalised coordinates θ_i, I_i by means of a (generating) function $S(\mathbf{q},\mathbf{I})$, such that

$$p_i = \frac{\partial S}{\partial q_i}, \quad \theta_i = \frac{\partial S}{\partial I_i}; \tag{1.32}$$

it follows that if we define[3]

$$H\left(\mathbf{q}, \frac{\partial S}{\partial \mathbf{q}}\right) = K(I), \tag{1.33}$$

then

$$p_i\,dq_i - H\,dt = d[S - \theta_i I_i] + I_i\,d\theta_i - K\,dt, \tag{1.34}$$

and therefore in view of (1.31), the Hamiltonian structure is retained for $\boldsymbol{\theta}$ and $\mathbf{I}$, and Hamilton's equations imply

$$\boldsymbol{\theta}' = \boldsymbol{\omega} = \frac{\partial K}{\partial \mathbf{I}}, \tag{1.35}$$

while $\mathbf{I}$ is constant. The variables $\mathbf{I}$, $\boldsymbol{\theta}$ are called *action-angle variables*, and give the solution of this integrable system.

It seems some magic has occurred somewhere, but in fact all we have done is to replace one hard problem (solving $2n$ ordinary differential equations in (1.23)) by another (solving a first order partial differential equation for a function of $2n$ variables in (1.33)). There is not even any guarantee that a solution of (1.33) exists, since the system may not in fact be integrable.

1.1.5 Perturbation theory

A way to proceed is by *perturbation theory*. In this, we assume that there is an unperturbed Hamiltonian system with Hamiltonian $H_0(\mathbf{I})$, and that this is perturbed to

$$H = H_0(\mathbf{I}) + \varepsilon H_1(\boldsymbol{\theta}, \mathbf{I}), \tag{1.36}$$

where $\varepsilon \ll 1$, and we then seek a near-identity canonical transformation $\boldsymbol{\theta}, \mathbf{I} \to \boldsymbol{\phi}, \mathbf{J}$ determined through the generating function $S = \boldsymbol{\theta}.\mathbf{J} + \ldots$. Because $\boldsymbol{\theta}$ is a vector of angles (and thus periodic), we can write H_1 as a Fourier series, and S_1 can be explicitly determined. In principle, the procedure can be repeated.

A problem arises when the different components ω_{0i} of the underlying frequency vector $H_0'(\mathbf{I})$ are *resonant*, which occurs when $\mathbf{m}.\boldsymbol{\omega}_0 = 0$ for any vector $\mathbf{m}$ with

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[3] We are assuming that H is independent of t, but this assumption can be relaxed.

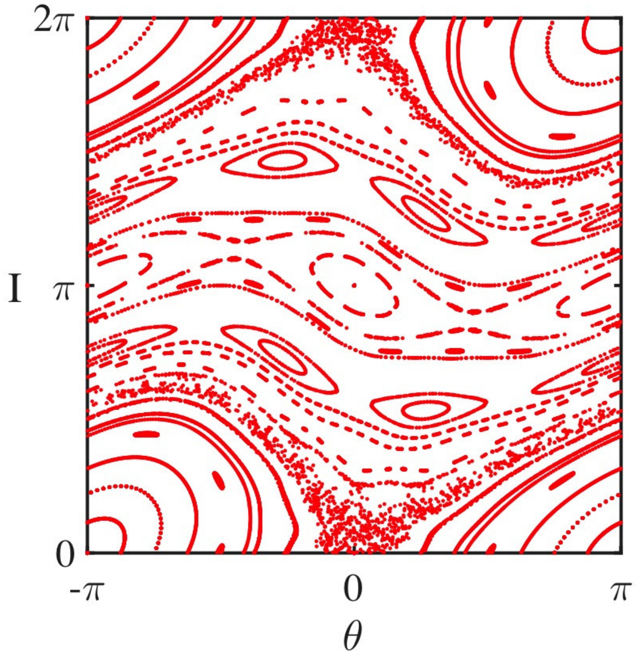

Figure 1.1: Standard map section: iterates of (1.37), for $K = 0.85$. The continuous sub-horizontal curves represent primitive invariant tori, the island chains are formed by resonance, and chaotic motion can be seen near the top and bottom of the figure. Figure courtesy of Mark McGuinness.

integer components. Resonance occurs sparsely but densely (like the distribution of the rationals in the reals), and the achievement of the celebrated KAM theorem (for Kolgomorov, Arn'old and Moser) is to show that despite this, most invariant tori are perturbed under the perturbation. On the other hand, resonance causes the break-up of tori into discrete chains of invariant loops, in whose vicinity *chaotic* behaviour can occur. Generally as ε increases, these chaotic regions take over the phase space.

Figure 1.1 shows an example of the break-up of invariant tori for a map called the *standard map*:

$$\begin{aligned} \theta_{n+1} &= \theta_n + I_{n+1}, \\ I_{n+1} &= I_n + K \sin \theta_n, \end{aligned} \tag{1.37}$$

here K is a parameter. One might wonder how this map relates to a Hamiltonian system. For a two degree of freedom near-integrable Hamiltonian, the phase space is four-dimensional, with two angle variables and two action variables; however, any given motion conserves the energy, which restricts the motion to a three-dimensional subspace with only one independent action variable, I say. An invariant torus thus correpsonds to motion on an actual two-torus (like a doughnut) with two angle variables θ and ϕ, and the action variable can be taken as measuring the radius. The dynamics of the motion can then be understood by selecting a Poincaré section at

$\phi = 0 \mod 2\pi$, say, and intersections of the trajectory with the section define a two-dimensional area-preserving Poincaré map on the plane, parameterised by the essentially polar coordinates I and θ; (1.37) is simply one artificial example of such a map.

1.2 Probability

Probability concerns the laws of chance and uncertainty, and carries with it an element of philosophy, lack of understanding of which is one cause of the public's lack of understanding of science. As for applied mathematics, the philosophy is easy to deal with, once one realises that the theory is not reality itself, but only a mirror, a representation, an image of reality. The statement, there is a 40% probability that it will rain in Oxford tomorrow, is not in itself very meaningful, although it can be made so with respect to ensemble predictions. The connection of probability with reality is through the law of large numbers, but probability theory is an abstraction, just as a mathematical model is.

Probability deals with a set of events, forming an event space or sample space E. To each event $a \in E$, we associate a number $P(a) \in [0,1]$, called the probability, which is additive, i. e., $P(a \cup b) = P(a) + P(b)$ for distinct events a and b, and

$$\sum_E P(a) = 1, \tag{1.38}$$

i. e., something happens. A probability of one indicates certainty, and of zero indicates impossibility. Roughly, we associate the actual value of the probability of a as being equal to the proportion of times a occurs in a (large) number of trials. More precisely, this is the law of large numbers, which we come to later. For example, in coin tossing, excluding the possibility of landing on its side, the event space consist of the two events h (heads) and t (tails), each of which has a probability of $\frac{1}{2}$, so that in a sequence of 1,000 trials, we would expect about half to be heads. This expectation is framed mathematically as a limit, where the number n of trials becomes very large; however, the likelihood of obtaining exactly $\frac{1}{2}n$ successes in n trials is not actually very large (and indeed tends to zero at large n).

The conditional probability (the probability of A given B, where now A and B are a possibly overlapping set of events) is defined following common sense as

$$P(A|B) = \frac{P(A \cap B)}{P(B)}, \tag{1.39}$$

and similarly two sets A and B are independent if

$$P(A \cap B) = P(A)P(B). \tag{1.40}$$

We next have the concept of a random variable, simply a variable X which takes values in E. Typically, we are interested in a succession of trials X_k, $k = 1, 2, \ldots$, and then $P(X_k = a) = P(a)$. Often we are interested in the total number of successes, i. e.,

$$S_n = \sum_1^n I(X_k), \tag{1.41}$$

where the indicator function satisfies

$$I(a) = 1; \qquad I(x) = 0, \quad x \neq a. \tag{1.42}$$

In some sense, we expect $\dfrac{S_n}{n} \to P(a)$ as $n \to \infty$, but the limit is a probabilistic limit, as explained below.

Random variables may be continuous, where a typical sample space would be $\mathbf{R}^m$, and in this case we define a *probability density function* $f(\mathbf{x})$, where $f(\mathbf{x})\,d\mathbf{x}$ is the probability of X being in a neighbourhood of $\mathbf{x}$ of volume $d\mathbf{x}$. For discrete random variables, the probability density is a sum of delta functions, and a typical sample space is $\mathbf{Z}$, which we use for illustration below. There are various named distributions, which can be found in any probability text. An important one is the normal distribution of mean μ and variance σ^2, written $N(\mu, \sigma^2)$, whose density is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]; \tag{1.43}$$

more on it below.

The mean of a probability distribution is the average value, or expectation, written variously as

$$\bar{X} = E(X) = \mu = \int_E x f(x)\,dx = \sum_E x P(X = x) \tag{1.44}$$

for continuous and discrete distributions, respectively. We also define higher moments[4] as

$$\overline{X^n} = E(X^n) = \int_E x^n f(x)\,dx = \sum_E x^n P(X = x), \tag{1.45}$$

and the variance is defined as

$$\sigma^2 = E[(X - \bar{X})^2] = E(X^2) - \mu^2; \tag{1.46}$$

it is a measure of the spread of the distribution about its mean, and its square root σ is called the standard deviation. Again, looking ahead, we can expect the way in which the average number of successes $\dfrac{S_n}{n}$ tends to μ to involve a non-zero standard deviation which, however, tends to zero at large n.

The *moment generating function* is defined as

$$G(s) = E(s^X), \tag{1.47}$$

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[4] By analogy with the moment exerted about the origin by a beam of density $f(x)$.

and is used mostly for discrete distributions, where (over $\mathbf{Z}$), it is just

$$G(s) = \sum_{\mathbf{Z}} p_n s^n, \tag{1.48}$$

where $p_n = P(X = n)$. As an example, consider the random walk on the integers (of which more later), where at each step j, there is a probability of $\frac{1}{2}$ of stepping left or right. Defining X as position and $p_{n,j} = P(X = n \text{ at step } j)$, we have the difference equation

$$p_{n,j} = \tfrac{1}{2} p_{n-1,j-1} + \tfrac{1}{2} p_{n+1,j-1}, \tag{1.49}$$

from which we derive the difference equation for the generating functions $G_j(s) = \sum_{\mathbf{Z}} p_{n,j} s^n$,

$$G_j = \tfrac{1}{2}\left(s + \frac{1}{s}\right) G_{j-1}, \tag{1.50}$$

with solution

$$G_j(s) = \left\{\tfrac{1}{2}\left(s + \frac{1}{s}\right)\right\}^j, \tag{1.51}$$

assuming a start at the origin.

For continuous distributions, it is more common to use the characteristic function, defined by

$$\phi(t) = E(e^{itX}) = \int_E f(x) e^{itx}\, dx, \tag{1.52}$$

which is just the Fourier transform of f (and so ϕ determines f uniquely through the inverse transform). As an example, the normal distribution $N(0,1)$ has characteristic function $\exp(-\frac{1}{2}t^2)$. Note that

$$\phi(t) = 1 + i\mu t - \tfrac{1}{2}(\sigma^2 + \mu^2)t^2 + \dots. \tag{1.53}$$

Now suppose a sequence of n trials are carried out, generating a sequence $\{X_k\}$ whose vales are independent and drawn from a distribution with mean μ and variance σ^2, and let $S_n = \sum_1^n X_i$. We define

$$U_n = \frac{S_n - n\mu}{\sigma\sqrt{n}}, \quad Y = \frac{X - \mu}{\sigma}, \tag{1.54}$$

so that $\phi_Y = 1 - \frac{1}{2}t^2 \dots$. The independence of the trials then shows that

$$\phi_{U_n}(t) = \left[\phi_Y\left(\frac{t}{\sqrt{n}}\right)\right]^n, \tag{1.55}$$

and from this it follows that $\phi_{U_n} \to e^{-\frac{1}{2}t^2}$ as $n \to \infty$. It follows that

$$\frac{S_n - n\mu}{\sigma\sqrt{n}} \overset{D}{\to} N(0,1) \quad \text{as} \quad n \to \infty, \tag{1.56}$$

meaning the distribution of S_n tends to a normal distribution[5] $N(\mu n, \sigma^2 n)$, *independently of the distribution of X*. This is the *central limit theorem*, of enormous use in statistics. It encompasses the *law of large numbers*, which states that

$$\frac{S_n}{n} \overset{D}{\to} \mu \text{ (or } \delta(x-\mu)) \quad \text{as} \quad n \to \infty, \tag{1.57}$$

and this is the underlying point connecting reality to theory, as it provides an experimental tool for estimating probability.

1.3 Fluid mechanics

The motion of a fluid is described by laws of conservation of mass, momentum and energy, and these provide equations for the variables of the motion, which are the density ρ, velocity $\mathbf{u}$ and temperature T, which is itself a measure of internal energy e. A further quantity, the pressure p, is determined by means of a constitutive law, which for example prescribes density as a function of pressure and temperature.

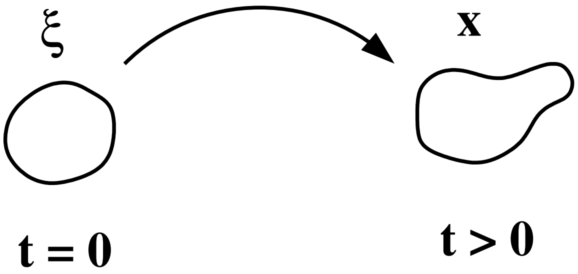

Figure 1.2: The map induced by the velocity field is assumed to be smooth.

We conceive of blobs of fluid, sometimes termed parcels, or fluid elements, moving around coherently, in such a way that a region $V(0)$ at time $t = 0$ is mapped smoothly to a region $V(t)$ at time $t > 0$. If $\boldsymbol{\xi}$ is the coordinate parameterisation of the element at time $t = 0$, then the map from $\boldsymbol{\xi}$ to $\mathbf{x}$ at time t is smooth, that is to say, $\mathbf{x}(\boldsymbol{\xi}, t)$ is a continuously differentiable function (see figure 1.2).

This is the *continuum assumption*, and as we shall see later, it is not one that is immediately reasonable. Providing we accept it, however, we can deduce appropriate governing equations more or less axiomatically.

First we need to define the *material derivative.* This distinguises time derivatives holding $\boldsymbol{\xi}$ fixed and holding $\mathbf{x}$ fixed. The *Lagrangian*, or material, time derivative, written $\dfrac{d}{dt}$, is related to the Eulerian time derivative $\dfrac{\partial}{\partial t}$ by the relation

$$\left.\frac{\partial}{\partial t}\right|_{\xi} \equiv \frac{d}{dt} = \left.\frac{\partial}{\partial t}\right|_{\mathbf{x}} + \mathbf{u}.\boldsymbol{\nabla}, \tag{1.58}$$

---

[5] More precisely, the probability distribution function $F(x) = \int_{-\infty}^{x} f(x)\,dx$ tends to the distribution function of the normal distribution; the actual discrete density is always actually a sum of delta functions.

which follows from the chain rule (here $\boldsymbol{\nabla} = \mathbf{e}_i \dfrac{\partial}{\partial x_i}$), and where the velocity field is

$$\mathbf{u} \equiv \left.\frac{\partial \mathbf{x}}{\partial t}\right|_{\xi}. \tag{1.59}$$

The material derivative is the time derivative following the fluid element.

We can derive an equation of conservation of mass in two ways. The straightforward way uses the usual volume integral conservation law. If V is a volume fixed in space, then from first principles, we have

$$\frac{d}{dt}\int_V \rho\, dV = -\int_{\partial V} \rho u_n\, dS, \tag{1.60}$$

where $u_n = \mathbf{u}.\mathbf{n}$ is the normal velocity at the surface ∂V. Taking the time derivative inside the integral, using the divergence theorem, and assuming ρ and $\mathbf{u}$ are continuously differentiable ($\in C^1$) leads us to the point form of the equation of mass conservation,

$$\rho_t + \boldsymbol{\nabla}.\,(\rho\mathbf{u}) = 0. \tag{1.61}$$

A useful alternative derivation uses the material derivative. Suppose now that $V(t)$ is a material volume element; in particular, its boundary ∂V always consists of the same fluid particles. Conservation of mass is simply

$$\frac{d}{dt}\int_V \rho\, dV = 0. \tag{1.62}$$

Now notice that dV changes in time; a first principles argument shows that

$$\frac{d(dV)}{dt} = \boldsymbol{\nabla}.\,\mathbf{u}\, dV, \tag{1.63}$$

and thus (1.62) implies, for ρ, $\mathbf{u} \in C^1$,

$$\frac{d\rho}{dt} + \rho\boldsymbol{\nabla}.\,\mathbf{u} = 0, \tag{1.64}$$

and this is readily seen to be equivalent to (1.61). A particular case of importance is that of the *incompressible* fluid, for which the density is conserved following the fluid, so that consequently

$$\boldsymbol{\nabla}.\mathbf{u} = 0. \tag{1.65}$$

Momentum conservation is an expression of Newton's second law. We will ignore body forces such as gravity. The only force acting on a fluid element is then that due to the surrounding fluid, and this acts on the surface ∂V of the element. We suppose that the force per unit area in the i component direction on a surface element dS with normal $\mathbf{n}$ is denoted σ_{in}. Consideration of the force balance (Newton's third law) on a tetrahedron, as shown in figure 1.3, implies that

$$\sigma_{in}\, dS = \sum_j \sigma_{ij} dS_j, \tag{1.66}$$

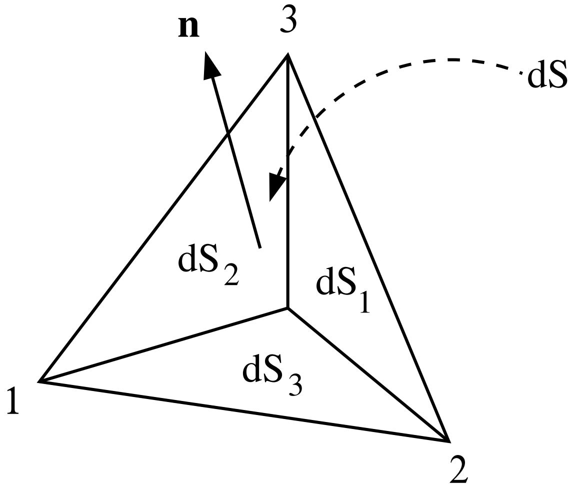

Figure 1.3: Force balance on a tetrahedron.

where dS_j is the face with normal in the j direction. Since additionally $dS_j = n_j\,dS$, where $\mathbf{n}$ is the normal to the oblique face dS, it follows that

$$\sigma_{ij} n_j = \sigma_{in}, \tag{1.67}$$

where, as is common in this subject, repeated suffixes indicates summation (the summation convention).

The elements σ_{ij} define a *tensor* $\boldsymbol{\sigma}$, which is a frame indifferent quantity just as a vector is, and with an obvious interpretation, (1.67) defines $\sigma_{in} = \boldsymbol{\sigma}.\mathbf{n}$, and Newton's second law takes the simple form

$$\frac{d}{dt}\int_V \rho \mathbf{u}\,dV = \int_{\partial V} \boldsymbol{\sigma}.\mathbf{n}\,dS, \tag{1.68}$$

where V is a material volume. The point form is derived in the usual way (noting that $\rho\,dV$ is constant):

$$\rho\frac{d\mathbf{u}}{dt} = \boldsymbol{\nabla}.\,\boldsymbol{\sigma}. \tag{1.69}$$

The issue now is to constitute the strss tensor $\boldsymbol{\sigma}$. Two particular choices are well known. The first is when $\boldsymbol{\sigma}$ is isotropic and the fluid is inviscid (frictionless):

$$\sigma_{ij} = -p\delta_{ij}, \tag{1.70}$$

where p is the pressure and δ_{ij} is the Kronecker delta; this leads to the Euler equation

$$\rho\frac{d\mathbf{u}}{dt} = -\boldsymbol{\nabla} p. \tag{1.71}$$

More realistically, the fluid is *viscous*, and the assumption of a *Newtonian* fluid, where the stress is linearly dependent on strain rate, leads to

$$\sigma_{ij} = -p\delta_{ij} + \tau_{ij}, \quad \tau_{ij} = \eta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \tfrac{2}{3}\boldsymbol{\nabla}.\,\mathbf{u}\,\delta_{ij}\right). \tag{1.72}$$

For the particular case of an *incompressible* fluid, for which $\boldsymbol{\nabla}.\,\mathbf{u}=0$, this leads to the common form of the Navier–Stokes equations:

$$\begin{aligned} \boldsymbol{\nabla}.\,\mathbf{u} &= 0, \\ \rho\frac{d\mathbf{u}}{dt} &= -\boldsymbol{\nabla}p+\eta\nabla^2\mathbf{u}; \end{aligned} \tag{1.73}$$

the quantity η is known as the (dynamic) viscosity. Note that we must interpret

$$\nabla^2\mathbf{u}=\boldsymbol{\nabla}\left(\boldsymbol{\nabla}.\,\mathbf{u}\right)-\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times\mathbf{u} \tag{1.74}$$

for coordinates other than cartesian.

The energy equation describes conservation of energy. Notice that in Newtonian particle mechanics, conservation of energy (where the forces are derived from a potential) is a consequence of Newton's second law. This is no longer true for fluid flow, and the reasons for this have to do with the nature of the continuum approximation, and will only emerge when we consider the statistical mechanics of particles.[6] Apart from the kinetic energy per unit mass, $\frac{1}{2}u^2$, there is an *internal* energy e, which is associated with the fluctuations of motion of the molecules of the fluid about the macroscopic mean velocity. Starting from an integral conservation law of kinetic and internal energy, we are led to the conservation law

$$\frac{\partial}{\partial t}\left[\tfrac{1}{2}\rho u^2+\rho e\right]+\boldsymbol{\nabla}.\left[\left(\tfrac{1}{2}\rho u^2+\rho e\right)\mathbf{u}\right]=\boldsymbol{\nabla}.\left[\boldsymbol{\sigma}.\mathbf{u}\right]-\boldsymbol{\nabla}.\,\mathbf{q}, \tag{1.75}$$

where the terms on the right represent the rate of work done on a volume element by the viscous forces, and the heat or internal energy flux $\mathbf{q}$, which in the present context arises phenomenologically due to spatial gradients of temperature or internal energy. Simplification of this using the Navier-Stokes equation leads to the form

$$\rho\frac{de}{dt}=\sigma_{ij}\dot{\varepsilon}_{ij}-\boldsymbol{\nabla}.\,\mathbf{q}, \tag{1.76}$$

where we use the summation convention on repeated indices. The kinetic energy pool feeds the internal energy pool through the first term on the right, which is called the viscous dissipation and is positive, while the second term representing heat transport provides a dissipative mechanism which spreads this created heat spatially. In practice (but not always) the frictional heating term is generally small, but heat conduction is commonly significant.

The vigour of a viscous flow is measured by a number called the Reynolds number, which is defined by

$$Re=\frac{\rho UL}{\eta}, \tag{1.77}$$

---

[6] Actually, the presence of the viscous term in the Navier-Stokes equation is a manifestation of the same feature, since the underlying equations of Newtonian mechanics possess no such dissipative terms. The transition from a microscopic conservative system to a macroscopic dissipative one is associated with a change from reversible to irreversible, and introduces a direction to the arrow of time, which provides one of the fundamental philosophical difficulties of statistical mechanics.

where U and L are typical sizes of velocity and size for the flow; for example, flow in a pipe is characterised by the mean velocity and the pipe diameter. When $Re < 1$, the flow is *slow*, and the acceleration terms are negligible; for values $Re \gg 1$, the flow is rapid, and viscous terms are negligible except in *boundary layers* adjoining solid surfaces. More importantly, when $Re \gtrsim 10^3$, the flow becomes disordered and chaotic; this is *turbulence*. One of the central problems of fluid mechanics is to understand the mechanism whereby turbulent flow occurs. It is generally thought that turbulence in fluids is a manifestation of chaos in the underlying governing (Navier-Stokes) equations, but little is known about chaos in partial differential equations, and the problem is not yet resolved.[7]

The practical modelling of turbulent flows uses a method of averaging, whereby the velocity and pressure fields are split into mean and fluctuation:

$$u_i = \bar{u}_i + u_i', \quad p = \bar{p} + p', \tag{1.78}$$

where overbar denotes mean and prime denotes fluctuation. The question arises, what sort of mean is defined here? A natural definition would be a local space average or a local time average, but these have the possible disadvantage of requiring a distinct separation of scales. A more natural choice is the *ensemble average*, which represents an average over many different realisations of the flow.

An issue now arises: since we are dealing with solutions of a partial differential equation with, it is hoped, a unique solution, how can one average over different realisations, given this uniqueness once the initial condition is prescribed. The resolution of this lies in the fact that the averaging procedure allows the same initial state for averaged quantities, although the small scale chaotic fluctuations can differ. The connection between ensemble, space and time averages lies in the hope that all three will be equivalent, which would be a consequence of the *ergodic theorem*, which essentially says that a single trajectory of a chaotic system on an invariant set in the phase space has the same probability of being in a region on this set as a large number of trajectories over a finite time; this equates ensemble averages to time averages; if the density is uniform over the set, it includes also space averages. The ergodic theorem is intuitive and reasonable, but it is an assumption, and in practice can not be generally proved.

Averaging of the Navier–Stokes equations leads to the Reynolds equations (for an incompressible flow):

$$\begin{aligned} \boldsymbol{\nabla} . \bar{\mathbf{u}} &= 0, \\ \rho \frac{d\bar{\mathbf{u}}}{dt} &= -\boldsymbol{\nabla}\bar{p} + \eta\nabla^2\bar{\mathbf{u}} + \boldsymbol{\nabla} . \boldsymbol{\tau}^{\mathrm{Re}}, \end{aligned} \tag{1.79}$$

where the *Reynolds stresses* $\boldsymbol{\tau}^{\mathrm{Re}}$ are defined by

$$\tau_{ij}^{\mathrm{Re}} = -\rho\overline{u_i' u_j'}. \tag{1.80}$$

---

[7] Indeed, even the existence of solutions of the equations is not certain, and the proof of existence or non-existence forms one of the Clay Institute's seven millennium prize questions (see `http://www.claymath.org/millennium/`).

Turbulence modelling in this way always has the problem of closure: the Reynolds stresses must be constituted, and a common simplistic assumption is to define an *eddy viscosity* η_T such that

$$\tau_{ij}^{\text{Re}} = \eta_T \left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i} \right). \tag{1.81}$$

In order of magnitude, $\eta_T \sim UL \gg \eta$, and is not realistically constant.

Higher order models can be obtained by averaging second moments of the momentum equation, to obtain equations for the Reynolds stress, which then involves closure by prescription of averages of third degree terms. This leads to the popular 'k–ε' models which have been used computationally. It is worth emphasising that, although common undergraduate courses deal largely with *laminar* (non-turbulent) flow, turbulence is by far the more common case: rivers, winds, ocean currents, are all turbulent; laminarity is the exception.

1.4 Brownian motion

Brownian motion, named for Robert Brown who first reported it in 1828, is the apparently random motion of small particles suspended in a fluid (Brown observed the motion of pollen grains). The explanation advanced by Einstein in 1905 and von Smoluchowski in 1906 is based on the idea that the motions are caused by a constant battering of the particles by the molecules of the fluid, and they model this effect by considering the displacement of a particle in a small time interval to be a continuous random variable $\boldsymbol{\Delta}$, with a density function $\phi(\boldsymbol{\Delta})$. Suppose the number of particles per unit volume at time t is $f(\mathbf{x}, t)$, then Einstein's model computes the change of f in a small time interval Δt as

$$f(\mathbf{x}, t + \Delta t) = \int_{\mathbf{R}^3} f(\mathbf{x} + \boldsymbol{\Delta}, t)\phi(\boldsymbol{\Delta})\, d\boldsymbol{\Delta}, \tag{1.82}$$

where we assume displacements are symmetric, $\phi(\boldsymbol{\Delta}) = \phi(-\boldsymbol{\Delta})$, and in fact we may take $\phi = \phi(\Delta)$ for an isotropic medium. Expanding for small Δ and Δt, we derive the result

$$\frac{\partial f}{\partial t} = D\nabla^2 f, \tag{1.83}$$

assuming

$$\int_{\mathbf{R}^3} \phi\, d\boldsymbol{\Delta} = 1, \quad \int_{\mathbf{R}^3} \phi \boldsymbol{\Delta}\, d\boldsymbol{\Delta} = \mathbf{0}, \tag{1.84}$$

where

$$D = \frac{1}{6\Delta t} \int_{\mathbf{R}^3} \Delta^2 \phi(\boldsymbol{\Delta})\, d\boldsymbol{\Delta}. \tag{1.85}$$

The equation (1.82) actually indicates that f (more precisely f/n) is a probability density, so that (1.83) is an evolution equation for the density of particles.

1.4.1 The Langevin equation

A different approach to the same problem considers the Newtonian mechanics of a particle subjected to a stream of molecular impacts. We may conceive of the molecular velocities as consisting of a (spatial) average, here taken as zero, together with a fluctuating component. The acceleration of the particle of mass m is then represented in the form

$$m\ddot{\mathbf{r}} = -\lambda\dot{\mathbf{r}} + \mathbf{X}, \tag{1.86}$$

where the terms on the right hand side represent the forces due to the average motion of the molecules and due to the fluctuations. The first is a linear damping term, which is appropriate for small Reynolds number, and the value of λ appropriate for Stokes flow past a sphere is

$$\lambda = 6\pi\eta a, \tag{1.87}$$

where a is the particle radius. From (1.86), we have

$$\tfrac{1}{2}m\ddot{(r^2)} - mv^2 = -3\pi\eta a\dot{(r^2)} + \mathbf{X}.\mathbf{r}, \tag{1.88}$$

where $\mathbf{v} = \dot{\mathbf{r}}$, and taking an ensemble average over a large number of particles, we have

$$\tfrac{1}{2}m\ddot{(\overline{r^2})} - m\overline{v^2} = -3\pi\eta a\dot{(\overline{r^2})} + \overline{\mathbf{X}.\mathbf{r}}. \tag{1.89}$$

At this point we make two assumptions; later we will find that the temperature is defined by the relation

$$kT = \tfrac{1}{3}m\overline{v^2}, \tag{1.90}$$

where k is Boltzmann's constant, and we are tacitly assuming that the mean square fluctuation velocity of the molecules is the same as that of the Brownian particle, though this seems at first sight somewhat arbitrary. If we conceive of the particle as equivalent to a volume of molecules with an impermeable surface, the argument becomes more reasonable, however. So we assume (1.90).

The other assumption we make is that

$$\overline{\mathbf{X}.\mathbf{r}} = 0. \tag{1.91}$$

The basis of this assumption is the randomness of the impact force $\mathbf{X}$, and its independence of particle position $\mathbf{r}$. This seems reasonable, but note that from (1.86), we have, after a rapid transient of length $t \sim \dfrac{m}{6\pi\eta a}$,

$$\overline{v^2} = \frac{\overline{\mathbf{X}.\dot{\mathbf{r}}}}{6\pi\eta a}, \tag{1.92}$$

which from the above discussion is evidently not zero.

With these assumptions, we can then solve (1.89). The transient time $t \sim \dfrac{m}{6\pi\eta a}$ is typically around 10^{-8} s, after which we have the diffusive mean square drift

$$\overline{r^2} \approx 6Dt, \tag{1.93}$$

where

$$D = \frac{kT}{6\pi\eta a}. \tag{1.94}$$

1.4.2 Random walks

Yet another approach to diffusion is to model the motion of a particle as a random walk. To do so, we consider a particle which moves in discrete steps on a one-dimensional lattice with locations at the integers. The extension to three dimensions is essentially trivial, assuming motions in each direction are independent. Let $p_{k,j}$ be the probability that the particle is at point k at time step j, and suppose that the particle moves to right or left with equal probability. It then follows by conditioning on the previous step that

$$p_{k,j+1} = \tfrac{1}{2}p_{k-1,j} + \tfrac{1}{2}p_{k+1,j}, \tag{1.95}$$

and if the particle originates at the origin at time step 0, then

$$p_{k,0} = \delta_{00}, \tag{1.96}$$

where δ_{rs} is the Kronecker delta.

We can solve (1.95) using a generating function $G_j(\xi) = \sum_{k=-\infty}^{\infty} p_{k,j}e^{ik\xi}$, whence we find

$$G_{j+1} = G_j \cos\xi, \quad G_0(\xi) = 1, \tag{1.97}$$

whence

$$G_j(\xi) = \cos^j \xi. \tag{1.98}$$

To find the solution at large time (large j), we write

$$\xi = \frac{\zeta}{\sqrt{j}}, \quad k = \sqrt{j}K, \quad \Delta K = \frac{1}{\sqrt{j}}, \quad p_{k,j} = \frac{1}{\sqrt{j}}P_{K,j}, \tag{1.99}$$

so that

$$\sum_K P_{K,j}e^{iK\zeta}\Delta K = \left[1 - \frac{\zeta^2}{2j} + \dots\right]^j, \tag{1.100}$$

where the sum over K is in increments of $\Delta K \ll 1$. For large j and small ΔK, writing $P_{K,j} = P_j(K)$, we have approximately

$$\hat{P}_j(\zeta) = e^{-\frac{1}{2}\zeta^2}, \tag{1.101}$$

where $\hat{P}$ is the Fourier transform, and the inverse is

$$P_j(K) = \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}K^2}, \tag{1.102}$$

and in terms of the original variables,

$$p_{k,j} = \frac{1}{\sqrt{2\pi j}} \exp\left(-\frac{k^2}{2j}\right). \tag{1.103}$$

Alternatively, we can consider the lattice points to be separated by a 'small' distance Δx, and the time steps to be of 'small' duration Δt, and then writing

$$x = k\Delta x, \quad t = j\Delta t, \quad p_{k,j} = \Delta x\, u(x,t), \tag{1.104}$$

(1.95) can be written in the form[8]

$$u(x,t+\Delta\, t)-u(x,t)=\tfrac{1}{2}\left[u(x-\Delta x,t)-2u(x,t)+u(x+\Delta x,t)\right]; \qquad (1.105)$$

expanding this in a Taylor series up to quadratic terms yields

$$\Delta t\, u_t+\tfrac{1}{2}(\Delta t)^2 u_{tt}+\ldots=\tfrac{1}{2}(\Delta x)^2 u_{xx}+\ldots, \qquad (1.106)$$

whence at leading order (ignore the small second time derivative term) we obtain the diffusion equation

$$u_t=Du_{xx}, \qquad (1.107)$$

where

$$D=\frac{(\Delta x)^2}{2\Delta t}. \qquad (1.108)$$

Note that in terms of (1.104), (1.103) is just

$$u=\frac{1}{2\sqrt{\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right], \qquad (1.109)$$

which is the similarity solution of the diffusion equation following initial release of a delta function at the origin.

Finite spread

One of the more obvious things about the exact solution for the random walk and its approximating diffusion equation is that the walker's position probability spreads at a finite rate, specifically $p_{k,j}=0$ for $|k|>j$, whereas the diffusion equation allows immediate propagation to infinity. This discrepancy arises because the approximation (1.101) is not uniformly valid; specifically (1.101) assumes $\zeta\sim O(1)$, whereas it is clear from (1.98) that the approximation is invalid when $\xi=\frac{1}{2}\pi$, and more generally when $\zeta\sim\sqrt{j}$. It is a bit impenetrable to see what to do with the difference equation, but a simple recipe follows by consideration of the expansion of (1.105). We simply retain the second derivative term in (1.106), so that the diffusion equation (1.107) is replaced by

$$u_t+\tau u_{tt}=Du_{xx}, \qquad (1.110)$$

where $\tau=\frac{1}{2}\Delta\, t$. This is a form of the telegraph equation; it is hyperbolic, and information propagates at finite speeds. The diffusion equation is accurate while $u\sim O(1)$, but fails when u is small, when the problem can be treated further using asymptotic methods. For more details, see Keller (2004).

1.5 Chaos

Chaos refers to the behaviour of a dynamical system which is erratic and 'unpredictable'. Chaos occurs in discrete systems (maps) and in continuous systems (differential equations), and indeed the two are intertwined, because the use of a Poincaré

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[8] The scaling for u is to represent the initial condition as a delta function.

section allows a differential equation to be converted to a map, although not usually explicitly.

The central property of a chaotic system is that it has *sensitive dependence on initial conditions*: two arbitrarily close initial conditions diverge, usually exponentially, in time. This is not enough on its own, as instanced by the system

$$\ddot{x} + zx = 0, \quad \dot{z} = 0, \tag{1.111}$$

and various extra ingredients are usually appended, for example that there are an infinite number of periodic and aperiodic orbits.

1.5.1 Maps

Maps come in two principal flavours: area-preserving and dissipative. But in both cases, the central architect of chaotic behaviour is that there is simultaneous expansion and contraction. The simplest example arises in the *logistic equation*

$$x_{n+1} = \lambda x_n(1 - x_n), \tag{1.112}$$

for which the transition to chaos is nicely illustrated by the bifurcation tree in figure 1.4.

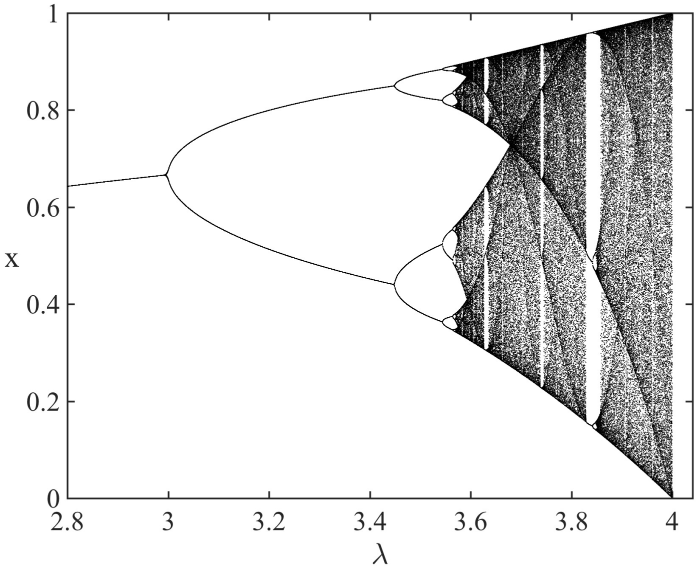

Figure 1.4: The bifurcation tree for the logistic map.

The tree is constructed by plotting the solution (after an initial transient, which is excised) for a sequence of different λ values. The single value for $\lambda < 3$ indicates a (stable) fixed point $\{x_n\} = \{x_0, x_0, \ldots\}$, which then bifurcates at $\lambda = 3$ to a period two cycle $\{x_n\} = \{x_1, x_2, x_1, x_2, \ldots\}$, and subsequently to cycles of period 4, period 8, and so on. This period-doubling sequence accumulates until at $\lambda \approx 3.57$, the trajectories become chaotic: all periodic solutions are unstable, and the trajectories become ‘smeared out’ in the tree. As λ increases further, the size of the chaotic region increases, until at $\lambda = 4$ it is the whole interval $[0, 1]$. It can be seen also that this progression is interrupted by a number (actually infinite) of ‘windows of stability’; the most obvious is the stable period 3 orbit which emerges at $\lambda \approx 3.81$.

The fully chaotic régime when $\lambda = 4$ is easily analysed by putting

$$x_n = \sin^2 \pi\phi_n, \tag{1.113}$$

from which we see that if we define

$$\phi_{n+1} = 2\phi_n \mod 1, \tag{1.114}$$

then x_n satisfies (1.112) with $\lambda = 4$.[9] This map is simply analysed by means of the following stratagem. Write the initial value of ϕ_n as

$$\phi_0 = .a_1a_2a_3\ldots \equiv \tfrac{1}{2}a_1 + \tfrac{1}{4}a_2 + \ldots, \tag{1.115}$$

being the binary fraction representation of ϕ_0; it is then clear that

$$\begin{aligned} \phi_1 &= .a_2a_3a_4\ldots, \\ \phi_2 &= .a_3a_4a_5\ldots, \end{aligned} \tag{1.116}$$

and so on, and thus the map (1.114) is encoded by the *shift map* σ on the space of semi-infinite sequences of two symbols $\Sigma_2^+ = \{.a_1a_2\ldots;\ a_i = 0 \text{ or } a_i = 1\}$:

$$\sigma(.a_1a_2a_3\ldots) = (.a_2a_3a_4\ldots). \tag{1.117}$$

It is immediate to see that the trajectories are completely encoded by the initial value, and that there is a countably infinite number of periodic orbits (ϕ_0 rational),[10] an uncountable number of aperiodic orbits (ϕ_0 irrational), and that trajectories are sensitive to initial conditions: these are the harbingers of chaos.

The logistic equation is an example of a dissipative map, and it is non-invertible. The Poincaré maps which arise from conservative Hamiltonian systems are invertible, but typically they too exhibit chaos. A simple but beautiful example of this is the baker map. This is illustrated in figure 1.5. The square is compressed, then cut in two and reassembled, thus mimicking the action of the baker in kneading a loaf (though the baker folds rather than cuts).

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[9] The same is also true for the tent map $\phi_{n+1} = 1 - |1 - 2\phi_n|$ which has the advantage of being continuous, and was also famously used as an example by Lorenz (1963) in his seminal work on chaos in differential equations.

[10] Any rational number $\phi = m/n$ where n is not a power of two has the form $.a_1\ldots a_pa_1\ldots$, and this corresponds to a period p cycle. To show this, suppose for simplicity that n has no factors of two, and can thus be written as a product of odd prime factors (possibly repeated) $n = p_1\ldots p_j$. Fermat’s theorem in number theory states that each $p_i \mid 2^{p_i} - 1$ (p_i divides $2^{p_i} - 1$), and therefore $n \mid 2^{\sum_i p_i} - 1$, i.e., $qn = 2^p - 1$ for some integers q and $p = \sum_i p_i$. From this we can deduce the statement above.

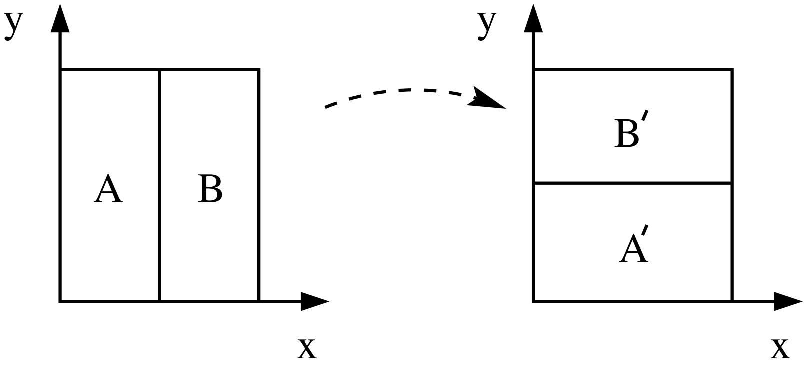

Figure 1.5: The baker map on the unit square.

The map can be written as

$$\begin{aligned} x_{n+1} &= 2x_n \mod 1, \\ y_{n+1} &= \tfrac{1}{2}y_n + \tfrac{1}{2}H(x_n - \tfrac{1}{2}), \end{aligned} \tag{1.118}$$

where H is the Heaviside step function[11]. Note that the map is area-preserving and indeed invertible. It can also be explicitly solved just as we did for the logistic map. Let the initial value of x be written as the binary fraction

$$x_0 = .a_1a_2a_3\ldots; \tag{1.119}$$

then each succeeding iterate simply shifts the binary point to the right and excises the leading digit; thus $x_1 = .a_2a_3\ldots$, and in general

$$x_n = .a_{n+1}a_{n+2}\ldots. \tag{1.120}$$

Note that $a_{n+1} = 0$ if $x_n < \frac{1}{2}$, and $a_{n+1} = 1$ if $x_n > \frac{1}{2}$. Therefore

$$y_{n+1} = \tfrac{1}{2}y_n + \tfrac{1}{2}a_{n+1}, \tag{1.121}$$

and the solution for y_n can be written in terms of the inverted n-th rational approximant

$$q_n = .a_na_{n-1}\ldots a_1 \tag{1.122}$$

as

$$y_n = \frac{y_0}{2^n} + q_n. \tag{1.123}$$

The solutions can be encoded in the same way as for the logistic equation. We denote the initial value of y_n as the binary fraction

$$y_0 = .a_0a_{-1}a_{-2}\ldots; \tag{1.124}$$

---

[11] Some extra book-keeping is necessary if $x_n = \frac{1}{2}$, which we will ignore.

then the solutions of the baker map are encoded by the shift map on the space Σ_2 of bi-infinite sequences of two symbols,

$$\sigma(\ldots a_{-2}a_{-1}a_0.a_1a_2a_3\ldots) = (\ldots a_{-1}a_0a_1.a_2a_3a_4\ldots). \tag{1.125}$$

From this we can see that the solutions give all the characteristics of chaos. There is clearly sensitive dependence on initial conditions, there are countably many periodic solutions (repeating sequences $\phi \in \Sigma_2$), and there are uncountably many aperiodic orbits (non-repeating sequences).

What is the evolution of a small cloud of points in a small box of side $\frac{1}{2^n}$? If we select all the points in the box (thus we know $a_{-(n-1)}, a_{-(n-2)}, \ldots, a_0, a_1, \ldots, a_n$), then after n iterations the y values sit in a small interval of length 2^{-2n}, while the x values have expanded to fill the unit interval. This just looks like an enhanced version of the baker map, with expansion and contraction by 2^n, and no cut. However, the following iterate introduces the cut, and the y range is split into sub-intervals near $.0a_n\ldots a_1$ and $.1a_n\ldots a_1$. After $2n$ iterates, the $O(2^{-n})$ knowledge of the initial neighbourhood is completely lost.

At this point, mathematical nicety and practical prediction diverge. We come back to the question: why is an invertible map in practice chaotic and not invertible? The answer to this lies in the fundamental nature of what a model is. We think the baker map is invertible because we know the initial position as a pair of infinite binary fractions. But already we are in a fictitious model place. There is no such thing as an infinite precision prescription of the coordinates of a point. The reality is that we can only measure initial positions to some finite level of accuracy. The myth of invertibility is something which diverts us because we mistake the mathematical precision of the real number system for reality, whereas it is no such thing.

1.5.2 Circle maps

In section 1.1.5 we alluded to the use of two-dimensional maps in describing the break-up of invariant tori in Poincaré maps for Hamiltonian systems. Much of the behaviour mentioned there can be understood by the study of *circle maps* of the form

$$\Theta \to \Theta + 2\pi\Omega + \beta \sin q\Theta. \tag{1.126}$$

Here Θ is the polar angle on a circle, and Ω and β are parameters. (1.126) arises in the context of dissipative systems, and specifically in the analysis of secondary Hopf bifurcations, when a limit cycle becomes oscillatorily unstable. In that case, Ω is the ratio of the bifurcation frequency to that of the underlying limit cycle, and β is a measure of nonlinearity, discussed further below. In the derivation of (1.126), the parameter $\beta = 0$ unless the ratio of frequencies $\Omega = p/q$ is rational, in which case $\beta \sim \mu^{(q-2)/2}$. The occurrence of the extra term is due to resonance between the two frequencies of the motion. In the analysis of (1.126) for small μ and Ω close to p/q, it is fairly straightforward to show that stable period q cycles occur if

$$\left|\Omega - \frac{p}{q}\right| \leq c\mu^{(q-2)/2}, \tag{1.127}$$

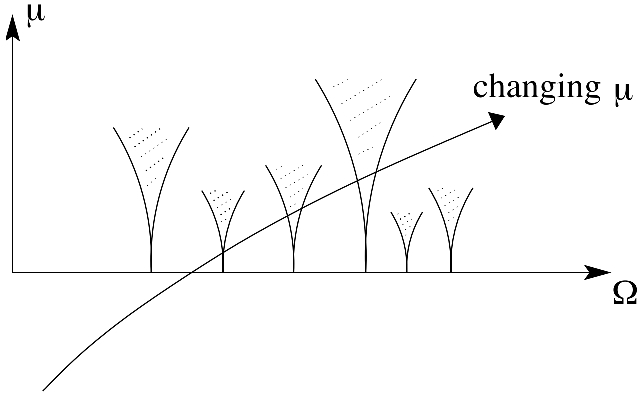

Figure 1.6: Arn'old tongues. Within the shaded regions, the motion is periodic, and elsewhere it is quasi-periodic; in general, Ω will change as μ increases, so that the system passes through a number of periodic windows; such behaviour is commonly seen in practice.

where we write $\beta = 2\pi c \mu^{(q-2)/2}$, and take $q \geq 5$ as part of the condition that (1.126) applies. The result of this is shown in figure 1.6. From each rational value of Ω, an *Arn'old tongue* emerges, within which the trajectories are periodic, and outside which they are quasi-periodic. Because the tongues are of finite but small width, and emerge from the rational values of Ω when $\mu = 0$, we have the paradox that periodic motion is structurally stable, but extremely unlikely to occur, whereas quasi-periodic motion has the inverse property. The same applies to the break-up of invariant tori in Hamiltonian systems, essentially for the same reason: most invariant tori remain, but it is the island chains which are structurally stable.

Continued fractions

Between the tongues and their periodic orbits, the trajectories are quasi-periodic and in fact dense in the unit circle, that is to say, they come arbitrarily close to every value of Θ. To see this, we take an excursion into number theory.

Begin with two relatively prime positive integers $n > m$, and successively apply the Euclidean algorithm:

$$\begin{aligned} n &= a_1 m + r_1, \\ m &= a_2 r_1 + r_2, \\ r_1 &= a_3 r_2 + r_3, \\ &\ldots \\ r_{k-1} &= a_{k+1} r_k + 1. \end{aligned} \tag{1.128}$$

Here, a_i are positive integers, and $m > r_1 > r_2 \ldots$ is a decreasing sequence of positive integers which are mutually relatively prime. The sequence must terminate with $r_{k+1} = 1$, otherwise m and n would have a common factor.

From this we construct successively

$$\begin{aligned}
\frac{m}{n} &= \frac{1}{a_1 + \dfrac{r_1}{m}}, \\
\frac{m}{n} &= \frac{1}{a_1 + \dfrac{1}{a_2 + \dfrac{r_2}{r_1}}}, \\
&\cdots, \\
\frac{m}{n} &= \frac{1}{a_1 + \dfrac{1}{a_2 + \dfrac{1}{\ldots + \dfrac{1}{a_{k+1} + \dfrac{1}{r_k}}}}},
\end{aligned} \tag{1.129}$$

and this is called the continued fraction representation of $\frac{m}{n}$. Exactly the same algorithm produces an infinite continued fraction representation of an irrational number.

The approximants

$$\frac{p_1}{q_1} = \frac{1}{a_1}, \quad \frac{p_2}{q_2} = \frac{1}{a_1 + \dfrac{1}{a_2}}, \ldots, \tag{1.130}$$

have a number of useful properties. By direct calculation, $(p_i, q_i) = 1$ for $i = 1, 2, 3$ (i. e., these pairs are relatively prime). Next, suppose inductively that

$$\begin{aligned}
p_n &= a_n p_{n-1} + p_{n-2}, \\
q_n &= a_n q_{n-1} + q_{n-2};
\end{aligned} \tag{1.131}$$

again, direct calculation shows this to be true for $n = 3$. To calculate $\frac{p_{n+1}}{q_{n+1}}$, we may simply note that it is obtained from $\frac{p_n}{q_n}$ by replacing a_n by $a_n + \frac{1}{a_{n+1}}$. Carrying out the calculation, we find

$$\frac{p_{n+1}}{q_{n+1}} = \frac{a_n p_n + p_{n-1}}{a_n q_n + q_{n-1}}, \tag{1.132}$$

and the inductive step is proved providing the definitions

$$p_{n+1} = a_n p_n + p_{n-1}, \quad q_{n+1} = a_n q_n + q_{n-1} \tag{1.133}$$

have $(p_{n+1}, q_{n+1}) = 1$. To show this, note that

$$p_n q_{n+1} - p_{n+1} q_n = -(p_{n-1} q_n - p_n q_{n-1}), \tag{1.134}$$

whence in fact

$$p_n q_{n+1} - p_{n+1} q_n = (-1)^{n+1} \tag{1.135}$$

(via evaluation at $n = 1$), and the relative primeness of (p_{n+1}, q_{n+1}) follows inductively.

(1.135) tells us other things also. The sequence of approximant differences is an alternating series, and thus the error of the approximant $\frac{p}{q}$ is less than $\frac{1}{q^2}$, and this clearly applies more generally to the continued fraction representation of an irrational number α.

As we suggested, this observation has its uses in understanding the dynamics of circle maps, of which the simplest example is the pure rotation $\theta \to \theta + \phi$, or equivalently $x \to x + \alpha \mod 1$. Clearly if α is rational, then the trajectories consist of periodic orbits; and clearly if α is irrational, there are no periodic orbits. We might then expect the resultant trajectory to be dense in the unit interval, i. e., to approach any particular value $y \in (0, 1)$ arbitrarily closely.

To see this, we first use continued fractions to choose relatively prime p and q such that $\left|\alpha - \frac{p}{q}\right| < \frac{1}{q^2}$, and then also r such that $\left|y - \frac{r}{q}\right| < \frac{1}{q}$. Now because p and q are relatively prime, the values of $np \mod q$ for $p = 0, 1, \dots, q-1$ cycle non-repetitively through the integers $q = 0, 1, \dots, q-1$. Thus there is a value $n < q$ such that $np = r \mod q$, and hence for some integer m, $|n\alpha - m - y| < \frac{2}{q}$. Since $q \to \infty$ as the approximants converge to α, we see that indeed the rotation map for irrational $\phi/2\pi$ has trajectories which are dense on the circle. See also question 3.1.

1.6 Notes and references

Reynolds (1895)

Brown (1828)[12] Einstein (1905) and Smoluchowski (1906)

In the context of dynamical systems, continued fractions are discussed expertly and compactly by Arn'old (1983). But their study is an old subject, and useful sources are the books by Todhunter (1875) and the classic by Birkhoff and MacLane (1965). Todhunter's book illuminates by its subtitle, 'for the use of colleges and schools'; a good deal of it is present day second year undergraduate material, and it indicates the extent to which educational prowess has changed in the intervening period.

Exercises

1.1 A number of particles with positions $\mathbf{r}_i$ are subjected to internal forces $\mathbf{F}_{ij}$, where $\mathbf{F}_{ij}$ is the force exerted by particle j on particle i.

What is meant by a virtual displacement? And what does it mean to say that a virtual displacement does no virtual work?

Show that if the forces have the form

$$\mathbf{F}_{ij} = f(r_{ij})\mathbf{r}_{ij},$$

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[12] The reference is given incorrectly by Gardiner (2009), and even on one online repository!

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and if the particles are connected as a rigid body, the virtual work is zero.

1.2 Use the chain rule to show that for a change of variable $\mathbf{r} = \mathbf{r}(\mathbf{q}, t)$,

$$\begin{aligned} \frac{d}{dt}\left(\frac{\partial \mathbf{r}_i}{\partial q_j}\right) &= \frac{\partial \mathbf{v}_i}{\partial q_j}, \\ \frac{\partial \mathbf{v}_i}{\partial \dot{q}_j} &= \frac{\partial \mathbf{r}_i}{\partial q_j}, \end{aligned}$$

where $\mathbf{v}_i = \dot{\mathbf{r}}_i$, and deduce that Newton's equations can be written in the form

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j} = Q_j,$$

where you should define the generalised forces Q_j and the kinetic energy T.

Hence deduce the form of Lagrange's and Hamilton's equations.

Show that Lagrange's equations also follow from a variational principle for the *action*

$$I = \int_{t_1}^{t_2} L\, dt,$$

where t_1 and t_2 are fixed, as are the values of q_i at these times. Why do $\dot{q}_i$ not have to be specified at the endpoints of the interval?

1.3 For a Lagrangian L, why does it make sense to define the generalised momenta as

$$p_i = \frac{\partial L}{\partial \dot{q}_i}?$$

Show how the definition of the Hamiltonian function

$$H = \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i, t),$$

together with Lagrange's equations, can be used to derive Hamilton's equations.

Show also how Hamilton's equations can be derived from a variational principle for the action

$$I = \int_C \sum_i p_i\, dq_i - H\, dt,$$

under variations of the trajectory C in (q_i, p_i, t) space such that the values of q_i and t are fixed at the endpoints.

A *homogeneous* function $f(\mathbf{r})$ of degree n satisfies $f(\lambda\mathbf{r}) = \lambda^n f(\mathbf{r})$. Prove Euler's theorem on homogeneous functions,

$$\mathbf{r}.\boldsymbol{\nabla} f = nf.$$

Using this result, show that if the kinetic energy T is quadratic in the generalised velocities $\dot{q}_i$, and the potential $V = V(q_i)$, then $H = T + V$.

1.4 A particle undergoes a random walk on the integers $\mathbf{Z}$, and the probability of being at position n at step j is $p_{n,j}$. Suppose the events move left, move right, remain stationary, have probabilities l, r and $1-l-r$ respectively. By using conditional probabilities, show that

$$p_{n,j} = lp_{n+1,j-1} + (1-l-r)p_{n,j-1} + rp_{n-1,j-1},$$

and if the particle starts at the origin, show that

$$p_{n,0} = \delta_{n0},$$

where δ_{ij} is the Kronecker delta. Find an equation for the generating function

$$G_j(s) = \sum_{\mathbf{Z}} p_{n,j}s^n, \quad (*)$$

and hence show that

$$G_j(s) = \left[\frac{l}{s} + (1-l-r) + rs\right]^j. \quad (\dagger)$$

For the case $l = r = \frac{1}{2}$, find the large time behaviour of the distribution as follows. Write

$$s = \exp\left(\frac{it}{\sqrt{j}}\right), \quad n = \sqrt{j}x, \quad p_{n,j} = \frac{1}{\sqrt{j}}f(x),$$

and find two approximations for G_j from $(*)$ and $(\dagger)$, one as a Fourier integral. Hence deduce that f is a normal distribution, independently of j. What are its mean and variance?

Find the equivalent result for general l and r.

1.5 Find the characteristic functions $\phi(t)$ for the following distributions:

Normal, $f(x) = \dfrac{1}{\sigma\sqrt{2\pi}}\exp\left[-\dfrac{(x-\mu)^2}{2\sigma^2}\right]$;

Gamma, $f(x) = \dfrac{\lambda^s x^{s-1}e^{-\lambda x}}{\Gamma(s)}$ on $(0,\infty)$;

Cauchy, $f(x) = \dfrac{1}{\pi(1+x^2)}$.

What are the mean and variance of each distribution?

1.6 Let $\{X_i\}$ be a series of independent trials from a distribution of mean μ and variance σ^2, and let $S_n = \sum_1^n X_i$. By consideration of appropriate characteristic functions, show that

$$S_n \sim N(\mu n, \sigma^2 n) \quad \text{as} \quad n \to \infty,$$

and deduce the law of large numbers,

$$\frac{S_n}{n} \overset{D}{\to} \delta(x-\mu) \quad \text{as} \quad n \to \infty.$$

Explain how this result can be used to provide a practical tool for the estimation of probability of an event $a \in E$.

1.7 Show from first principles that if $dV = dx_1\, dx_2\, dx_3$ is a material volume element, then

$$\frac{d(dV)}{dt} = (\boldsymbol{\nabla}.\,\mathbf{u})\, dV,$$

where $\mathbf{u}$ is the velocity field. Show this in two ways: using Eulerian coordinates, and using Lagrangian coordinates.

By consideration of Newton's second law applied to an infinitesimal tetrahedron, explain why Newton's third law applies, and deduce that the surface force on a volume element can be written in the form $\boldsymbol{\sigma}.\mathbf{n}$.

Hence derive the Navier-Stokes equation in the form

$$\rho \frac{d\mathbf{u}}{dt} = \boldsymbol{\nabla}.\,\boldsymbol{\sigma}.$$

1.8 In cartesian coordinates, and using the summation convention, the term $\nabla^2 \mathbf{u}$ is defined by

$$\nabla^2 \mathbf{u} \equiv \mathbf{e}_i \frac{\partial^2 u_i}{\partial x_j \partial x_j},$$

where $\mathbf{e}_i$ is an orthonormal basis for $\mathbf{R}^3$. Use the definitions of

$$\boldsymbol{\nabla}\phi = \mathbf{e}_i \frac{\partial \phi}{\partial x_i},$$

$$\boldsymbol{\nabla}.\,\mathbf{a} = \frac{\partial a_k}{\partial x_k},$$

$$\boldsymbol{\nabla} \times \mathbf{v} = \varepsilon_{ijk} \mathbf{e}_i \frac{\partial v_j}{\partial x_k},$$

where ε_{ijk} is the alternating tensor:

$$\varepsilon_{ijk} = \begin{cases} +1, & \{ijk\} = \{123\}, \{231\}, \{312\}, \\ -1, & \{ijk\} = \{132\}, \{213\}, \{321\}, \\ \;\;0 & \text{otherwise}, \end{cases}$$

to show that

$$\nabla^2 \mathbf{u} \equiv \boldsymbol{\nabla}(\boldsymbol{\nabla}.\,\mathbf{u}) - \boldsymbol{\nabla} \times \boldsymbol{\nabla} \times \mathbf{u},$$

which thus provides a coordinate-free definition of this term.

Hint: the alternating tensor satisfies the relation

$$\varepsilon_{ijk}\varepsilon_{ipq} = \delta_{jp}\delta_{kq} - \delta_{jq}\delta_{kp}.$$

1.9 Write down an integral form of the conservation of kinetic and internal energy for a fluid flow, allowing for work done by viscous stresses and for a heat flux vector due to spatial internal energy gradients. By reducing this to point form, and making use of the Navier-Stokes equations, show that the energy equation can be written in the form

$$\rho\frac{de}{dt}=\sigma_{ij}\dot{\varepsilon}_{ij}-\boldsymbol{\nabla}.\,\mathbf{q}.$$

1.10 Starting from the Navier–Stokes equations in the form

$$\boldsymbol{\nabla}.\,\mathbf{u}=0,$$

$$\rho\left[\frac{\partial\mathbf{u}}{\partial t}+\boldsymbol{\nabla}.\,(\mathbf{uu})\right]=-\boldsymbol{\nabla}p+\eta\nabla^2\mathbf{u},$$

derive average equations for the mean velocity and pressure by writing

$$\mathbf{u}=\bar{\mathbf{u}}+\mathbf{u}',\quad p=\bar{p}+p',$$

where the overbar denotes an ensemble average and the prime denotes fluctuations (thus $\overline{\mathbf{u}'}=\mathbf{0}$, $\overline{p'}=0$). Show that the Reynolds shear stress at a solid surface, where the fluid velocity vanishes, is necessarily zero, and hence explain why, if an eddy viscosity closure is assumed, the eddy viscosity should vanish at a solid surface.

1.11 A large number of particles undergo Brownian motion in one spatial dimension x, and the probability density function $p(x,t)$ of being at position x at time t is determined by a probability density $\phi(\Delta)$ of moving a distance Δ in a small time τ. Using conditional probability and the independence of successive events in time τ, write down an equation for $p(x+\Delta,t)$, and assuming Δ and τ are small, show that p satisfies a diffusion equation, where the diffusivity is

$$D=\frac{1}{2\tau}\int_{-\infty}^{\infty}\Delta^2\phi(\Delta)\,d\Delta.$$

Find the solution if all the particles are initially at $x=0$, and hence show that the mean square displacement

$$\overline{x^2}=2Dt.$$

For motion in three dimensions, the density satisfies the diffusion equation

$$\frac{\partial p}{\partial t}=D\left[\frac{\partial^2 p}{\partial r^2}+\frac{2}{r}\frac{\partial p}{\partial r}\right],$$

together with $p=\delta(\mathbf{r})$ at $t=0$. Noting that

$$\int_0^\infty 4\pi r^2 p\,dr\equiv 1,$$

find a suitable similarity solution for p, and hence show that

$$\overline{r^2} = 6Dt.$$

Is this consistent with the one-dimensional result?

1.12 Show that if p, q are relatively prime integers, then the Diophantine equation

$$np - mq = 1$$

has integer solutions n and m.

Chapter 2

Stochastic processes

2.1 The Chapman–Kolmogorov equation

A Markov process is one for which successive events $X_1, X_2, \ldots$ have conditional probabilities which only retain 'most recent memory'. Thus

$$P(X_n \,|\, X_{n-1}, X_{n-2}, \ldots) = P(X_n \,|\, X_{n-1}). \tag{2.1}$$

Here $\{X_n\}$ can be either a discrete or continuous (X_t) process.

We consider sequential events z, y, x at respective times $t_3 < t_2 < t_1$, with associated probability density functions denoted by f (of various arguments). The laws of conditional probability then state that for a Markov process

$$f(x, y, z) = f(x \,|\, y, z) f(y, z) = f(x \,|\, y) f(y \,|\, z) f(z). \tag{2.2}$$

Strictly, we should have various subscripts on the fs. Dividing by $f(z)$ and integrating over the range Y of y, we have (since $\displaystyle\int_Y f(x, y, z)\, dy = f(x, z)$)

$$f(x \,|\, z) = \int_Y f(x \,|\, y) f(y \,|\, z)\, dy; \tag{2.3}$$

this is the *Chapman–Kolmogorov equation.*

For a discrete time series, we define the n-step transition probability

$$p_{ij}^{(n)} = P(X_{m+n} = i \,|\, X_m = j), \tag{2.4}$$

and then the Chapman–Kolmogorov equation takes the form

$$p_{ij}^{(m+n)} = \sum_k p_{ik}^{(m)} p_{kj}^{(n)}, \tag{2.5}$$

for any positive integers m, n.

In the above, we have assumed the conditional probabilities or densities are independent of time, i. e., the processes are *stationary.* This is not essential, but we will assume it in the sequel. In this case, we can write the conditional density

$$f(x_t \,|\, z_\tau) = T_{t-\tau}(x \,|\, z), \tag{2.6}$$

where the subscripts on the variables x and z denote the time of observation. T_t is called the transition probability, and depends only on the time interval between observations. Note in particular that

$$\int_X T_t(x \,|\, z)\, dx = 1 \tag{2.7}$$

for any t or z, through one of the axioms of probability, and also

$$T_0(x \,|\, z) = \delta(x - z). \tag{2.8}$$

The Chapman–Kolmogorov equation now takes the form

$$T_{t-\tau}(x \,|\, z) = \int_Y T_{t-t'}(x \,|\, y) T_{t'-\tau}(y \,|\, z)\, dy, \tag{2.9}$$

for any $t' \in (\tau, t)$. Much of stochastic dynamics is concerned with the solution of this equation, under a variety of simplifying assumptions, which we detail in subsequent sections.

An incremental form of (2.9) is

$$T_{t+\Delta t}(x \,|\, z) = \int_Y T_{\Delta t}(x \,|\, y) T_t(y \,|\, z)\, dy. \tag{2.10}$$

Additionally, (2.8) implies

$$T_t(x \,|\, z) = \int_Y T_0(x \,|\, y) T_t(y \,|\, z)\, dy, \tag{2.11}$$

hence we can deduce that

$$\frac{\partial T_t(x \,|\, z)}{\partial t} = \int_Y S(x, y) T_t(y \,|\, z)\, dy, \tag{2.12}$$

where we define (if we can)

$$S(x, y) = \lim_{\Delta t \to 0} \left[\frac{T_{\Delta t}(x \,|\, y) - T_0(x \,|\, y)}{\Delta t} \right]. \tag{2.13}$$

It is convenient to write the differential form of the Chapman–Kolmogorov equation (2.12) in terms of either an evolving probability distribution, or in terms of an initial distribution of points. If we let $\phi(x, t)$ denote the probability density function of X at time t, then

$$\phi(x, t) = \int_Z T_t(x \,|\, z) \phi_0(z)\, dz, \tag{2.14}$$

where $\phi = \phi_0(x)$ at $t = 0$, and

$$\frac{\partial \phi}{\partial t} = \mathcal{S}\phi \equiv \int_Y S(x, y) \phi(y, t)\, dy. \tag{2.15}$$

In terms of the operator $\mathcal{S}$, the solution of (2.15) is simply

$$\phi = e^{t\mathcal{S}}\phi_0, \tag{2.16}$$

although this is of little use unless the eigenvalues of $\mathcal{S}$ are known. The equivalent for the discrete case (both in time and sample space) follows from (2.5). Defining the matrix

$$\mathcal{P} = (p_{ij}^{(1)}) \tag{2.17}$$

and the state vector of probabilities at step n to be $\mathbf{u}_n$, with prescribed $\mathbf{u_0}$, then the solution of (2.5) is simply (analogously to (2.16))

$$\mathbf{u}_n = \mathcal{P}^n\mathbf{u}_0. \tag{2.18}$$

2.2 The master equation

There are two essential types of process which lead to simplifications of (2.10). These can be called *jump* processes and *diffusive* processes. In the former we allow finite jumps from z to x in small time intervals. An example of this is the process of successive fragmentation of rocks (e. g., Kolmogorov 1941). An initial rock, or collection of rocks, is successively fragmented. At each stage of the process, new fragments can be created which are not necessarily close to the size of the parent rock.

In a Poisson-like assumption, we assume that for $x \neq z$,

$$T_{\Delta t}(x\,|\,z) = W(x,z)\Delta t, \quad x \neq z; \tag{2.19}$$

it is then a consequence of (2.7) that

$$T_{\Delta t}(x\,|\,z) = W(x,z)\Delta t + \left\{1 - \Delta t\int_X W(x',z)\,dx'\right\}\delta(x-z). \tag{2.20}$$

Substituting this into (2.10) and taking the limit $\Delta t \to 0$ then leads to the *master equation*

$$\frac{\partial T_t(x\,|\,y)}{\partial t} = \int_Y \left[W(x,y)T_t(y\,|\,z) - W(y,x)T_t(x\,|\,z)\right]\,dy, \tag{2.21}$$

or, in terms of the density of X,

$$\frac{\partial\phi(x,t)}{\partial t} = \int_Y \left[W(x,y)\phi(y,t) - W(y,x)\phi(x,t)\right]\,dy. \tag{2.22}$$

As mentioned above, a practical application of the master equation lies in the fragmentation of rocks. As ever, there is also a discrete analogue of (2.22). If $p_n(t) = P(X_t = n)$, for example (here the state space is discrete but time is continuous), then the master equation takes the form

$$\dot{p}_n = \sum_k \left(W_{nk}p_k - W_{kn}p_n\right). \tag{2.23}$$

Examples of this are the random walk on the integers

$$\dot{p}_n = \tfrac{1}{2}(p_{n-1} + p_{n+1}), \tag{2.24}$$

whose generating function

$$G(s,t) = \sum_{\mathbf{Z}} p_n s^n \tag{2.25}$$

is

$$G = \exp\left[\tfrac{1}{2}t\left(s + \frac{1}{s}\right)\right], \tag{2.26}$$

and the birth-death-immigration process where n is the size of a population at time t, each of whose souls can die, stay alive or reproduce with probability $\lambda\,\Delta t$ in time Δt, and in so doing produce r individuals from the previous one with probability q_r ($r = 0$, death; $r = 1$, stay alive; $r > 1$, stay alive and produce $r - 1$ offspring). In addition we suppose immigration of an individual occurs with probability $\nu\,\Delta t$. This leads to the master equation

$$\dot{p}_n = -(\nu + n\lambda)p_n + \lambda\sum_0^n (n - m + 1)q_m p_{n-m+1} + \nu p_{n-1}, \tag{2.27}$$

which is of the form (2.23) with

$$\begin{aligned} W_{n,k} &= \lambda k q_{n+1-k}, \quad k \le n+1, \quad k \ne n-1, \\ W_{n,n-1} &= \lambda(n-1)q_2 + \nu. \end{aligned} \tag{2.28}$$

The evolution of the population p.d.f. in this case can lead to negative binomial distributions (Bartlett 1960), of relevance in human infectious diseases (Anderson and May 1991).

2.3 The Fokker–Planck equation

The Fokker–Planck equation is an approximate form of the (continuous) master equation which arises when only near-neighbour transitions are allowed. Its origins lie in the explanation of Brownian motion by Einstein at the beginning of the twentieth century. We start with the master equation in the form (2.22):

$$\frac{\partial\phi(x,t)}{\partial t} = \int_Y [W(x,y)\phi(y,t) - W(y,x)\phi(x,t)]\,dy. \tag{2.29}$$

Now define

$$W(x,y) \equiv w(y, x-y), \tag{2.30}$$

whence also $W(y,x) \equiv w(x, y-x)$. Substituting into (2.29) and putting $y = x - \Delta$ in the first integral and $y = x + \Delta$ in the second leads to

$$\frac{\partial\phi}{\partial t} = \int_{\mathbf{R}} [w(x-\Delta,\Delta)\phi(x-\Delta,t) - w(x,\Delta)\phi(x,t)]\,d\Delta, \tag{2.31}$$

where we may take $\mathbf{Y} = \mathbf{R}$ whether it is or not, as we assume $w(\xi, \eta)$ is only non-zero for small η. More precisely, w is rapidly varying in η but not in ξ.

A formal Taylor series expansion in powers of Δ about x (expand the first argument in w and ϕ but not the second) leads to the Kramers-Moyal expansion

$$\frac{\partial \phi}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} [M_n \phi], \tag{2.32}$$

where the moments M_n are

$$M_n = \int_{\mathbf{R}} \Delta^n w(x, \Delta)\, d\Delta. \tag{2.33}$$

Because Δ is small, M_n decreases sharply wth n, and the series can be truncated; the Fokker–Planck equation follows from retaining only the first two moments, thus

$$\frac{\partial \phi}{\partial t} + \frac{\partial (M_1 \phi)}{\partial x} = \frac{\partial^2 (M_2 \phi)}{\partial x^2}. \tag{2.34}$$

The advective term is referred to as the drift term, while the second is the diffusive term. In the description of Brownian motion, the odd moments are zero if there is no bias in the molecular random impacts, and then we simply obtain the diffusion equation.

2.4 Stochastic differential equations

A stochastic differential equation is one of the form

$$\dot{x} = ax + b\xi, \tag{2.35}$$

where a and b may be functions of x and t, and ξ represents a random noise term. The presence of the term ξ renders the meaning of (2.35) opaque, and it is more common to consider a sequence of values x to form a (random) process for the random variable X, in which the increments Δx satisfy

$$\Delta x = a\,\Delta t + b\,\Delta W, \tag{2.36}$$

where commonly W is defined to be a *Wiener* process, that is to say it is continuous, not differentiable, and $W(t)$ is a Gaussian random variable with mean zero and variance t. Our object is to determine a master equation to describe the evolution of the density of X.

We begin by supposing that a and b are constant, so that the process X is stationary, and our previous discussion is relevant. From (2.10), we have

$$\phi(x, t + \Delta t) = \int_Y T_{\Delta t}(x \,|\, y) \phi(y, t)\, dy, \tag{2.37}$$

and we wish to calculate the transition probability density $T_{\Delta t}(x\,|\,y)$. To do this we use the fact that

$$\Delta x = x - y = a\Delta t + b\Delta W, \tag{2.38}$$

and thus

$$\begin{aligned} T_{\Delta t}(x\,|\,y)\,dy &= f\left[\Delta W = \frac{x-y-a\Delta t}{b}\,|\,y\right] d\left\{\frac{x-y-a\Delta t}{b}\right\} \\ &= f\left[\Delta W = \frac{x-y-a\Delta t}{b}\right]\frac{dy}{b}, \end{aligned} \tag{2.39}$$

if we assume that the Wiener process is independent of X and symmetric (as it is). It follows that

$$T_{\Delta t}(x\,|\,y) = \frac{1}{b\sqrt{2\pi\Delta t}}\exp\left[-\frac{(x-y-a\Delta t)^2}{2b^2}\right], \tag{2.40}$$

since $\Delta W \sim \mathcal{N}(0, \Delta t)$. Substituting this into (2.37), we find, after a change of variable,

$$\phi(x, t+\Delta t) = \int_{\mathbf{R}} \frac{1}{\sqrt{2\pi}}\exp(-\tfrac{1}{2}r^2)\phi\left(x - a\Delta t - br\sqrt{\Delta t}\right)\,dr, \tag{2.41}$$

and expanding this to terms of $O(\Delta t)$ leads to the Fokker–Planck equation in the form

$$\phi_t + a\phi_x = \tfrac{1}{2}b^2\phi_{xx}, \tag{2.42}$$

where the subscripts here denote partial derivatives.

It is possible to extend this result for variable a and b. Most simple is the extension for variable a, which follows from the realisation that since ϕ is itself a density, there is a (cancelled) dx missing from each side of (2.41). The increment dx' at $t + \Delta t$ is stretched from its value dx at t so that

$$dx' = dx(1 + a'\Delta t), \tag{2.43}$$

where $a' = \dfrac{\partial a}{\partial x}$. This leads to a modification of the expansion of (2.41) as

$$\phi(x, t+\Delta t)(1 + a'\Delta t) = \phi + \Delta t[-a\phi_x + \tfrac{1}{2}b^2\phi_{xx}], \tag{2.44}$$

and thus

$$\phi_t + (a\phi)_x = \tfrac{1}{2}b^2\phi_{xx}. \tag{2.45}$$

The issue of variable b is more complicated, and is discussed further below.

2.4.1 Liouville's equation

In the absence of noise ($b = 0$), the Fokker–Planck equation becomes Liouville's equation:

$$\phi_t + (a\phi)_x = 0, \tag{2.46}$$

which is the usual conservation law for a cloud of deterministic particles moving with velocity $\dot{x} = a$.

2.4.2 Ornstein–Uhlenbeck process

2.4.3 The Itô–Stratonovich dilemma

2.5 Notes and references

Two principal sources are the books by Gardiner (2009) and Van Kampen (2007). Risken (1989)

Exercises

2.1

Chapter 3

Statistical mechanics

The subject of statistical mechanics comes squarely from physics. It is an important subject, providing as we shall see a unifying interface between diverse areas of applied mathematics, including mechanics, probability, stochastic dynamics, fluid dynamics, thermodynamics, quantum mechanics (though we will not touch this), and even philosophy.

For such a powerful subject, it is compellingly opaque. I have yet to meet an applied mathematician who professed to understand thermodynamics in any useful sense of the word. Why, for example, do you minimise Gibbs free energy at constant temperature and pressure, but Helmholtz free energy at constant temperature and volume? What, indeed, is entropy?

In vain does one seek answers in any of the proliferation of books on the matter. They are relentlessly full of imprecision and obfuscation. No wonder so many authors have complained of other books which provide labyrinthine explanations whose contortions provide conclusions without any measurable logical process. You can see that I am in sympathy with such complaints, and will have more to say on this matter in the notes at the end of the chapter.

The path we tread will be logically different from most of the other books you may read, and we will explicitly avoid entirely some of the constructivist explanations (Carnot engines, heat baths, and the like) which in my view serve merely to confuse the precise eye of the mathematician. For sure, we will have to step off the rational path of mechanics at some point, but at least we will not resort to simply making it up, which is what a good deal of the subject apparently involves. We begin at the beginning, resuming a knowledge of classical particle mechanics.

3.1 The Liouville equation

We chanced on Liouville's equation in chapter 2, which obscured the fact that it is the central equation on which what one might call deterministic statistical mechanics is based. We are interested in the motion of N particles described by a Hamiltonian system

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\partial H}{\partial \mathbf{p}_i},\\ \dot{\mathbf{p}}_i &= -\frac{\partial H}{\partial \mathbf{q}_i},\end{aligned}\tag{3.1}$$

$i = 1, \ldots, N$, where we may suppose that

$$H = T(\mathbf{p}) + V(\mathbf{q}),\tag{3.2}$$

and the kinetic energy T is quadratic in $\mathbf{p}$. It follows that under the transformation

$$\mathbf{q} \to \mathbf{q}, \quad \mathbf{p} \to -\mathbf{p}, \quad t \to -t,\tag{3.3}$$

the equations of motion are invariant, and thus the motion of the system of particles is *time-reversible.* As we shall see, this time reversibility is lost when we come to consider the statistical evolution of the system, and this will lead us to the central philosophical problem of statistical mechanics, prosaically referred to as 'the arrow of time': why is the collective behaviour of a system of particles irreversible (i. e., time goes in one demonstrable direction), while the individual particle motions are reversible? We return to this conundrum in due course.

The motion of N particles in 6–dimensional $(\mathbf{q}, \mathbf{p})$ space can equally be thought of as a single trajectory of the coordinate $\gamma = (\mathbf{q}_i, \mathbf{p}_i)$ in $6N$–dimensional phase space Γ. We may reasonably take H to be an analytic function, and in this case the trajectory is uniquely defined (via Picard's theorem), and it also depends smoothly on the initial state, and it therefore follows that if we take a cloud of points in a volume element of density $\rho(\gamma, t)$, the density evolves according to the conservation of mass equation (1.61), derived in the same way from first principles:

$$\rho_t + \boldsymbol{\nabla} . \, (\rho \mathbf{u}) = 0,\tag{3.4}$$

where now

$$\mathbf{u} = \left(\frac{\partial H}{\partial \mathbf{p}_i}, -\frac{\partial H}{\partial \mathbf{q}_i} \right).\tag{3.5}$$

The velocity in Γ is indeed a smooth function of position in Γ, and no extra continuum hypothesis is necessary. (3.4) can be written in the form

$$\rho_t + \{\rho, H\} = 0,\tag{3.6}$$

where the curly brackets denote the Poisson bracket, formed from the Jacobian,

$$\{\rho, H\} = \frac{\partial(\rho, H)}{\partial(\mathbf{q}, \mathbf{p})}.\tag{3.7}$$

Notice that from (3.5), the velocity $\mathbf{u}$ in Γ is *incompressible.* Not only that, but the Liouville equation is time reversible under the transformation $t \to -t$, $\mathbf{q} \to \mathbf{q}$, $\mathbf{p} \to -\mathbf{p}$. We shall see that our efforts to solve it introduce irreversibility.

The alert reader will complain that in practice, H has singularities, assuming we do not allow particles to pass through each other in our present classical phase space. This is indeed true, but the conclusion on the smoothness of the solutions follows from the fact that we assume that the initial state is non-singular (the particles are non-overlapping) and the singularities act as repellers. The argument can be illustrated by means of the motion in the interval $(0, 1)$ governed by the Hamiltonian

$$H = \tfrac{1}{2}p^2 + V(q), \quad V = \frac{\delta}{q(1-q)}, \tag{3.8}$$

which for small δ simply represents a particle bouncing back and forth between the boundaries at 0 and 1. Picard's theorem applies for any motion with the initial value of $q \in (0, 1)$, since the singularities at 0 and 1 are inaccessible.

Liouville's equation may be exact, but it is not of much use, because we cannot hope to follow a trajectory in Γ when $N \gg 1$. Our only hope lies in approximating it in some way, and this is where the statistical part of the subject begins. In particular, it leads to the *ergodic theorem*, or more accurately the *ergodic hypothesis*.

3.1.1 The ergodic hypothesis

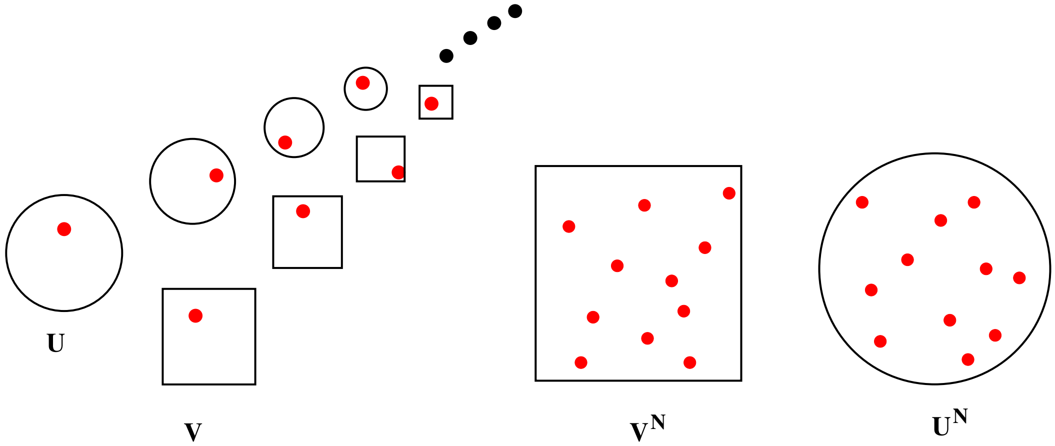

Figure 3.1: Alternative visualisations of $\Gamma = (V \times U)^N$ (left) or $\Gamma = V^N \times U^N$ (right). The circles indicate an expected spherically symmetric distribution in velocity space.

It is helpful to try and get some idea of what the phase space Γ looks like. As a typical example, we will think of a large number N of spherical particles (the hard sphere gas) moving and interacting via Newtonian collision in a box. This is a limit of the motion encountered with a Hamiltonian analogous to (3.8). The physical coordinate space V spanned by $\mathbf{q}$ is simply the box, and generally we expect the particles to be equidistributed throughout it. Velocities are not so bounded, and thus the velocity space U spanned by $\mathbf{p}$ is simply $\mathbf{R}^3$, although we do not expect the particles to be equidistributed in U; we do, however, expect their velocities to be equidistributed in direction, and in fact as we shall see their density is Gaussian with

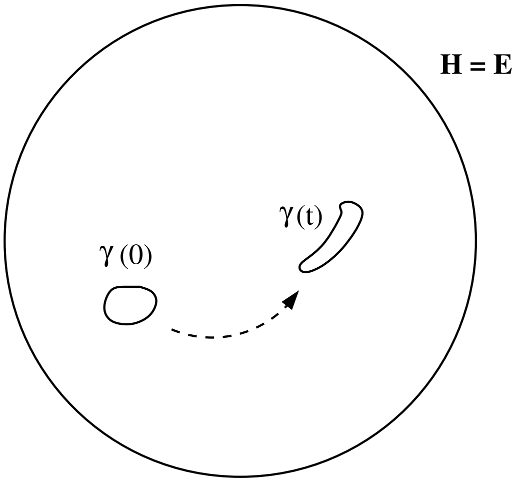

Figure 3.2: The Liouville picture of (an ensemble of trajectories) γ on the hypersurface $H = E$.

radius. Thus a large number of particles have velocities distributed as a Gaussian cloud in U, and the space inhabited by each particle is just $P = V \times U$. The $6N-$dimensional space Γ is then simply $P^N = (V \times U)^N$, and we can think of it as N copies of V and U, each with one point in each of V and U (representing position and velocity), thus $\Gamma = (V \times U)^N$; or as all of the N copies superimposed, which thus gives an image of N points in V (the particle positions) together with their velocities in U; thus $\Gamma = V^N \times U^N$.

A more schematic visualisation uses the fact that the trajectory in Γ lives on the surface of the hypersphere $H = E$, where E is the total energy of the system. The Liouville picture thinks of a small element of this hypersurface being mapped under the flow to another hypersurface of equal volume, and a trajectory of a cloud of points in Γ can be thought of as the motion of a deformable constant volume blob as it moves round the surface of the hypersurface.

The ergodic hypothesis is best understood in terms of figure 3.2. A collection (ensemble) of initial states $\gamma(0)$ in Γ evolve under the flow on the hypersurface $H = E$, conserving their volume as they go. The ergodic hypothesis supposes not only that γ covers the whole of the hypersphere as it evolves (which is by no means obvious), but over the course of its evolution it visits each part of the hypersphere equally frequently. Reducing γ to a single trajectory, we are led to the ergodic hypothesis in the following form:

> The time average of a quantity A as it evolves on (almost every) single trajectory $\gamma(t) \in \Gamma$ is equal to the phase space average of A over the constant energy hypersurface on which A resides.

We will use the ergodic hypothesis when we come later (section 3.5) to classical statistical mechanics, which in essence starts from its assumption. For the moment, we consider also some other natural averages. To begin, we realise that ρ is described by an ensemble average, and it therefore also describes a probability density for the evolution of a trajectory in Γ. It is also natural, for a collection of N particles, to suppose that the probability density (now in P) for a single particle is independent of which particle is chosen: all particles are equivalent: but it is a matter of care to determine this, because it is also clear that the motion of a single particle is not independent of all the others. For example, it is obvious that the density in P of a single particle in a box is not the same as that of one of N particles in a box, since the single particle has a velocity distribution which resides on a sphere in U. The effort to determine what is called the single particle distribution function for the motion of any of N particles in a box leads us to the *Boltzmann equation*.

3.2 The Boltzmann equation

It is common practice in fluid mechanics texts to derive the equations of mass, momentum and energy from first principles, assuming that one can define an average density[1] ρ, average velocity $\mathbf{u}$, and average internal energy e of the medium, and that these are continuously differentiable functions. Mass conservation causes no difficulties, and nor does energy, provided one adds in some thermodynamics, and in addition uses the momentum equation. However, the momentum equation involves the introduction of a stress tensor, and the properties of this quantity are largely, if reasonably, made up.

A more fundamental approach begins with the concept that a fluid consists of a large number of molecules, whose position and velocity fluctuate in time and space, and which interact through the action of short range forces whose effect can be conceived of as enabling collisions. In order to describe the collective motion, we define a *velocity distribution function* $f(\mathbf{r},\mathbf{v},t)$, which is the expected number density function of molecules of position $\mathbf{r}$ and velocity $\mathbf{v}$. More precisely,

$$f(\mathbf{r},\mathbf{v},t)\,d\mathbf{v}\,d\mathbf{r} \tag{3.9}$$

is the expected number of molecules in the six-dimensional hypervolume element $d\mathbf{v}\,d\mathbf{r}$ centred at $(\mathbf{r},\mathbf{v})$, where $d\mathbf{v}$ is a (positive) volume element in velocity space, and $d\mathbf{r}$ is a volume element in physical space. In practice, if N is the total number of particles in the volume under consideration, then f/N is the single particle probability density function.

There is a specific connection between f and the Liouville density ρ, which describes the density of an ensemble of trajectories in the $6N$-dimensional phase space Γ. The s-particle probability density is defined as

$$\rho_s=\int_{\Gamma_{s+1}}\rho\,d\Gamma_{s+1},\quad d\Gamma_{s+1}=\prod_{s+1}^{N}d\gamma_k,\quad d\gamma_k=d\mathbf{q}_k\,d\mathbf{p}_k, \tag{3.10}$$

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[1] In a confusing subject, it does not help that the fluid density ρ, which is the number of particles per unit volume multiplied by their mass, has the same symbol as that used for the ensemble density of trajectories in $6N$-dimensional space Γ; but it does. Keep your wits about you!

where $\mathbf{p}_k = m\mathbf{v}_k$, $\mathbf{q}_k = \mathbf{r}_k$, and the s-particle distribution function is given by

$$f_s(\gamma_1, \ldots, \gamma_s) = \frac{N!}{(N-s)!}\rho_s(\gamma_1, \ldots, \gamma_s). \tag{3.11}$$

The distinction between f_s and ρ_s lies in the fact that f_s is not concerned with particle identity; the number of ways of selecting s particles from N is $\dfrac{N!}{(N-s)!}$, and this is the number of the distinct realisations in Γ_s which are indistinguishable for f_s. An equivalent statement is that ρ_s can be assumed to be invariant under permutations of $\gamma = (\gamma_1, \ldots, \gamma_s)$, so that f_s is a density over the space of permutations of γ.

It can be shown (see question 3.2) that the velocity distribution functions f_s satisfy the BBGKY hierarchy equations

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int_P \sum_{i=1}^{s} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i}\, d\gamma_{s+1}, \tag{3.12}$$

where $\{f, H\}$ is the Poisson bracket, and $W_{ij} = W(|\mathbf{r}_i - \mathbf{r}_j|)$ is the inter-particle potential; the space $P = V \times U$ is the position-velocity space inhabited by each particle.

The left hand side of this equation represents conservation of particle density in the space (call it P_s) spanned by $(\gamma_1, \ldots, \gamma_s)$. The density of these points is not conserved however, because collisions can provide a source or sink to a neighbourhood of P_s through changes to $\mathbf{p}$. The integral term on the right provides the description of this collision term.

We can rewrite (3.12) in a slightly more accessible fashion by defining

$$\mathbf{a}_{ij} = -\frac{1}{m}\boldsymbol{\nabla}_{\mathbf{r}_i} W_{ij} \tag{3.13}$$

(not summed) as the force per unit mass on particle i due to particle j; here $\boldsymbol{\nabla}_{\mathbf{r}_i}$ indicates the gradient with respect to $\mathbf{r}_i$. If in addition $\mathbf{g}$ is the external force per unit mass acting on the particles, then the BBGKY equations take the form

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^{s}\left[\mathbf{v}_i.\boldsymbol{\nabla}_{\mathbf{r}_i} f_s + \left\{\mathbf{g} + \sum_{j=1}^{s}\mathbf{a}_{ij}\right\}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_s\right] = -\sum_{i=1}^{s}\int_P \mathbf{a}_{i,s+1}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_{s+1}\, d\gamma_{s+1}. \tag{3.14}$$

In particular, the velocity distribution function $f = f_1$ satisfies

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = -\int_P \mathbf{a}_{12}.\boldsymbol{\nabla}_{\mathbf{v}} f_2\, d\gamma_2. \tag{3.15}$$

The right hand side of (3.15) is the collision integral, denoted as Q, and the Boltzmann equation follows from the assumption that the number of particles N is large, and that the joint probability density function $\rho_2(\mathbf{r}, \mathbf{v}; \mathbf{s}, \mathbf{w}, t) = \rho_1(\mathbf{r}, \mathbf{v}, t)\rho_1(\mathbf{s}, \mathbf{w}, t)$, that is to say the probability of a particle being at $\mathbf{r}$ with velocity $\mathbf{v}$ is independent of its probability of being at $\mathbf{s}$ with velocity $\mathbf{w}$. This assumption seems reasonable, providing the range of the inter-particle force is much less than the mean distance between particles, and this we assume; this is the hard-sphere gas assumption. In that case, the collision term takes the form

$$Q = -\int_P \mathbf{a}(\mathbf{r}-\mathbf{s}).\boldsymbol{\nabla}_{\mathbf{v}} f(\mathbf{r},\mathbf{v},t) f(\mathbf{s},\mathbf{w},t)\, d\mathbf{s}\, d\mathbf{w}. \tag{3.16}$$

The Boltzmann equation is a master equation for f, with the added piquancy that the time derivative is one which follows the particles in their six-dimensional position-velocity space. Because the particles satisfy

$$\dot{\mathbf{r}} = \mathbf{v}, \quad \dot{\mathbf{v}} = \mathbf{g}, \tag{3.17}$$

and because we take the body force per unit mass $\mathbf{g} = \mathbf{g}(\mathbf{r})$ to be independent of $\mathbf{v}$, it follows that the Boltzmann equation takes the form

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}}.(f\mathbf{v}) + \boldsymbol{\nabla}_{\mathbf{v}}.(f\mathbf{g}) = Q, \tag{3.18}$$

which also results from the usual form of integral conservation law applied to a volume fixed in $(\mathbf{r}, \mathbf{v})$ space. The collision integral plays the same rôle as the integral term in the master equation (2.22), and is indeed analogous to it.

3.2.1 The collision integral

In question 3.5, we show that for short range forces, Q takes the particularly simple form

$$Q = -\mathbf{A}.\boldsymbol{\nabla}_{\mathbf{v}} f, \quad \mathbf{A} = K\boldsymbol{\nabla} n, \tag{3.19}$$

and $n(\mathbf{r}, t)$ is number density. However, this is not the form which the Boltzmann equation usually takes. In this section, we start from the equation (3.18), and we derive an expression for Q from first principles, based on an assumption of instantaneous elastic collisions between molecules, which we thus conceive of as a collection of hard spheres. More generally, this should be appropriate where the intermolecular forces are conservative and of short range (compared with the molecular mean free path), so that the collision process is very rapid. We will then find a conundrum, since our first principles calculation yields a result quite different to (3.19), and we shall have something to say about this in due course.

Our calculation for Q is based on a master equation approach. Contributions to Q occur via losses (collisions remove particles from the neighbourhood in $\mathbf{v}$), but also gains, whereby collisions beyond $d\mathbf{r}\, d\mathbf{v}$ cause production of particles with velocities near $\mathbf{v}$. As in (2.22) we separate Q into two components,

$$Q = Q_+ - Q_-, \tag{3.20}$$

where Q_+ is the source to $\mathbf{v}$ due to other collisions, and Q_- is the loss from $\mathbf{v}$ in collisions.

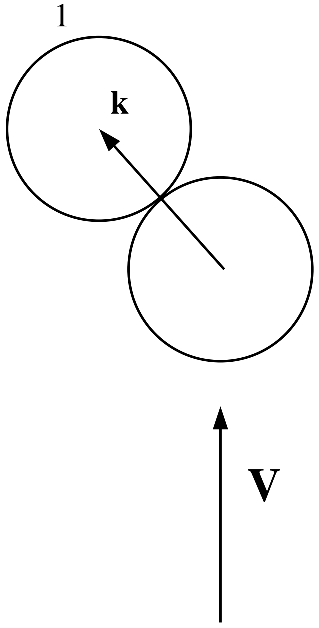

Figure 3.3: Geometry of impact, relative to molecule 1.

Impact

Suppose two molecules (of equal masses and diameters) with velocities $\mathbf{v}$ and $\mathbf{w}$, and labelled respectively 1 and 2, collide as indicated in figure 3.3, which represents the point of impact. Momentum conservation implies

$$\mathbf{v}+\mathbf{w}=\mathbf{v}'+\mathbf{w}', \tag{3.21}$$

where $\mathbf{v}'$ and $\mathbf{w}'$ are the respective velocities of the molecules 1 and 2 after impact. We let $\mathbf{k}$ denote the unit vector along the line of centres, from 2 to 1, at impact, and

$$\mathbf{V}=\mathbf{w}-\mathbf{v} \tag{3.22}$$

denotes the relative velocity. Note that collision requires $\mathbf{V}.\mathbf{k}>0$.

For a purely elastic impact, the relative normal velocity is reversed, while the tangential velocity is continuous (and it is easy to show that energy is then conserved). If $\mathbf{V}'=\mathbf{w}'-\mathbf{v}'$ is the relative velocity following impact, we then have

$$\begin{aligned} -\mathbf{V}.\mathbf{k} &= \mathbf{V}'.\mathbf{k}, \\ \mathbf{V}-(\mathbf{V}.\mathbf{k})\mathbf{k} &= \mathbf{V}'-(\mathbf{V}'.\mathbf{k})\mathbf{k}, \end{aligned} \tag{3.23}$$

and using these together with (3.21), we find

$$\begin{aligned} \mathbf{v}' &= \mathbf{v}+(\mathbf{V}.\mathbf{k})\mathbf{k}, \\ \mathbf{w}' &= \mathbf{w}-(\mathbf{V}.\mathbf{k})\mathbf{k}, \end{aligned} \tag{3.24}$$

which give the post-collisional velocities in terms of the arbitrary $\mathbf{V}$ and $\mathbf{k}$.

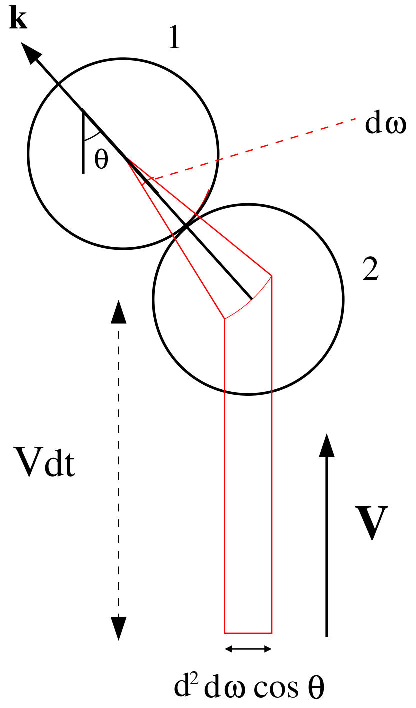

Figure 3.4: Calculation of impact frequency. **V** here is the velocity of molecule 2 relative to molecule 1.

Impact frequency

Next we need to know the frequency at which these impacts occur. The number of molecules in the vicinity of $\mathbf{r}, \mathbf{v}$ is $f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v}$, and the number of impacts in time dt within a solid angle $d\omega(\mathbf{k})$ at the point of contact in direction $\mathbf{k}$ of molecule 1 with molecules moving at relative speed $\mathbf{V}$ is $f(\mathbf{r} - d\mathbf{k}, \mathbf{w}, t)\, dV_{\text{cyl}}\, d\mathbf{w}$, where d is the molecular diameter, and dV_{cyl} is the volume of the cylinder indicated in figure 3.4, and is given by

$$dV_{\text{cyl}} = d^2 \mathbf{k}.\mathbf{V}\, d\omega(\mathbf{k})\, dt. \tag{3.25}$$

The displacement $-d\mathbf{k}$ represents the offset of the centre of molecule 2 evident in figure 3.3, but is small and will be ignored. We thus gain an expression for the loss of molecules in collisions,

$$Q_-\, d\mathbf{r}\, d\mathbf{v}\, dt = f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)\, d^2 \mathbf{k}.\mathbf{V}\, d\omega(\mathbf{k})\, d\mathbf{w}\, d\mathbf{r}\, d\mathbf{v}\, dt; \tag{3.26}$$

integrating over $\mathbf{V}$ and $\mathbf{k}$ such that $\mathbf{V}.\mathbf{k} > 0$, we have

$$Q_- = \int_U \int_{\Omega_+} f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)\, d\Omega\, d\mathbf{w}, \tag{3.27}$$

where we write

$$\begin{aligned} \Omega_+ &= \{\mathbf{k} \mid \mathbf{V}.\mathbf{k} > 0\} \\ d\Omega &= d^2 \mathbf{k}.\mathbf{V}\, d\omega(\mathbf{k}). \end{aligned} \tag{3.28}$$

Calculation of collision integral

It remains to compute the source term for molecules of velocity $\mathbf{v}$. This is done by simply relabelling $\mathbf{v} \leftrightarrow \mathbf{v}'$ and $\mathbf{w} \leftrightarrow \mathbf{w}'$. Since the collision is reversible, the change in velocity formulae in (3.24) remain valid, and the source term is (cf. (3.26))

$$Q_+ \, d\mathbf{r} \, d\mathbf{v} \, dt = f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) \, d^2\mathbf{k}'.\mathbf{V}' \, d\omega(\mathbf{k}') \, d\mathbf{w}' \, d\mathbf{r} \, d\mathbf{v}' \, dt; \tag{3.29}$$

note the primes on the velocities (and the corresponding volume elements) on the right hand side.

We have also written the direction vector as $\mathbf{k}'$, which is cosmetic, but useful, as we now show. As a consequence, the formulae (3.24) apply with the same cosmetic change. The point is that in writing (3.29), the restriction to collisions requires $\mathbf{V}'.\mathbf{k}' > 0$, that is $\mathbf{V}.\mathbf{k}' < 0$. To obtain the same integration range as in (3.27), it is therefore convenient to write

$$\mathbf{k}' = -\mathbf{k}, \tag{3.30}$$

so that $\mathbf{V}.\mathbf{k} > 0$ as before. The formulae (3.24) remain valid as they stand.

Finally, we want to change variables on the right hand side of (3.29) from $\mathbf{v}', \mathbf{w}'$ to $\mathbf{v}, \mathbf{w}$ so that we can carry out the same division by the hypervolume $d\mathbf{r} \, d\mathbf{v} \, dt$ to find Q_+. The transformation (3.24) is linear, and the change of variable yields

$$d\mathbf{v}' \, d\mathbf{w}' = J \, d\mathbf{v} \, d\mathbf{w}, \tag{3.31}$$

where J is the Jacobian of the transformation,

$$J = \left| \frac{\partial(\mathbf{v}', \mathbf{w}')}{\partial(\mathbf{v}, \mathbf{w})} \right|. \tag{3.32}$$

Evaluating the coefficients, we find that J is the modulus of the determinant of the matrix $\mathcal{J}$, in block form,

$$\mathcal{J} = \begin{pmatrix} I - K & K \\ K & I - K \end{pmatrix}, \tag{3.33}$$

where I is the three-by-three identity matrix, and K is the three-by-three orthogonal matrix

$$K_{ij} = k_i k_j. \tag{3.34}$$

Note that $K\mathbf{k} = \mathbf{k}$, and $K\mathbf{m} = K\mathbf{n} = \mathbf{0}$ if $\mathbf{m}$ and $\mathbf{n}$ are independently orthogonal to $\mathbf{k}$. By direct calculation, the following vectors are eigenvectors of $\mathcal{J}$:

$$\begin{pmatrix} \mathbf{m} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{n} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{m} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{n} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ \mathbf{k} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ -\mathbf{k} \end{pmatrix}, \tag{3.35}$$

with respective eigenvectors $1, 1, 1, 1, 1, -1$; thus $\det \mathcal{J} = -1$, and $J = 1$. Hence

$$d\mathbf{v}' \, d\mathbf{w}' = d\mathbf{v} \, d\mathbf{w} \tag{3.36}$$

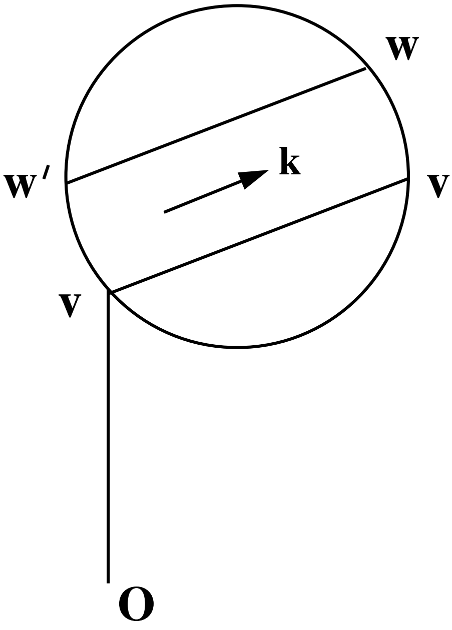

Figure 3.5: Geometric interpretation of Ω_+. O is the origin in velocity space.

in (3.29). Dividing by the hypervolume element and noting that

$$\mathbf{k}'.\mathbf{V}' = \mathbf{k}.\mathbf{V}, \tag{3.37}$$

we obtain the source term for (3.18) in the form

$$Q_+ = \int_U \int_{\Omega_+} f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{w}',t)\, d\Omega\, d\mathbf{w}, \tag{3.38}$$

and the collision term takes the final form

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{w}',t) - f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{w},t)]\, d\Omega\, d\mathbf{w}, \tag{3.39}$$

in which $\mathbf{v}'$ and $\mathbf{w}'$ are given by (3.24).

$Q\{f, f\}$ is a quadratic integral operator in which the integral is five-dimensional, over the three dimensions of velocity space and the two of the solid angle space Ω_+. A useful characterisation of this latter is illustrated in figure 3.5. Given $\mathbf{v}$ and $\mathbf{w}$, we construct the sphere in which $\mathbf{v}$ and $\mathbf{w}$ are diametrically antipodal points: we call this the *antipodal sphere*. The diameter is the vector $\mathbf{V}$, as shown in figure 3.6. For any unit vector $\mathbf{k}$ such that $\mathbf{V}.\mathbf{k} > 0$, $\mathbf{v}'$ and $\mathbf{w}'$ lie on this sphere (and are diametrically antipodal); the simplest way to show this by showing that $\mathbf{v}' - \mathbf{v}$ is orthogonal to $\mathbf{w} - \mathbf{v}'$. Integration over Ω is thus represented as the integration over solid angle subtended by $\mathbf{v}$ on this sphere. In more detail (see figure 3.6), if θ is the polar angle and ϕ the azimuthal angle, then

$$d\Omega = d^2\mathbf{V}.\mathbf{k}\, d\omega = d^2 V \cos\theta \sin\theta\, d\theta\, d\phi = \frac{d^2\, dS}{V}, \tag{3.40}$$

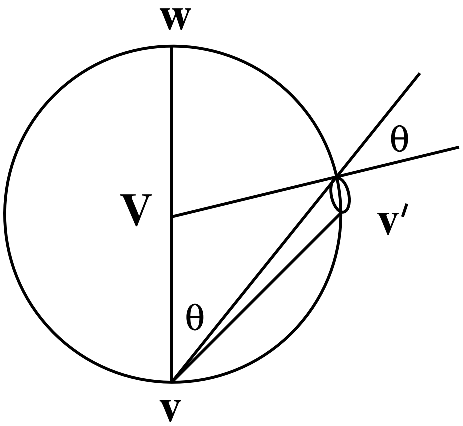

Figure 3.6: Integration with repect to (scaled) solid angle Ω over the antipodal sphere.

where dS is the element of surface area on the sphere. (This last follows from using the spherical polar definition of dS about the centre of the sphere.)

The expression in (3.39), derived from first principles for a hard-sphere gas, can be compared with (3.16), or the simpler hard-sphere expression (3.19); it is quite different! Importantly, (3.16) changes sign under time reversal, while (3.39) does not; thus the Boltzmann equation coming from the BBGKY hierarchy is time-reversible, but that from the first principles calculation is not. Why is this? And why does the hard-sphere calculation not give the same result as the BBGKY one?

The closure of (3.15) by assuming independence of the two particles in ρ_2 to obtain (3.16) does not seem unreasonable, and it maintains reversibility. If one accepts this approximation as fact, then the consequent simplification in question 3.5, which leads to the BBGKY-derived definition

$$Q = -\mathbf{A}.\boldsymbol{\nabla}_{\mathbf{v}} f, \quad \mathbf{A} = \int_P \mathbf{a}(\boldsymbol{\xi}) f(\mathbf{r}-\boldsymbol{\xi}, \mathbf{w}, t)\, d\boldsymbol{\xi}\, d\mathbf{w} \tag{3.41}$$

is also exact, for the same reason that Liouville's equation is exact: the velocity (but let us call it the hyper-velocity) $\dot{\gamma} = (\dot{\mathbf{r}}, \dot{\mathbf{v}})$ is a smooth function of hyper-position $\gamma \in P$.

Exact or not, this prescription is not of much practical use, since during a collision, smooth and singular though $\mathbf{a}$ may be, the velocity changes rapidly. The difference between the BBGKY model and the hard-sphere model is that the latter allows many collisions to occur in its short time interval $\Delta t \gg t_f$, where t_f is the mean time between collisions. In this short time an initially smooth hyper-volume element $d\gamma$ is distorted through collisions into a highly nonlinear hyper-volume element with multiple branching pseudopodia extending, like a fungus, throughout hyperspace Γ: see figure 3.7. It is this chaotic behaviour, analogous to that described for Hamiltonian systems in section 1.5, and particularly for the baker map, which causes the distinction between the exact but useless BBGKY hierarchy and the inexact but effective Boltzmann collision integral (3.39), which is in fact constructed, like Einstein's theory of Brownian motion, or the derivation of the master equation,

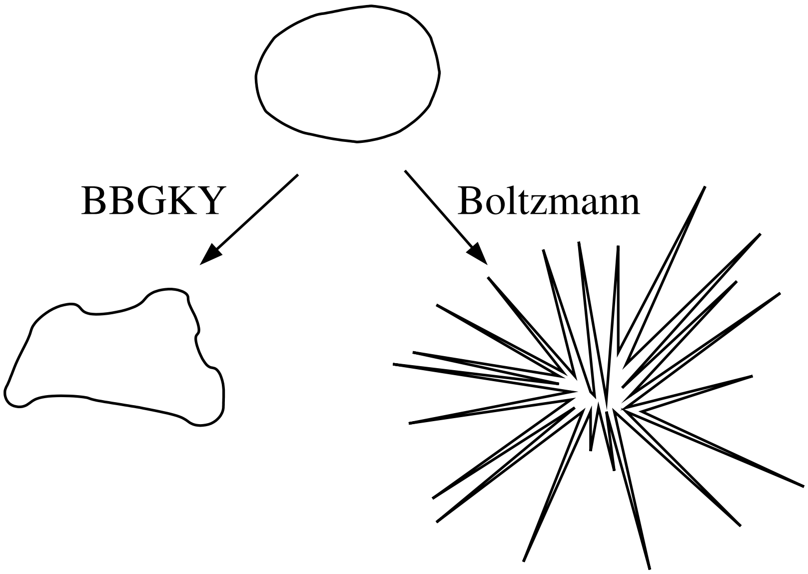

Figure 3.7: The distinction between the smooth BBGKY evolution and the chaotic Boltzmann evolution is one of time scale.

on the basis of probabilistic time-stepping. Another, rather precise, analogy is to compare the Navier-Stokes equations with the Reynolds-averaged equations of fluid mechanics, described in section 1.3. The 'exact' Navier-Stokes equations have chaotic, turbulent solutions at high Reynolds number which they are useless to describe. This is best done with the Reynolds-averaged equations, assuming a good closure for the Reynolds stresses. However, whereas a microscale model for particle mechanics successfully produces a closure for the Boltzmann equation, no comparable microscale solution for the Navier-Stokes equations is known which can provide a mechanistically derived closure for the Reynolds equations. This is the fundamental problem in turbulent fluid flow modelling.

3.2.2 Conservation laws

Note that, because of the conservation of particle number, momentum and energy in the collision, it follows that

$$\int_U \psi(\mathbf{v}) Q \, d\mathbf{v} = 0, \tag{3.42}$$

for the three quantities

$$\psi(\mathbf{v}) = 1,\ \mathbf{v},\ \tfrac{1}{2}v^2, \tag{3.43}$$

though it seems that this is hardly obvious. The integral in (3.42) consists of two parts, corresponding to the division of $Q = Q_+ + Q_-$ in (3.27) and (3.38). For brevity, we write $f(\mathbf{r}, \mathbf{v}, t) = f(\mathbf{v})$, and then

$$\int_U \psi(\mathbf{v}) Q_+ \, d\mathbf{v} = \int_\Sigma \psi(\mathbf{v}) f(\mathbf{v}') f(\mathbf{w}') \, d\Sigma, \tag{3.44}$$

where we write

$$\begin{aligned}\Sigma &= U^2 \times \Omega_+,\\ d\Sigma &= d\Omega\, d\mathbf{w}\, d\mathbf{v}.\end{aligned}\tag{3.45}$$

We change variables from $\mathbf{v}, \mathbf{w}$ to $\mathbf{v}', \mathbf{w}'$. As earlier, the Jacobian is one, and we define $\mathbf{k}' = -\mathbf{k}$. Using (3.24) and (3.37), we then have, on dropping the primes,

$$\int_U \psi(\mathbf{v}) Q_+\, d\mathbf{v} = \int_\Sigma \psi(\mathbf{v}') f(\mathbf{v}) f(\mathbf{w})\, d\Sigma,\tag{3.46}$$

and thus

$$\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = \int_\Sigma [\psi(\mathbf{v}') - \psi(\mathbf{v})] f(\mathbf{v}) f(\mathbf{w})\, d\Sigma.\tag{3.47}$$

In this integral we now interchange $\mathbf{v}$ and $\mathbf{w}$, and we define $\mathbf{k}' = -\mathbf{k}$. Then also, from (3.24), $\mathbf{v}'$ is replaced by $\mathbf{w}'$, and the integral (3.47) can also be written in the form

$$\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = \int_{U^2} \int_{\mathbf{V}.\mathbf{k}'>0} [\psi(\mathbf{w}') - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w})\, d^2\mathbf{k}'.\mathbf{V}\, d\omega\, d\mathbf{w}\, d\mathbf{v}.\tag{3.48}$$

Adding the two expressions (noting that $\mathbf{k}'$ is a dummy variable),

$$2\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = \int_\Sigma [\psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w})\, d\Sigma.\tag{3.49}$$

It follows from this that (3.42) is satisfied identically if (and only if)

$$\psi(\mathbf{v}') + \psi(\mathbf{w}') = \psi(\mathbf{v}) + \psi(\mathbf{w}),\tag{3.50}$$

i. e., ψ is conserved in collisions, which is the case for (3.43), and for no other independent quantity, as mass, momentum and energy are the only conserved quantities. (While this seems reasonable, it is by no means obvious; the result is proved later.)

We define the number density of molecules n at a point in physical space to be

$$n = \int_U f\, d\mathbf{v},\tag{3.51}$$

where we suppose $f \to 0$ as $|\mathbf{v}| \to \infty$. If the molecules have mass m, then the density is defined as

$$\rho = mn.\tag{3.52}$$

We also define the mean velocity by

$$n\mathbf{u} = \int_U f\mathbf{v}\, d\mathbf{v},\tag{3.53}$$

and more generally the mean $\bar{\phi}$ of a quantity ϕ is defined by

$$n\bar{\phi} = \int_U f\phi\, d\mathbf{v}.\tag{3.54}$$

We have the following identity:

$$\int_U \left[\frac{\partial (f\psi)}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}}.(f\psi\mathbf{v}) + \boldsymbol{\nabla}_{\mathbf{v}}.(f\psi\mathbf{g})\right] d\mathbf{v} =$$

$$\int_U \psi \left[\frac{\partial f}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}}.(f\mathbf{v}) + \boldsymbol{\nabla}_{\mathbf{v}}.(f\mathbf{g})\right] d\mathbf{v}$$

$$+ \int_U f \left[\frac{\partial \psi}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}}\psi + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}}\psi\right] d\mathbf{v}. \tag{3.55}$$

On the left hand side, we remove the t and $\mathbf{r}$ derivatives outside the integral, and apply the divergence theorem to the $\mathbf{v}$ derivative, together with the (necessary) assumption $f \to 0$ as $|\mathbf{v}| \to \infty$.[2] Through the definition of the average in (3.54), together with the Boltzmann equation (3.18), (3.55) thus implies (after multiplication by m)

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \boldsymbol{\nabla}.\,(\rho\bar{\psi}\mathbf{u}) + \boldsymbol{\nabla}.\,\mathbf{J}_\psi = \int_U m\psi Q\,d\mathbf{v} + \rho\,\overline{\left[\psi_t + \mathbf{v}.\boldsymbol{\nabla}\psi + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}}\psi\right]}\,, \tag{3.56}$$

where

$$\mathbf{J}_\psi = \rho\overline{\psi\mathbf{u}'} \tag{3.57}$$

is the molecular flux of ψ, the velocity fluctuations $\mathbf{u}'$ are defined by

$$\mathbf{u}' = \mathbf{v} - \mathbf{u}, \tag{3.58}$$

and we have written $\boldsymbol{\nabla} = \boldsymbol{\nabla}_{\mathbf{r}}$.

The averaged term on the right hand side is simplified if we suppose ψ depends only on $\mathbf{v}$, since then $\psi_t = \boldsymbol{\nabla}\psi = 0$, since these partial derivatives are taken with $\mathbf{v}$ constant. Now we take the three values of $\psi = 1,\ \mathbf{v},\ \frac{1}{2}v^2$, as in (3.43), for which the integral term in (3.56) vanishes (see (3.42)), so that the conservation law (3.56) takes the form

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \boldsymbol{\nabla}.\,(\rho\bar{\psi}\mathbf{u}) + \boldsymbol{\nabla}.\,\mathbf{J}_\psi = \rho\overline{\mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}}\psi}. \tag{3.59}$$

For $\psi = 1$, we obtain the conservation of mass equation

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}.\,(\rho\mathbf{u}) = 0; \tag{3.60}$$

for $\psi = \mathbf{v}$, we obtain conservation of momentum in the form

$$\frac{\partial\rho\mathbf{u}}{\partial t} + \boldsymbol{\nabla}.\,(\rho\mathbf{u}\mathbf{u}) = \boldsymbol{\nabla}.\,\boldsymbol{\sigma} + \rho\mathbf{g}, \tag{3.61}$$

where the stress tensor is defined by

$$\boldsymbol{\sigma} = -\rho\overline{\mathbf{u}'\mathbf{u}'}, \tag{3.62}$$

and we follow the tensor notation where $\mathbf{ab}$ denotes the tensor with components $a_i b_j$.

---

[2] Necessary, because f is a density and must integrate over U to a finite quantity.

Finally, we obtain the energy equation by putting $\psi = \frac{1}{2}v^2$. The result of this is

$$\frac{\partial}{\partial t}(\tfrac{1}{2}\rho u^2 + \rho e) + \boldsymbol{\nabla}.\,[(\tfrac{1}{2}\rho u^2 + \rho e)\mathbf{u}] = -\boldsymbol{\nabla}.\,\mathbf{q} + \boldsymbol{\nabla}.\,(\boldsymbol{\sigma}.\mathbf{u}) + \rho\mathbf{g}.\mathbf{u}, \tag{3.63}$$

where the internal energy per unit mass is defined by

$$e = \tfrac{1}{2}\overline{u'^2}, \tag{3.64}$$

and the conductive heat flux is

$$\mathbf{q} = \tfrac{1}{2}\rho\overline{u'^2\mathbf{u}'}. \tag{3.65}$$

A note on kinetic theory

The assumption in the derivation of the collision integral is that the molecules are relatively far apart, in the sense that a typical distance between them, l, is much greater than the molecular diameter d. As we shall see, this will typically be the case for gases, but not for liquids, and so the derivation of the Navier–Stokes equations from the Boltzmann equation is most usually thought to apply to gases. In fact, the formalism can still be applied to liquids, only the form of the collision integral will not be of the Boltzmann form; also the internal energy will not just be given by (3.64), as it will also involve the potential energy associated with intermolecular forces.

For gases, the internal energy per molecule is related to the macroscopic measure, the temperature, by the relation

$$\tfrac{1}{2}m\overline{u'^2} = \tfrac{3}{2}kT, \tag{3.66}$$

where $k = 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant. In addition, we define the pressure in the usual way as

$$p = -\tfrac{1}{3}\sigma_{kk} = \tfrac{1}{3}\rho\overline{u'^2}, \tag{3.67}$$

from which we can derive the perfect gas law

$$p = nkT = \frac{\rho RT}{M}, \tag{3.68}$$

where R is the perfect gas constant and M is the molecular weight, these being defined by

$$R = kA, \quad M = Am, \tag{3.69}$$

with $A = 6 \times 10^{23}$ being Avogadro's number, the number of molecules in a mole.

3.2.3 Boltzmann's H–theorem

We go back to (3.49), which we write in the form

$$\int_U \psi(\mathbf{v})Q\,d\mathbf{v} = \tfrac{1}{2}\int_\Sigma \Delta\psi(\mathbf{v},\mathbf{w})f(\mathbf{v})f(\mathbf{w})\,d\Sigma, \tag{3.70}$$

where

$$\Delta\psi \equiv \psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w}). \tag{3.71}$$

In the integral, we change variables from $\mathbf{v}, \mathbf{w}$ to $\mathbf{v}', \mathbf{w}'$, and in addition we define $\mathbf{k}' = -\mathbf{k}$. We then change the dummy labelling between the primed and unprimed variables, noting (3.24) and its inverses; the result is

$$\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = -\tfrac{1}{2} \int_\Sigma \Delta\psi(\mathbf{v}, \mathbf{w}) f(\mathbf{v}') f(\mathbf{w}')\, d\Sigma. \tag{3.72}$$

Adding the two results, we obtain

$$\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = \tfrac{1}{4} \int_\Sigma \Delta\psi(\mathbf{v}, \mathbf{w}) [f(\mathbf{v}) f(\mathbf{w}) - f(\mathbf{v}') f(\mathbf{w}')]\, d\Sigma. \tag{3.73}$$

Now suppose that f is independent of $\mathbf{r}$, or more generally that it is slowly varying in $\mathbf{r}$, in a sense which will be made clearer later. It may depend on t, though we do not write this dependence explicitly. Define a function

$$H = \int_U f \ln f\, d\mathbf{v}. \tag{3.74}$$

H is a function of t, and its derivative is

$$\dot{H} = \int_U (1 + \ln f) Q\, d\mathbf{v} \tag{3.75}$$

(the term involving $\mathbf{g}$ vanishes identically by an application of the relation

$$\int_U \boldsymbol{\nabla}_{\mathbf{v}} G\, d\mathbf{v} = \int_{\partial U} G \mathbf{n}\, dS, \tag{3.76}$$

if $G \to 0$ as $|\mathbf{v}| \to \infty$). Applying (3.73),

$$\dot{H} = \tfrac{1}{4} \int_\Sigma \ln\left[\frac{f(\mathbf{v}') f(\mathbf{w}')}{f(\mathbf{v}) f(\mathbf{w})}\right] [f(\mathbf{v}) f(\mathbf{w}) - f(\mathbf{v}') f(\mathbf{w}')]\, d\Sigma. \tag{3.77}$$

Since $f > 0$ and $(1-\zeta)\ln\zeta \le 0$, it follows that $\dot{H} \le 0$. In addition, H is bounded below,[3] and thus H tends to a constant, in which

$$\Delta \ln f = 0. \tag{3.78}$$

---

[3] This seems intuitively reasonable, since $f \ln f$ is bounded below, and generally it will be true; however, it is possible to construct pathological sequences of f for which it might not be true. For example, take $f_M = \dfrac{1}{4\pi v^3 \ln^2 v}$ for $e < v < M$, and zero otherwise: then n remains bounded as $M \to \infty$, while $H \sim -3 \ln\ln M \to -\infty$. However, for systems of finite total energy (as we assume), the integral $\displaystyle\int v^2 f\, d\mathbf{v}$ is bounded and remains so; if H were to become unbounded, we would then have to have $f < \exp[-O(v^2)]$, in which case the integral defining H is finite. This is the argument given by Chapman and Cowling (1970, p. 67, footnote), but even this argument is insufficient; a more complete demonstration is given in question 3.9.

This is Boltzmann's H–theorem. The state $\dot{H} = 0$ defines an equilibrium distribution, called the *Maxwellian distribution.*

(3.78) expresses the fact that $\ln f$ is conserved in collisions, and because Δ is a linear operator, $\ln f$ must be a linear combination of the three conserved quantities in (3.43), i. e.,

$$f = A \exp[\mathbf{B}.\mathbf{v} - \tfrac{1}{2}Cv^2], \tag{3.79}$$

or equivalently, completing the square,

$$f = \hat{A} \exp[-\tfrac{1}{2}C|\mathbf{v} - \hat{\mathbf{v}}|^2]. \tag{3.80}$$

We can now determine the constants in terms of the mean number density, velocity, and temperature, defined, using (3.51), (3.53) and (3.66), by

$$n = \int_U f\,d\mathbf{v}, \quad n\mathbf{u} = \int_U f\mathbf{v}\,d\mathbf{v}, \quad \frac{nkT}{m} = \tfrac{1}{3}\int_U f|\mathbf{v} - \mathbf{u}|^2\,d\mathbf{v}. \tag{3.81}$$

Carrying out the calculations, we find

$$\hat{\mathbf{v}} = \mathbf{u}, \quad C = \frac{m}{kT}, \quad \hat{A} = n\left(\frac{m}{2\pi kT}\right)^{3/2}, \tag{3.82}$$

and thus

$$f = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{mu'^2}{2kT}\right]. \tag{3.83}$$

This is the Maxwellian distribution, a Gaussian in the velocity fluctuation $\mathbf{u}'$. Note that (3.83) can be written in the form

$$f = \frac{n}{(2\pi c^2)^{3/2}} \exp\left[-\frac{u'^2}{2c^2}\right], \tag{3.84}$$

where

$$c = \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}} = \sqrt{\frac{p}{\rho}} \tag{3.85}$$

is the isothermal sound speed.

Non-dimensional estimates

The use of the above theory in the macroscopic description of fluids introduces the important concept of scale. In particular, we may expect macroscopic quantities such as density and velocity to vary on a macroscopic length scale, which for simplicity we will identify as the dimension L of our box, with its N particles. In solving the Boltzmann equation, it is then natural to non-dimensionalise the variables, and this will give us some idea of the relative sizes of the terms.

As we are about to allow spatial variations in the macroscopic variables n, T and u, we define typical scales for these variables as n_0, T_0 and

$$v_0 = \sqrt{\frac{kT_0}{m}}. \tag{3.86}$$

The particle number density scale n_0 defines a mean inter-particle distance

$$l = \frac{1}{n_0^{1/3}}, \tag{3.87}$$

and we take v_0 in (3.86) to be a typical fluctuation velocity scale. The intermolecular potential varies over an interaction distance which we may take to be the molecular diameter d (this is discussed further in section 3.6), and the hard sphere gas assumption presumes $d \ll l$.

The inter-particle length is much less than the mean free path, which is the typical distance a particle progresses between collisions. A single particle travelling in its domain of cross-sectional area l^2 encounters another particle every distance l, but typically not in the same position. Looking ahead of itself, it needs to encounter $\sim (l/d)^2$ particles (which thus cover the cross section), before it is likely to collide with one. The mean free path is thus[4]

$$l_f \sim \frac{l^3}{d^2} = \frac{1}{n_0 d^2}. \tag{3.88}$$

We can also define a corresponding mean free time between collisions,

$$t_f = \frac{l_f}{v_0}, \tag{3.89}$$

and a mean collision time

$$t_c = \frac{d}{v_0}. \tag{3.90}$$

We non-dimensionalise the variables as

$$\begin{gathered} n \sim n_0, \quad f \sim \frac{n_0}{v_0^3}, \quad Q \sim \frac{n_0^2 d^2}{v_0^2}, \quad \mathbf{r} \sim L, \\ \mathbf{v} \sim v_0, \quad \mathbf{g} \sim g, \quad t \sim \frac{L}{v_0}, \quad T \sim T_0, \end{gathered} \tag{3.91}$$

and denote the dimensionless values of n and T as n^* and T^* (the asterisk is omitted from the velocities, however); then the Boltzmann equation (3.18) with (3.39) takes the dimensionless form

$$\begin{gathered} \varepsilon \left[\frac{\partial f}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}} . (f\mathbf{v}) + \frac{1}{F^2} \boldsymbol{\nabla}_{\mathbf{v}} . (f\mathbf{g}) \right] = Q, \\ Q = \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)] \, d\Omega \, d\mathbf{w}, \end{gathered} \tag{3.92}$$

where

$$\varepsilon = \frac{l_f}{L} = \frac{1}{n_0 d^2 L}, \quad F = \frac{v_0}{\sqrt{gL}}. \tag{3.93}$$

F is a kind of Froude number (actually the Mach number times the Froude number), and is typically large. The parameter ε is known as the Knudsen number, often written as Kn, and is usually very small. This allows us to develop a perturbative solution of the Boltzmann equation when f also depends on $\mathbf{r}$.

---

[4] Chapman and Cowling (1970, p. 88) use a more elaborate calculation to show that $l_f = \dfrac{1}{\pi\sqrt{2} n d^2}$.

3.2.4 The Chapman-Enskog method

The terms in the conservation of mass, momentum and energy equations which need to be specified are the stress tensor and the conductive heat flux. From (3.62) and (3.65), these are

$$\boldsymbol{\sigma} = -\rho\overline{\mathbf{u}'\mathbf{u}'}, \quad \mathbf{q} = \tfrac{1}{2}\rho\overline{u'^2\mathbf{u}'}. \tag{3.94}$$

If we use the Maxwellian distribution for f to provide expressions for these, we find

$$\boldsymbol{\sigma} = -p\mathbf{I}, \quad \mathbf{q} = \mathbf{0}; \tag{3.95}$$

hardly surprising, since our assumption of spatial independence implies uniform temperature and velocity. Thus in order to compute viscosity and thermal conductivity, we must consider corrections to the equilibrium Maxwellian distribution due to variation of f with $\mathbf{r}$; the way to do this is generally referred to as the *Chapman–Enskog method*.

We write the material derivative of f in $P = V \times U$ as $\dot{f}$, so that the dimensionless Boltzmann equation in (3.92) is just

$$\varepsilon\dot{f} = Q(f, f), \tag{3.96}$$

where it is now useful to define the collision integral Q in terms of the symmetric bilinear operator

$$Q\{f, g\}(\mathbf{v}) = \tfrac{1}{2}\int_U\int_{\Omega_+}[f(\mathbf{v}')g(\mathbf{w}') + f(\mathbf{w}')g(\mathbf{v}') - f(\mathbf{v})g(\mathbf{w}) - f(\mathbf{w})g(\mathbf{v})]\,d\Omega\,d\mathbf{w}. \tag{3.97}$$

First note that by putting

$$f = e^{\Phi}, \tag{3.98}$$

(3.96) can be written in the form

$$\varepsilon\dot{\Phi} = \int_U\int_{\Omega_+}[\exp(\Delta\Phi) - 1]\,f(\mathbf{w})\,d\Omega\,d\mathbf{w}. \tag{3.99}$$

The Maxwell solution in dimensionless form is

$$\Phi_0 = \ln\left[\frac{n^*}{(2\pi T^*)^{3/2}}\right] - \frac{u'^2}{2T^*}, \tag{3.100}$$

and is the first term in an asymptotic expansion of the solution in powers of ε. Calculation of the viscosity and thermal conductivity requires computation of the solution to the next order.

We expand the solution as

$$\Phi = \Phi_0 + \varepsilon\phi + \dots; \tag{3.101}$$

noting that $\Delta\Phi_0 = 0$, it follows that ϕ satisfies the linear equation

$$\mathcal{L}\phi = \dot{\Phi}_0, \tag{3.102}$$

where we define the linear integral operator

$$\mathcal{L}\phi = \int_U \int_{\Omega_+} f_0(\mathbf{w})\Delta\phi \, d\Omega \, d\mathbf{w}, \tag{3.103}$$

where here $f_0 = e^{\Phi_0}$ is the Maxwellian. Alternatively, by direct calculation from (3.96),

$$\mathcal{L}\phi = \frac{2}{f_0} Q(f_0, f_0\phi). \tag{3.104}$$

(3.102) is a linear Fredholm integral equation, and can be treated using standard methods, as described below.

Useful properties of $\mathcal{L}$ follow from consideration of the properties of the collision integral operator $Q(f, g)$. We consider the integral

$$I = \int_U \psi(\mathbf{v}) Q\{f, g\}(\mathbf{v}) \, d\mathbf{v}, \tag{3.105}$$

using the definition of Q in (3.97). We can then write I in three further ways, analogously to the manipulations following (3.44), that is, we firstly re-label the variables by swapping $\mathbf{v}$ with $\mathbf{w}$ (and thus also $\mathbf{v}'$ with $\mathbf{w}'$); secondly, we change variables from $\mathbf{v}, \mathbf{w}$ to $\mathbf{v}', \mathbf{w}'$; and thirdly, we repeat the first manoeuvre on the formula obtained from the second. This gives four different definitions of I; adding, and dividing by four, we obtain the relation

$$I = \tfrac{1}{8} \int_\Sigma \Delta\psi [f(\mathbf{v})g(\mathbf{w}) + f(\mathbf{w})g(\mathbf{v}) - f(\mathbf{v}')g(\mathbf{w}') - f(\mathbf{w}')g(\mathbf{v}')] \, d\Sigma. \tag{3.106}$$

Now we put $f = f_0$, $g = f_0\phi$ into this; using the definition of I in (3.105), we find (noting that $f_0(\mathbf{v}')f_0(\mathbf{w}') = f_0(\mathbf{v})f_0(\mathbf{w})$)

$$\int_U f_0(\mathbf{v})\psi(\mathbf{v})\mathcal{L}\phi(\mathbf{v}) \, d\mathbf{v} = -\tfrac{1}{4} \int_\Sigma f_0(\mathbf{v}) f_0(\mathbf{w}) \Delta\psi \Delta\phi \, d\Sigma, \tag{3.107}$$

and evidently because of the symmetry of this last expression, we also have

$$\int_U f_0(\mathbf{v})\psi(\mathbf{v})\mathcal{L}\phi(\mathbf{v}) \, d\mathbf{v} = \int_U f_0(\mathbf{v})\phi(\mathbf{v})\mathcal{L}\psi(\mathbf{v}) \, d\mathbf{v}. \tag{3.108}$$

We now define an inner product as

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v})\phi(\mathbf{v})\bar{\psi}(\mathbf{v}) \, d\mathbf{v} \tag{3.109}$$

(the overbar denotes the complex conjugate); it follows from (3.108) that $\mathcal{L}$ is self-adjoint, and therefore the integral equation (3.102) only has solutions if $\langle \phi, \eta \rangle = 0$ for all null solutions of $\mathcal{L}\eta = 0$. One can show that the null solutions are precisely the collision invariants $\chi \in \mathcal{N} = \operatorname{span}\{1, \mathbf{v}, \tfrac{1}{2}v^2\}$, and thus (3.102) only has solutions if

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \tag{3.110}$$

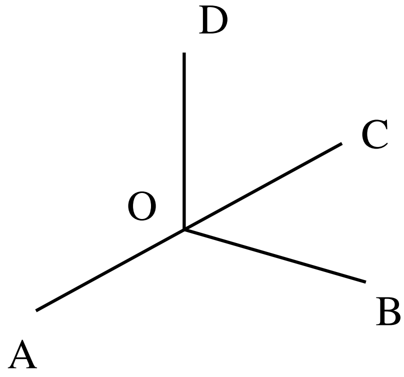

Figure 3.8: The initial grid used in the proof that $\mathcal{N}$ is the null space of $\mathcal{L}$.

for these null solutions ($\mathcal{N}$ is the null space of $\mathcal{L}$).

Although it is reasonable to imagine that the null space of $\mathcal{L}$ is precisely $\mathcal{N}$, it is not that simple to prove. An elegant argument due to Harold Grad is as follows. First, in view of (3.107), we see that

$$\langle \phi, \mathcal{L}\phi \rangle \leq 0, \tag{3.111}$$

and equals zero if and only if $\Delta\phi = 0$, i. e., ϕ is conserved in collision. It follows that $\mathcal{L}\phi = 0$ if and only if $\Delta\phi = 0$ for all points on the sphere with $\mathbf{v}$ and $\mathbf{w}$ as antipodal points, for any $\mathbf{v}$ and $\mathbf{w}$. Such functions are called *summational invariants.*

Suppose we can find a function ϕ which is a summational invariant and such that $\phi = 0$ on the five points indicated in figure 3.8, i. e., at O: $(0,0,0)$, A: $(0,-1,0)$, B: $(1,0,0)$, C: $(0,1,0)$ and D: $(0,0,1)$. Where there are three points of a square where $\phi = 0$, the property of summational invariance implies that $\phi = 0$ at the fourth point also (by drawing the circle through the four points). In this way, we can show that $\phi = 0$ at each of the other seven points of the cuboid spanned by $OABCD$. Additionally, completing the square formed from A, B and C yields $\phi = 0$ at B': $(-1,0,0)$, the reflection of B in the plane $AOCD$. Repeating the argument for the grid $OAB'CD$ shows that $\phi = 0$ at the vertices of the reflected cuboid, and indeed the argument extends to allow $\phi = 0$ at all points on the cubic grid surrounding the origin (with A, B, C and D on the faces) and thence to all points in U with integer coordinates.

Next we consider a square grid as shown in figure 3.9, with an interior square $abcd$. We then have $\phi_a + \phi_b = 0$ (by consideration of the square $OaCb$), and similarly $\phi_b + \phi_c = 0$, $\phi_c + \phi_d = 0$, and lastly from the square $abcd$ itself, $\phi_a + \phi_b + \phi_c + \phi_d = 0$. From these we find that $\phi = 0$ at all four points, and hence at all points of the subdivided grid in U. The subdivision can be iterated indefinitely, with the consequence that if ϕ is continuous, then it is identically zero. Finally, suppose that $\mathcal{L}\phi = 0$, ϕ is continuous, and that $\phi = \phi_A$ at A, etc. (not all zero); we can uniquely choose (five) coefficients a, $\mathbf{b}$ and c so that the function

$$\psi = a + \mathbf{b}.\mathbf{v} + \tfrac{1}{2}cv^2 \tag{3.112}$$

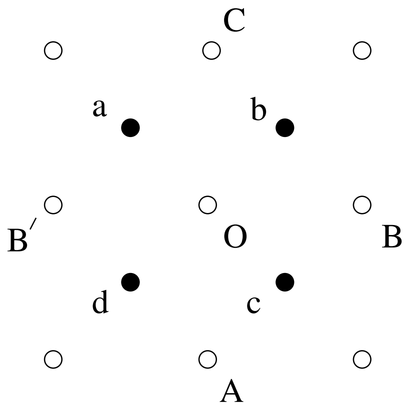

Figure 3.9: Subdividing the grid.

is equal to ϕ at these five points. Then $\mathcal{L}(\phi-\psi)=0$ and $\phi-\psi=0$ at the five points; thus $\phi\equiv\psi$, which shows that in fact $\phi\in\mathcal{N}$.

The derivation of the conservation laws from (3.55) involves multiplication of the Boltzmann equation by the null solutions χ. In the linear equation (3.102), this corresponds (since $\Phi_0=\ln f_0$) to projection on to $\mathcal{N}$ using the inner product (3.110). Thus the conditions (3.110) will simply reproduce the conservation laws which we already have; what we need to do is to find the parts of $\dot{\Phi}_0$ which are in the orthogonal complement $\mathcal{N}_\perp$ of $\mathcal{N}$.

First we calculate $\dot{\Phi}_0$. It is convenient to work with the functions $1, \mathbf{u}', \frac{1}{2}u'^2$, which also form a basis for $\mathcal{N}$. We write (3.100) in the form

$$\Phi_0 = A - \tfrac{1}{2}Cu'^2, \tag{3.113}$$

where

$$A = \ln\left[\frac{n^*}{(2\pi T^*)^{3/2}}\right], \quad C = \frac{1}{T^*}. \tag{3.114}$$

Calculation then yields

$$\dot{\Phi}_0 = \Phi_{\mathcal{N}} - \mathbf{W}.\boldsymbol{\nabla}C + CU_{ij}\frac{\partial u_i}{\partial x_j}, \tag{3.115}$$

where

$$\Phi_{\mathcal{N}} = \frac{dA}{dt} + \mathbf{u}'.\left[\boldsymbol{\nabla}A - \frac{C\mathbf{g}}{F^2} + C\frac{d\mathbf{u}}{dt} - \tfrac{5}{2}T^*\boldsymbol{\nabla}C\right] + \tfrac{1}{2}u'^2\left[\tfrac{2}{3}C\boldsymbol{\nabla}.\mathbf{u} - \frac{dC}{dt}\right], \tag{3.116}$$

and

$$\mathbf{W} = \left(\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*\right)\mathbf{u}', \quad U_{ij} = u'_iu'_j - \tfrac{1}{3}u'^2\delta_{ij}. \tag{3.117}$$

The term $\Phi_{\mathcal{N}}$ lies in the null space of $\mathcal{L}$, and as we now show, $\mathbf{W}$ and $\mathbf{U}$ are orthogonal both to each other and to $\mathcal{N}$. Therefore (3.110) implies $\Phi_{\mathcal{N}}=0$, and thus the particular solution we seek of (3.102) can be written as

$$\phi = -\boldsymbol{\xi}.\boldsymbol{\nabla}C + C\boldsymbol{\eta}\mathbin{:}\boldsymbol{\nabla}\mathbf{u}, \tag{3.118}$$

where

$$\mathcal{L}\boldsymbol{\xi} = \mathbf{W}, \quad \mathcal{L}\boldsymbol{\eta} = \mathbf{U}. \tag{3.119}$$

In general, one might add components of the homogeneous solution from $\mathcal{N}$, but in fact they can be taken to be zero without loss of generality by simply taking the solution for Φ_0 to contain the entire dependence on $\mathcal{N}$.

Norms and inner products

First we calculate the inner products and norms of the elements of the null space $\mathcal{N}$. Quantities of particular note are

$$M_2 = \overline{u'^2} = \int_U f_0 u'^2\, d\mathbf{v} = 3n^* T^*,$$

$$M_4 = \overline{u'^4} = \int_U f_0 u'^4\, d\mathbf{v} = 15 n^* T^{*2}. \tag{3.120}$$

Note that the dimensionless values of n and T can be taken to be one, but these values are not used yet. The inner products in $\mathcal{N}$ are easily found to be

$$\langle 1, 1\rangle = n, \quad \langle u_i', u_j'\rangle = \tfrac{1}{3} M_2 \delta_{ij}, \quad \langle \tfrac{1}{2}u'^2, \tfrac{1}{2}u'^2\rangle = \tfrac{1}{4} M_4,$$

$$\langle 1, u_i'\rangle = 0, \quad \langle 1, \tfrac{1}{2}u'^2\rangle = \tfrac{1}{2} M_2, \quad \langle \tfrac{1}{2}u'^2, u_i'\rangle = 0, \tag{3.121}$$

where we make liberal use of symmetry arguments. It is further straightforward to show that $\mathbf{W}, \mathbf{U} \perp \mathcal{N}$, and that additionally $\mathbf{W} \perp \mathbf{U}$, as we stated above.

The solutions of (3.119) have the form

$$\boldsymbol{\xi} = -F(u')\mathbf{u}', \quad \boldsymbol{\eta} = -G(u')\mathbf{U}. \tag{3.122}$$

Without loss of generality we may choose $\boldsymbol{\xi}, \boldsymbol{\eta} \perp \mathcal{N}$ (which thus specifies them uniquely). One can even with some labour find approximate expressions for F and G, but we do not pursue that here.

The justification for the forms in (3.122) is not so easy to deduce, and we now do so. It relies on a certain rotational invariance of the operator $\mathcal{L}$. We write (3.103) in the form

$$\mathcal{L}\phi = \int_U f_0(w) \left[\int_{\Omega_+} \Delta\phi(\mathbf{v}, \mathbf{w}, \boldsymbol{\Omega})\, d\Omega \right] d\mathbf{w}, \tag{3.123}$$

which recognises that the Maxwellian is a function of the magnitude of $\mathbf{w}$, and that $\Delta\phi$ is a function of both $\mathbf{v}$ and $\mathbf{w}$, which together define the sphere spanned by $\boldsymbol{\Omega}$, as well as the direction element $\boldsymbol{\Omega}$ (cf. figures 3.5 and 3.6).

Now suppose that

$$\boldsymbol{\phi} = g(v)\mathbf{v}; \tag{3.124}$$

thus $\mathcal{L}\boldsymbol{\phi}$ is a vector. Let us consider the effect on $\mathcal{L}\boldsymbol{\phi}$ of a rotation about the $\mathbf{v}$ axis, that is, we multiply $\mathcal{L}\boldsymbol{\phi}$ by a matrix R which is orthogonal, and which satisfies $R\mathbf{v} = \mathbf{v}$. If we define

$$\mathbf{w} = R^T \mathbf{w}^*, \quad \mathbf{k} = R^T \mathbf{k}^*, \tag{3.125}$$

then, noting also that $\mathbf{v} = R^T\mathbf{v}$, we find that

$$\mathbf{v}' = R^T\mathbf{v}^{*\prime}, \quad \mathbf{w}' = R^T\mathbf{w}^{*\prime}, \tag{3.126}$$

and thus

$$R\Delta\boldsymbol{\phi} = \Delta\boldsymbol{\phi}^* = \Delta\boldsymbol{\phi}(\mathbf{v}, \mathbf{w}^*, \boldsymbol{\Omega}^*), \tag{3.127}$$

where $\boldsymbol{\Omega}^*$ is the direction element associated with $\mathbf{k}^*$. The direction sphere Ω_+ is unaffected by the transformation, since $\mathbf{V}.\mathbf{k} = \mathbf{V}^*.\mathbf{k}^*$. It then follows that if we change variable to $\mathbf{w}^*$ in (3.123),

$$R\mathcal{L}\boldsymbol{\phi} = \mathcal{L}\boldsymbol{\phi}, \tag{3.128}$$

since the Maxwellian and the volume element are unchanged by the transformation.

If we suppose that

$$\mathcal{L}\boldsymbol{\phi} = \mathbf{u}. \tag{3.129}$$

It follows from (3.128) that

$$R\mathbf{u} = \mathbf{u} \tag{3.130}$$

for any rotation which leaves (only) $\mathbf{v}$ invariant, and this implies that in fact $\mathbf{u} \parallel \mathbf{v}$. Thus we always have

$$\mathcal{L}[g(v)\mathbf{v}] = h(v)\mathbf{v}, \tag{3.131}$$

where h must be a function only of $v = |\mathbf{v}|$.

Now let us extend the argument to tensors, and specifically we consider the tensor $\boldsymbol{\phi}$ to be of the form

$$\boldsymbol{\phi} = g(v)\mathbf{v}\mathbf{v}, \quad \phi_{ij} = g(v)v_iv_j. \tag{3.132}$$

Note that $\boldsymbol{\phi}$ is symmetric. Following through the argument used above, we find

$$R_{ik}R_{jl}\Delta\phi_{kl}(\mathbf{v}, \mathbf{w}, \boldsymbol{\Omega}) = \Delta\phi_{ij}(\mathbf{v}, \mathbf{w}^*, \boldsymbol{\Omega}^*), \tag{3.133}$$

and thus, analogously to (3.128),

$$R_{ik}R_{jl}\mathcal{L}\phi_{kl} = \mathcal{L}\phi_{ij}. \tag{3.134}$$

Now let us suppose that

$$\mathcal{L}[g(v)v_iv_j] = W_{ij}, \tag{3.135}$$

and note that W_{ij} is symmetric. It then follows from the invariance result (3.134) that

$$\mathcal{R}\mathbf{W} = \mathbf{W}, \quad \mathcal{R}_{ijkl} = R_{ik}R_{jl}, \quad R_{ik}R_{jl}W_{kl} = W_{ij}, \tag{3.136}$$

analogously to (3.130).

It is convenient to think of the components of $\mathbf{W}$ as a nine-dimensional vector in $U \times U$, and if $\mathbf{u}$, $\mathbf{v}$, $\mathbf{w}$ form an orthogonal basis in U, then the nine tensors $\mathbf{uu}$, $\mathbf{uv}$, etc. form an orthogonal basis in U^2. Let us temporarily write these with a central dot, thus $\mathbf{uu} = \mathbf{u}\cdot\mathbf{u}$, etc. We then have $\mathcal{R}_{ijkl}v_kv_l = R_{ik}v_kR_{jl}v_l = v_iv_j$, so $\mathcal{R}(\mathbf{v}\cdot\mathbf{v}) = \mathbf{v}\cdot\mathbf{v}$. In a similar fashion, $\mathcal{R}(\mathbf{u}\cdot\mathbf{v}) = R\mathbf{u}\cdot\mathbf{v}$, $\mathcal{R}(\mathbf{u}\cdot\mathbf{w}) = R\mathbf{u}\cdot R\mathbf{w}$, and so on.

Now since R is a rotation about the $\mathbf{v}$ axis, it is clear that both $R\mathbf{u}$ and $R\mathbf{w}$ lie in the $(\mathbf{u},\mathbf{w})$ plane, and thus are linear combinations of $\mathbf{u}$ and $\mathbf{w}$; more specifically,

$$\begin{aligned} R\mathbf{w} &= \mathbf{w}\cos\theta+\mathbf{u}\sin\theta, \\ R\mathbf{u} &= -\mathbf{w}\sin\theta+\mathbf{u}\cos\theta, \end{aligned} \qquad (3.137)$$

where θ is the angle through which R turns the $(\mathbf{w},\mathbf{u})$ coordinates. We thus see that in U^2, $\mathcal{R}$ leaves $\mathbf{vv}$ invariant, and the eight-dimensional orthogonal subspace is also invariant under $\mathcal{R}$. In fact, $\mathcal{R}$ is an orthogonal matrix in U^2 (see question 3.12), and so the conclusion is analogous to that for (3.130), with the exception that there is another invariant under $\mathcal{R}$, which is the unit tensor

$$\boldsymbol{\delta}=\tfrac{1}{3}\left(\mathbf{uu}+\frac{\mathbf{vv}}{v^2}+\mathbf{ww}\right), \qquad (3.138)$$

if we assume that $\mathbf{u}$ and $\mathbf{w}$ are unit vectors.[5] That this is an invariant follows from inspection of (3.136), and that $\mathbf{vv}$ and $\boldsymbol{\delta}$ are the only two such invariants under $\mathcal{R}$ follows straightforwardly but laboriously from using (3.137) (see question 3.13). Thus the general solution of (3.136) is a linear combination of $\mathbf{vv}$ and $\boldsymbol{\delta}$, and thus

$$\mathcal{L}[g(v)\mathbf{vv}]=h(v)\mathbf{vv}+k(v)\boldsymbol{\delta}. \qquad (3.139)$$

Since also $\mathcal{L}[p(v)]=q(v)$, it follows that

$$\mathcal{L}\left[g(v)\left\{\mathbf{vv}-\tfrac{1}{3}\boldsymbol{\delta}\right\}\right]=h(v)\left\{\mathbf{vv}-\tfrac{1}{3}\boldsymbol{\delta}\right\}, \qquad (3.140)$$

since the left hand side, and therefore also the right hand side, has zero trace.

These results do not prove that the solutions of (3.119) are of the forms in (3.122), but they show that such solutions are possible, providing suitable scalar functions F and G can be found, and this follows naturally from the fact that F and G satisfy inhomogeneous Fredholm equations in which the inhomogeneous terms are orthogonal to the null space of the integral operator. That the solutions then must be of the form of (3.122) follows from the fact that they are unique (if in $\mathcal{N}_\perp$).

3.2.5 Viscosity and thermal conductivity

We return to the definitions of the stress tensor and the heat flux in (3.94). First we write these in terms of the dimensionless coordinates. We then find

$$\sigma_{ij}=-p\delta_{ij}+\tau_{ij},\quad \tau_{ij}=-\frac{kT_0}{d^2L}\langle\phi,u'_iu'_j\rangle=-\frac{kT_0}{d^2L}\langle\phi,U_{ij}\rangle, \qquad (3.141)$$

since $\phi\perp\frac{1}{2}u'^2$. Now note that $\mathbf{u'u'}$ is orthogonal to $\boldsymbol{\xi}$ (using (3.122)), and so only the component of (3.118) proportional to $\boldsymbol{\eta}$ contributes to (3.141). Writing all this out,

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[5] The simplest way to see this is to choose axes parallel to $(\mathbf{u},\mathbf{v},\mathbf{w})$, so that $\mathbf{uu}=\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix}$, etc., and (3.138) follows in arbitrary coordinate systems since both sides are tensors.

and converting $\boldsymbol{\nabla}\mathbf{u}$ to dimensional form, we find (using the summation convention)

$$\tau_{ij} = \frac{\sqrt{mkT}}{d^2}\beta_{ijkl}\frac{\partial u_k}{\partial x_l}, \tag{3.142}$$

where T is dimensional temperature, and β_{ijkl} is the dimensionless fourth order tensor

$$\beta_{ijkl} = \frac{1}{T^{*3/2}}\langle GU_{kl}, U_{ij}\rangle. \tag{3.143}$$

To calculate β_{ijkl}, we note first that symmetry considerations show that all the components are zero unless $(k, l) = (i, j)$ or (j, i). There are then two cases. If $i \neq j$, then

$$\tau_{ij} = 2\mu\dot{\varepsilon}_{ij}, \tag{3.144}$$

where

$$\dot{\varepsilon}_{ij} = \tfrac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{3.145}$$

is the strain rate tensor, and the viscosity is

$$\mu = \frac{\sqrt{mkT}}{d^2}\mu^*, \quad \mu^* = \frac{1}{T^{*3/2}}\langle GU_{ij}, u_i' u_j'\rangle \tag{3.146}$$

(not summed). Evidently μ is independent of the particular choice of i and j; in fact, we have also

$$\mu^* = \frac{1}{T^{*3/2}}\langle GU_{ij}, U_{ij}\rangle = \frac{1}{T^{*3/2}}\left.\langle Gu_i'^2, u_j'^2\rangle\right|_{i\neq j}. \tag{3.147}$$

If $i = j$, then

$$\tau_{ii} = \frac{\sqrt{mkT}}{d^2}\sum_k \frac{1}{T^{*3/2}}\langle GU_{kk}, u_i'^2\rangle\frac{\partial u_k}{\partial x_k}, \tag{3.148}$$

and for each value of k, we find

$$\langle GU_{kk}, u_i'^2\rangle = \langle Gu_k'^2, u_i'^2\rangle - (\tfrac{1}{3}G_1 + \tfrac{2}{3}G_2), \tag{3.149}$$

where

$$G_1 = \langle Gu_i'^2, u_i'^2\rangle, \quad G_2 = \left.\langle Gu_i'^2, u_j'^2\rangle\right|_{i\neq j} \tag{3.150}$$

(and these are independent of i, j). By direct calculation, we have, putting $\mathbf{u}' = \sqrt{T^*}(x, y, z)$,

$$\begin{aligned} G_1 &= \frac{n^*T^{*2}}{(2\pi)^{3/2}}\int_U G(r)e^{-\frac{1}{2}r^2}x^4\,dV = \frac{n^*T^{*2}}{4}\sqrt{\frac{2}{\pi}}\int_0^\infty G(r)r^6e^{-\frac{1}{2}r^2}\,dr, \\ G_2 &= \frac{n^*T^{*2}}{(2\pi)^{3/2}}\int_U G(r)e^{-\frac{1}{2}r^2}x^2y^2\,dV = \frac{n^*T^{*2}}{12}\sqrt{\frac{2}{\pi}}\int_0^\infty G(r)r^6e^{-\frac{1}{2}r^2}\,dr, \end{aligned} \tag{3.151}$$

which gives $G_1 = 3G_2$. It follows from (3.148) that

$$\tau_{ii} = 2\mu \left[\frac{\partial u_i}{\partial x_i} - \tfrac{1}{3}\dot{\varepsilon}_{kk} \right] \tag{3.152}$$

(summed over k only), and this, together with (3.144), yields the general formula

$$\tau_{ij} = 2\mu(\dot{\varepsilon}_{ij} - \tfrac{1}{3}\dot{\varepsilon}_{kk}\delta_{ij}) \tag{3.153}$$

(summed over k). From (3.147) and (3.151), we have

$$\mu^* = \frac{G_2}{T^{*3/2}} = \frac{1}{12}\sqrt{\frac{2}{\pi}} \int_0^\infty G^*(r) r^6 e^{-\frac{1}{2}r^2}\, dr, \tag{3.154}$$

where we have written

$$G = \frac{G^*}{n^* T^{*1/2}} \tag{3.155}$$

(see question 3.14), or more simply just put $n^* = T^* = 1$.

The heat flux is calculated in the same way. From its definition in (3.65), we find

$$q_i = \frac{1}{d^2 L}\sqrt{\frac{k^3 T_0^3}{m}} \langle \phi, \tfrac{1}{2} u'^2 u'_i \rangle. \tag{3.156}$$

To calculate the inner product, note that since $\phi \perp \mathcal{N}$,

$$\langle \phi, \tfrac{1}{2} u'^2 u'_i \rangle = \langle \phi, W_i \rangle, \tag{3.157}$$

and in view of (3.118) and the fact that $\mathbf{U} \perp \mathbf{W}$, we have

$$\langle \phi, \tfrac{1}{2} u'^2 u'_i \rangle = -\langle \xi_j, W_i \rangle \frac{\partial C}{\partial x_j}, \tag{3.158}$$

summed over j. Since both $\boldsymbol{\xi}$ and $\mathbf{W}$ are proportional to $\mathbf{u}'$, it follows that $\langle \xi_j, W_i \rangle = 0$ if $i \neq j$, and thus

$$\langle \phi, \tfrac{1}{2} u'^2 u'_i \rangle = -\frac{1}{T^{*2}} \langle \xi_i, W_i \rangle \frac{\partial T^*}{\partial x_i} \tag{3.159}$$

(not summed). Converting the temperature gradient to dimensional units, we find

$$\mathbf{q} = -k_T \boldsymbol{\nabla} T, \tag{3.160}$$

where the thermal conductivity is

$$k_T = \frac{k^*}{d^2} \left(\frac{k^3 T}{m} \right)^{1/2}, \tag{3.161}$$

and

$$k^* = \frac{1}{T^{*5/2}} \langle \xi_i, W_i \rangle = \frac{1}{T^{*5/2}} \langle F u'_i, (\tfrac{1}{2} u'^2 - \tfrac{5}{2} T^*) u'_i \rangle = \frac{1}{3T^{*5/2}} \langle F, (\tfrac{1}{2} u'^2 - \tfrac{5}{2} T^*) u'^2 \rangle. \tag{3.162}$$

Making the substitution $u' = r\sqrt{T^*}$ and writing (see question 3.14)

$$F = \frac{T^{*1/2}F^*(r)}{n^*}, \tag{3.163}$$

this last integral can be explicitly written as

$$k^* = \frac{4\pi}{3}\int_0^\infty e^{-\frac{1}{2}r^2}F^*(r)\left(\tfrac{1}{2}r^2 - \tfrac{5}{2}\right)r^4\,dr. \tag{3.164}$$

The only remaining task is to show that μ and k_T are positive. This is a consequence of the negative definiteness of $\mathcal{L}$ on $\mathcal{N}_\perp$. More precisely, we see from (3.109) and (3.107) that

$$\langle\psi, \mathcal{L}\psi\rangle = -\tfrac{1}{4}\int_\Sigma f_0(\mathbf{v})f_0(\mathbf{w})(\Delta\psi)^2\,d\Sigma \leq 0, \tag{3.165}$$

and is equal to zero precisely if $\psi \in \mathcal{N}$. The eigenvalues of $\mathcal{L}$ on $\mathcal{N}_\perp$ are thus all strictly negative. Since we have taken $\boldsymbol{\xi}, \boldsymbol{\eta} \in \mathcal{N}_\perp$, it follows that (3.165) applies for $\psi = \boldsymbol{\xi}, \boldsymbol{\eta}$, and thus from (3.119)

$$\langle G(u')\mathbf{U}, \mathbf{U}\rangle > 0, \quad \langle\boldsymbol{\xi}, \mathbf{W}\rangle > 0, \tag{3.166}$$

where the inequalities apply separately to each component of the inner products. In particular, (3.147) implies that $\mu > 0$, and (3.162) implies $k_T > 0$.

Explicit expressions for μ^* and k^* are given in (3.154) and (3.164). Chapman and Cowling (1970, page 168) give estimates based on solving for F and G of

$$\mu^* = \frac{5}{16\sqrt{\pi}} \approx 0.176, \quad k^* = \frac{75}{64\sqrt{\pi}} \approx 0.661. \tag{3.167}$$

It is of interest to compare these values,

$$\mu \sim \frac{0.18\sqrt{mkT}}{d^2}, \quad k_T \sim \frac{0.66}{d^2}\left(\frac{k^3T}{m}\right)^{1/2}, \tag{3.168}$$

with actual measured values. We take

$$\begin{gathered} m \sim 5\times 10^{-26}\text{ kg}, \quad k = 1.38\times 10^{-23}\text{ J K}^{-1}, \\ d \sim 3.6\times 10^{-10}\text{ m}, \quad T \sim 300\text{ K} \end{gathered} \tag{3.169}$$

as representative values for air; these give $\mu \sim 1.8\times 10^{-5}$ Pa s and $k_T \sim 0.08$ W m^{-1} K^{-1}: the first is about right, whereas the actual value of k_T is about three times lower. The agreement of the viscosity is slightly illusory, since in effect one can estimate the molecular 'diameter' from the viscosity; however, the fact that the resultant thermal conductivity is close to the actual value provides an independent confirmation of the theory.

3.2.6 The Maxwell slip boundary condition

3.2.7 Dense gases

3.3 Entropy and free energy

From its definition in (3.74), we see that H is n times the particle mean of $\ln f$. It is convenient to define a particle mean entropy s by

$$ns = -\frac{kH}{m}, \quad s = -\frac{k}{m}\overline{\ln f}. \tag{3.170}$$

It follows that from an initial configuration, s increases during the evolution to the equilibrium Maxwellian distribution, and a direct calculation from (3.83) shows that in equilibrium,

$$s = \frac{k}{m}\left[\tfrac{3}{2} - \ln\left\{n\left(\frac{m}{2\pi kT}\right)^{3/2}\right\}\right] = \frac{k}{m}\left[\tfrac{3}{2} - \ln n + \tfrac{3}{2}\ln\left(\frac{4\pi e}{3}\right)\right], \tag{3.171}$$

since from (3.66),

$$e = \frac{3kT}{2m}. \tag{3.172}$$

In particular, at fixed n,

$$T\,ds = de. \tag{3.173}$$

If instead we vary n, then we find $T\,ds = p\,dv$, where

$$v = \frac{1}{\rho} \tag{3.174}$$

is the *specific volume*, and we use

$$p = nkT, \tag{3.175}$$

which follows from (3.68) and (3.69). In general, we therefore have

$$T\,ds = de + p\,dv. \tag{3.176}$$

We make a distinction between *intensive* and *extensive* variables. Intensive variables are those which refer to material properties. For example n, p and T are intensive variables, as are e and s defined above. Extensive variables are those which depend on the amount of material; for example particle number N and volume V are extensive variables. Extensive variables may be defined through an invariance under rescaling. For an ensemble of particles with fixed intensive properties, rescaling of volume V by λ should lead to comparable rescaling for other extensive variables. Some confusion arises because extensive definitions of energy and entropy are not per unit mass. Thus the extensive definitions of entropy, energy, particle number and volume are

$$S = mNs, \quad E = mNe, \quad N = nV, \quad V = mNv, \tag{3.177}$$

and thus for fixed N and V, we have from (3.176)

$$T\,dS = dE + p\,dV, \tag{3.178}$$

and

$$S = kN\left[\tfrac{3}{2} - \ln\frac{N}{V} + \tfrac{3}{2}\ln\left(\frac{4\pi E}{3mN}\right)\right]. \tag{3.179}$$

It can immediately be seen that the definition of entropy in (3.179) is indeed extensive. These relations apply at equilibrium, when the Maxwellian distribution has been obtained.

Although these results are derived specifically for the hard sphere gas, it seems reasonable to suppose that in general there is a specific entropy function $s[f]$, analogous to (3.170), such that s increases towards an equilibrium in which one can define an extensive function $S = mNs$, the entropy, which is determined as a function of $E = mNe$ and V, and such that (3.178) holds; indeed the enigmatic quantities T and p can be *defined* by (3.178) (or (3.176)), i. e.,

$$T = \left.\frac{\partial E}{\partial S}\right|_V, \quad p = -\left.\frac{\partial E}{\partial V}\right|_S, \tag{3.180}$$

and these replace (3.64) and (3.67), which rely on the specific nature of the hard sphere gas.

An extension of (3.178) to multi-component mixtures introduces the idea of chemical potentials. If a gas, say, consists of a mixture of different gases labelled by a suffix i, then the chemical potential μ_i can be defined as

$$\mu_i = \frac{\partial E}{\partial N_i}, \tag{3.181}$$

where N_i is the number of particles of phase i. Conventionally, N_i is measured in *moles* (one mole contains Avogadro's number $A \approx 6 \times 10^{23}$ particles mole^{-1}). Evidently the chemical potential is intensive, and the generalisation of (3.178) is

$$T\,dS = dE + p\,dV - \sum_i \mu_i\,dN_i. \tag{3.182}$$

It is more common to define chemical potentials in terms of the *Gibbs free energy*, which we define below.

The Gibbs–Duhem relation

The fact that $S = S(E, V, N_i)$ is an extensive function of its extensive variables implies that it is *homogeneous* of degree one, thus

$$S(\alpha E, \alpha V, \alpha N_i) = \alpha S(E, V, N_i) \tag{3.183}$$

for any α, and thus

$$E\frac{\partial S}{\partial E} + V\frac{\partial S}{\partial V} + N_i\frac{\partial S}{\partial N_i} = S, \tag{3.184}$$

where we use the summation convention. Noting from (3.182) that

$$\frac{\partial S}{\partial E}=\frac{1}{T},\quad \frac{\partial S}{\partial V}=\frac{p}{T},\quad \frac{\partial S}{\partial N_i}=-\frac{\mu_i}{T}, \tag{3.185}$$

we see that in fact

$$E=TS-pV+\mu_i N_i; \tag{3.186}$$

this is the Gibbs–Duhem relation. In differential form, it follows from (3.182) that

$$S\,dT-V\,dp+N_i\,d\mu_i=0, \tag{3.187}$$

from which further definitions can be gleaned; one in particular to which we will return is that for the rate of change of chemical potential with pressure:

$$\frac{\partial \mu_i}{\partial p}=\frac{V}{N_i}. \tag{3.188}$$

3.4 Thermodynamic relations

Classical thermodynamics is generally presented as a set of fairly arbitrary-seeming rules, but as we have seen, one can provide a coherent mechanical underpinning of the subject. In doing this, we need to keep in mind the distinction between the instantaneous state described by $f(\mathbf{r},\mathbf{v},t)$, for which there is a well-defined specific entropy s, internal energy e, and so on, and the (thermodynamic) equilibrium to which the local configuration converges. It is only in this equilibrium that the entropy (and other variables) can be taken to be defined in terms of particle number, internal energy and volume, and in which (3.178) applies. One might suppose that since we then *defined* temperature and pressure by (3.180), we could simply continue to do so even before equilibrium is attained. This loses sight of the fact that when not in equilibrium, the Boltzmann entropy s is not necessarily simply a function of n and e as in (3.171), and so one cannot take S to be purely dependent on E and V when out of equilibrium. Nevertheless, it should be noted that the conservation relations (3.60), (3.61) and (3.63) *do* apply when out of equilibrium, and this will be important below.

There are a number of subsidiary extensive variables which are commonly used. These include the enthalpy,

$$H=E+pV, \tag{3.189}$$

the Gibbs free energy

$$G=E-TS+pV, \tag{3.190}$$

and the Helmholtz free energy

$$F=E-TS. \tag{3.191}$$

As a spoiler, we may immediately note from (3.186) that

$$G=\mu_i N_i \tag{3.192}$$

(summed over i). It is straightforward to show that in thermodynamic equilibrium,

$$\begin{aligned} dH &= T\,dS + V\,dp, \\ dG &= V\,dp - S\,dT, \\ dF &= -p\,dV - S\,dT. \end{aligned} \tag{3.193}$$

Less clear to assert are the statements that G is minimised at fixed T and p, while F is minimised at fixed T and V. Here we go back to the non-equilibrium evolution of the Boltzmann specific entropy s, noting also that the energy equation (3.63) can be simplified using (3.60) and (3.61) (see also question 3.18) to the form

$$\rho\left[\frac{de}{dt} + p\frac{dv}{dt}\right] = \tau_{ij}\dot{\varepsilon}_{ij} - \boldsymbol{\nabla}.\,\mathbf{q} \equiv R, \tag{3.194}$$

where the strain rate tensor is $\dot{\boldsymbol{\varepsilon}} = \frac{1}{2}(\boldsymbol{\nabla}\mathbf{u} + (\boldsymbol{\nabla}\mathbf{u})^T)$. For a Maxwellian velocity distribution we can take $R = 0$, and in fact during the rapid time over which the equilibrium distribution is reached, the macroscopic transport terms R can be ignored. In this case, we have $\dot{s} \geq 0$, $\dot{e} + p\dot{v} = 0$ during approach to equilibrium.

Now let us consider evolution of a trajectory in Γ towards equilibrium, and we consider the evolution of the specific Gibbs free energy

$$g = e - Ts + pv. \tag{3.195}$$

There is a conceptual difficulty here, because although we can happily define T and p for the hard sphere gas, it is less obvious how to do so in general, and in particular the more general definitions in (3.180) presume an equilibrium distribution. In order to proceed, we suppose that the relaxation time for the solutions of the Boltzmann equation t_B is much less than the macroscopic time scale t_M of interest, and we then consider changes to the system on time scales $t_B \ll t \ll t_M$, so that local equilibrium prevails but the source term R in (3.194) is negligible.

If we now consider a process in which T and p (and N) remain constant, then we have

$$\dot{g} = \dot{e} - T\dot{s} + p\dot{v} = -T\dot{s} \leq 0, \tag{3.196}$$

and thus g (and so also G) tends to a minimum: *the Gibbs free energy is minimised at constant temperature and pressure.*

In a similar manner, we consider the evolution of the specific Helmholtz free energy

$$f = e - Ts \tag{3.197}$$

at constant T, V and N, whence also v is constant. Then $\dot{e} = \dot{e} + p\dot{v} = 0$, so that

$$\dot{f} = \dot{e} - T\dot{s} = -T\dot{s} \leq 0, \tag{3.198}$$

and thus f (and so also F) tends to a minimum: *the Helmholtz free energy is minimised at constant temperature and volume.*

3.5 Classical statistical mechanics

Having established a mechanical basis for the concepts of internal energy and entropy, we now proceed to re-derive these results in a much simpler but also more mystical way. In what follows, it should be borne in mind that a particle has three quantities of note: its existence, its position and its velocity. At the ensemble level, a collection of particles is thus described by its number, volume and internal energy: N, V and E. If we have more than one species present, then we have a sequence of numbers N_i. Much of thermodynamics consists of identification of a slew of other derived quantities, and relating them to each other through, in Sethna's phrase, a zoo of partial derivatives. This is also how classical statistical mechanics works.

Classical statistical mechanics is based on the concept of an *ensemble*, which we can think of as a cluster of points in the realisation space of the system; for our standard example of N particles in a box, this is the $6N$-dimensional space Γ. In practice, the ensemble will be a large number of points, but we can idealise it as having, or being drawn from, a probability density. Indeed, as we shall see, the large number of points allows us to cross from discrete sums to integrals with ease, and this will be useful.

What we might then call axiomatic statistical mechanics is based on two postulates:

> *Postulate 1*: The time average on an individual trajectory is the same as that of an ensemble average over the phase space.

We need to be a bit clearer what we mean by this. A single trajectory in Γ is given by $\gamma(t)$. We can think of this, as in figure 3.2, as being represented as a path on the surface of a hypersphere $\partial\Gamma_E$ in Γ. The time average of a quantity $\phi(\gamma)$ is then

$$\langle\phi\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T \phi\{\gamma(t)\}\,dt. \tag{3.199}$$

On the other hand, if we define a probability density ρ of states on $\partial\Gamma_E$, then the ensemble average of $\phi(\gamma)$ over $\partial\Gamma_E$ is

$$\bar{\phi} = \int_{\partial\Gamma_E} \rho(\gamma)\phi(\gamma)\,d\gamma. \tag{3.200}$$

Postulate 1 equates these two averages, and is the ergodic hypothesis of section 3.1.1.

The second postulate is simply an assumption of equiprobability:

> *Postulate 2:* All states in the state space are equally likely.

What this means is that

$$\rho(\gamma) = \frac{1}{\Omega}, \tag{3.201}$$

where Ω is the volume of $\partial\Gamma_E$. This assumption would not be true for dissipative systems, for example.

To explore the consequences of these postulates, we consider in turn three types of ensembles. The first of these is an isolated system (of particles), in which N, V and E are held fixed. Precisely, then, the particles live on a constant energy hypersurface $\partial\Gamma_E \in \Gamma$.

Microcanonical ensemble

We consider a set of N particles described by a Hamiltonian

$$H=\sum_1^N \frac{p_i^2}{2m}+W(\mathbf{q}_i) \tag{3.202}$$

having total energy E, residing in a volume V. The trajectory γ resides on the surface $H=E$ of a hypervolume $V_H(E)$ having a 'surface area'

$$\Omega(E)=\frac{\partial V_H}{\partial E}. \tag{3.203}$$

For the ideal hard sphere gas, we take $W=0$ (except for collisions or at the boundaries where W is infinite). The hypersurface $H=E$ is then the cross product of B^N, where B is the box inhabited by the particles, and the $3N$-sphere $\sum p_i^2=2mE$. The hypervolume of the state space is then just

$$V_H=V^N V_{3N}(\sqrt{2mE}), \tag{3.204}$$

where $V_M(R)$ is the hypervolume of the M-sphere, which is

$$V_M(R)=\frac{\pi^{M/2}R^M}{(M/2)!}. \tag{3.205}$$

The hypersurface area is then, from (3.203)

$$\Omega=\frac{3N}{2E}\frac{V^N\pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!}, \tag{3.206}$$

and this allows us to define the phase space density and thus entropy.

Definition of entropy

Classical statistical mechanics takes the results of solving the Boltzmann equation and extends them in a more extrapolative way to more general systems, by way of hypothesis. In particular, we define the entropy, and assume it satisfies the same thermodynamic relationships that apply to the hard sphere gas. We could actually define entropy to be anything we want, but it makes obvious sense to define it so that it is consistent with the Boltzmann entropy, and to do this we re-examine its definition in (3.170). This was $s=-\frac{k}{m}\overline{\ln f}$, and extension to the extensive definition in (3.177) suggests

$$S=-kN\overline{\ln f}. \tag{3.207}$$

To relate this to the Liouville density ρ, which itself is related to the N-particle distribution function by

$$f_N=N!\rho \tag{3.208}$$

(see (3.11)), it is tempting to take $f_N \approx f^N$, on the basis of a presumed independence of the particles, and then define the entropy as

$$S = -k\overline{\ln f_N} = -k\overline{\ln(N!\rho)}. \tag{3.209}$$

The relation (3.208) is not really quite right, since f is not itself a density, and it is better to identify

$$\rho = \frac{f_N}{N!} \approx \left(\frac{f}{N}\right)^N, \tag{3.210}$$

and if we use this together with the Maxwellian expression (3.83) for f, then we find

$$S = kN\left[\tfrac{5}{2} - \ln\frac{N}{V} + \tfrac{3}{2}\ln\left(\frac{4\pi E}{3mN}\right)\right], \tag{3.211}$$

in mild contrast to (3.179). In deriving this, we use *Stirling's approximation*

$$n! \sim n^n e^{-n}\sqrt{2\pi n} \quad \text{as} \quad n \to \infty, \tag{3.212}$$

which is derived using Laplace's method on the integral definition of the gamma function $\Gamma(z)$.

The difference between (3.211) and (3.179) simply represents an origin shift in the definition of the specific entropy, and is inconsequential. More generally, we might have expected to define entropy as

$$S = -k\ln\rho = k\ln\Omega, \tag{3.213}$$

and in fact this is the usual general definition. However it is important in defining the state space that its members are distinguishable, and this is not the case in the N-particle system, where there is no distinction between the $N!$ permutations of the particles. This explains the presence of the factor $N!$ in (3.209); if it is omitted, one obtains an expression for the entropy which is not extensive, and this is known as *Gibbs's paradox.*

Returning to the N-particle hypersurface (3.206), we avoid Gibbs's paradox by defining

$$S = k\ln\left(\frac{\Omega}{N!}\right), \tag{3.214}$$

and then a direct calculation using Stirling's formula leads again to (3.211), with an extra factor $3\ln m$ because the hyper-area (3.206) was calculated in momentum space.

Discrete state space

Commonly statistical mechanics deals with discrete state spaces, not for any obvious reason, but in practice this makes little difference, because if the number of states is very large, then the distinction between the consequent sums and their corresponding integrals is slight.

For a discrete state space, we suppose Ω is the number of (distinct) states, and that these are all equally likely. The entropy is then defined as

$$S = k \ln \Omega. \tag{3.215}$$

More generally, if the probability of the i-th state is p_i, we can define

$$S = -k \sum_i p_i \ln p_i, \tag{3.216}$$

which is familiar as the Shannon entropy of information theory. It reduces to (3.215) when all the states are equally likely.

Canonical ensemble

A more general ensemble to consider is the canonical ensemble, where we consider a box of N particles having volume V and (fixed) temperature T. Our conceptual picture which allows this is to have the box B in thermal contact with a large reservoir R, as shown in figure 3.10; heat exchange is possible through the common wall, but no particle exchange occurs. In this case the combined system is isolated, and thus has constant energy E_{tot}.

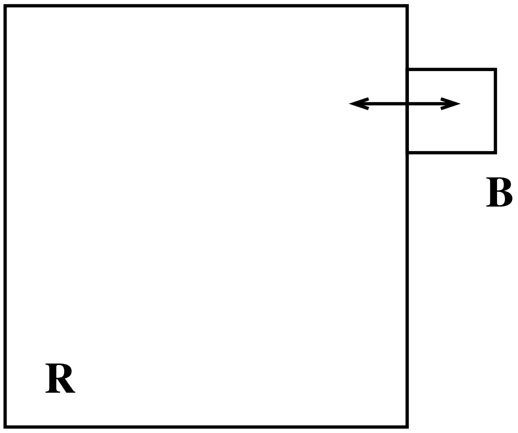

Figure 3.10: Box and reservoir for the canonical ensemble.

In our discussion, we will follow convention in thinking of discrete states, although in fact this is simply an approximation to the more appropriate continuous case. The number of distinct states is denoted as Ω, and is a function of the energy E (and of N and V, but these are fixed in each volume). The probability of any state is $p = \dfrac{1}{\Omega}$, and we define the entropy as

$$S = k \ln \Omega, \tag{3.217}$$

and it is an extensive variable. Consequently

$$\Omega_{R \oplus B} = \Omega_R \Omega_B, \tag{3.218}$$

which also follows directly from the independence of the states in the two reservoirs.

Consider now a state $\gamma \in B$ with energy $H(\gamma) = E_\gamma$. The energy in R is then $E_{\text{tot}} - E_\gamma$, so that (3.217) and (3.218) imply that the probability of the state γ is

$$p_\gamma = \frac{1}{\Omega_B(E_\gamma)} = \frac{\Omega_R(E_{\text{tot}} - E_\gamma)}{\Omega_{R\oplus B}(E_{\text{tot}})} \propto \exp\left[\frac{1}{k}\left(S_R(E_{\text{tot}}) - E_\gamma \frac{\partial S_R(E_{\text{tot}})}{\partial E} \dots\right)\right], \tag{3.219}$$

i. e.,

$$p_\gamma \propto \exp\left[\frac{-E_\gamma}{kT}\right], \tag{3.220}$$

since temperature is $T = \dfrac{\partial S_R}{\partial E}$. Since the sum of all the probabilities is one, we normalise this relation with the *partition function*

$$Z = \sum_\gamma \exp\left[\frac{-E_\gamma}{kT}\right], \tag{3.221}$$

and thus

$$p_\gamma = \frac{e^{-\beta E_\gamma}}{Z}, \quad \beta = \frac{1}{kT}. \tag{3.222}$$

Note that from its definition, Z is dimensionless.

The Boltzmann mean is $\bar{\phi} = \displaystyle\int_\gamma \rho_1 \phi \, d\gamma$, where ρ_1 is the one particle probability density; equivalently the mean for a discrete distribution is $\bar{\phi} = \displaystyle\sum_\gamma p_\gamma \phi$, and therefore the mean energy is

$$E = \sum_\gamma p_\gamma E_\gamma = -\frac{\partial}{\partial \beta} \ln Z. \tag{3.223}$$

In similar fashion, we can compute other quantities, thus

$$\begin{aligned} S &= \frac{E}{T} + k \ln Z, \\ Z &= e^{-\beta F}, \\ G &= kT \left[-\ln Z + V \left. \frac{\partial \ln Z}{\partial V} \right|_T \right]. \end{aligned} \tag{3.224}$$

Although we have derived the properties of the partition function assuming discrete states, there is little difference in considering continuous states, for which we define

$$Z = \int_\gamma e^{-\beta E_\gamma} \, d\gamma, \tag{3.225}$$

since the number of particles and thus also states is very large. Since commonly the state variable (i. e., γ) is dimensional, we should strictly divide by a suitable pixel dimension of $d\gamma$, but this makes little difference, since the quantities in (3.223) and (3.224) depend on $\ln Z$.

As an example, the partition function for N indistinguishable particles in a box is given by

$$Z = \int_0^\infty \frac{\Omega(E)e^{-\beta E}}{N!}\,dE, \tag{3.226}$$

where Ω is the surface area of the $(6N-1)$ dimensional energy surface, as given in (3.206). Carrying out the calculation, we obtain

$$Z = \frac{V^N}{N!}\left(\frac{2\pi kT}{m}\right)^{3N/2} \sim \frac{1}{\sqrt{2\pi N}}\left(\frac{Ve}{N}\right)^N\left(\frac{2\pi kT}{m}\right)^{3N/2}, \tag{3.227}$$

using Stirling's approximation for $N!$. The algebraic pre-factor is irrelevant, so that we have

$$\ln Z \sim N\left[1 - \ln\left(\frac{N}{V}\right) + \tfrac{3}{2}\ln\left(\frac{2\pi kT}{m}\right)\right], \tag{3.228}$$

from which we have

$$E = -\frac{\partial}{\partial\beta}\ln Z = \tfrac{3}{2}NkT, \tag{3.229}$$

in keeping with earlier results. Similarly, calculation of S from $(3.224)_1$ reproduces (3.211).

m-level systems

Suppose we consider N particles, each of which can exist in one of m different states, each having corresponding energies $E_1, \ldots, E_m$. We assume that the transition between these states conforms to the assumptions of statistical mechanics, and is described by a Hamiltonian, which is simply the energy. We denote the state variable of the i–th particle by the m–vector $(n_{i1}, \ldots, n_{im})$, where $n_{ij} = 1$ if the particle is in the j–th energy state, and $n_{ij} = 0$ otherwise. The energy of the system in a particular state $\gamma = \{n_{ij}\}$ is then

$$E_\gamma = \sum_{i,j} n_{ij}E_j, \tag{3.230}$$

and the corresponding probability p_γ of this state is

$$p_\gamma = \frac{e^{-\beta E_\gamma}}{Z} = \frac{1}{Z}\exp\left[-\beta\sum_{i,j} n_{ij}E_j\right], \tag{3.231}$$

and the partition function is

$$Z = \sum_\gamma \exp\left[-\beta\sum_{i,j} n_{ij}E_j\right]. \tag{3.232}$$

We denote the number of E_j states as $n_j = \sum_i n_{ij}$. Using the multinomial coefficient for the number of ways of selecting from $N = \sum_j n_j$ particles, it follows that

$$Z = \sum_{\{n_j\}} \frac{N!}{\prod_j n_j!}\exp\left[-\beta\sum_j n_jE_j\right] = \left(\sum_j e^{-\beta E_j}\right)^N. \tag{3.233}$$

From this we can compute various quantities; for example the energy is

$$E = -\frac{\partial}{\partial\beta}\ln Z = \frac{N\sum E_j}{\sum e^{-\beta E_j}}, \tag{3.234}$$

and other quantities can be computed similarly.

3.5.1 Chemical potential

Having discussed ensembles with fixed energy and then fixed temperature, the next generalisation is to allow a change in number of particles. The consequent change in energy associated with particle number change is the chemical potential. The chemical potential μ was defined earlier in (3.181) to be the change of internal energy when adding a particle to a system at constant V and S, thus

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}; \tag{3.235}$$

chemical potential is an intensive variable. The differential of E is thus modified to

$$dE = T\,dS - p\,dV + \mu\,dN, \tag{3.236}$$

and it follows from this that also

$$\mu = -T\left.\frac{\partial S}{\partial N}\right|_{E,V}. \tag{3.237}$$

Neither (3.235) nor (3.237) are particularly useful definitions, since entropy is an elusive quantity. However, consideration of the Gibbs free energy $G(N,p,T) = E + pV - TS$ yields a more useful definition

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{p,T}, \tag{3.238}$$

and this is the one that is commonly used.

The chemical potential plays the rôle for particle number that temperature does for internal energy. To see this, consider firstly two systems 1 and 2 which can exchange energy, but not volume or particles. The combined pair forms a microcanonical ensemble. If we add an increment of energy dE to system 1, then the same amount is removed from system 2, and the consequent change of entropy of the combined system is

$$dS = \left.\frac{\partial S}{\partial E}\right|_1 dE - \left.\frac{\partial S}{\partial E}\right|_2 dE = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE. \tag{3.239}$$

This must be non-negative, and so energy flows down temperature gradients, and at equilibrium $T_1 = T_2$, which is simply the zero-th law of thermodynamics.

Now let us allow a number of particles dN to be added to system 1, and thus the same quantity is removed from system 2, without any change in energy. The change in total entropy is then

$$dS = \left.\frac{\partial S}{\partial N}\right|_1 dN - \left.\frac{\partial S}{\partial N}\right|_2 dN = \left(-\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right) dN, \tag{3.240}$$

using (3.237), and since $T_1 = T_2$ in equilibrium, this states that particles flow down chemical potential gradients, and in equilibrium, $\mu_1 = \mu_2$. Just as energy transport down temperature gradients is described by Fourier's law of heat conduction, particle transport down chemical potential gradients is described by Fick's law of diffusion.

As always, we return to the perfect gas. The entropy is given by (3.211). Using (3.237), it follows that

$$\mu = kT\left[\ln\left(\frac{N}{V}\right) - \tfrac{3}{2}\ln\left(\frac{2\pi kT}{m}\right)\right]. \tag{3.241}$$

A direct calculation of the Gibbs free energy for the perfect gas then shows that in fact

$$G = \mu N \tag{3.242}$$

(in keeping with (3.192)).

Grand canonical ensemble

We return to the system illustrated in figure 3.10 consisting of a box B and a reservoir R, but now we allow exchange of both energy and particles: this is the grand canonical ensemble. The total energy is E_{tot} and the total number of particles is N_{tot}. The total number of states is $\Omega_{\text{tot}} = \Omega_R\Omega_B$. For a particular state $\gamma \in B$ with number N_γ and energy E_γ, the corresponding number and energy in the reservoir are $N_{\text{tot}} - N_\gamma$ and $E_{\text{tot}} - E_\gamma$; then the probability of the state γ is

$$p_\gamma = \frac{1}{\Omega_B} = \frac{\Omega_R}{\Omega_{\text{tot}}} = \frac{1}{\Omega_{\text{tot}}}\exp\left[\frac{S_R(E_{\text{tot}} - E_\gamma, N_{\text{tot}} - N_\gamma)}{k}\right], \tag{3.243}$$

and Taylor expanding this as we did for the canonical ensemble, we have

$$p_\gamma = \frac{1}{Q}\exp\left[\frac{(\mu N_\gamma - E_\gamma)}{kT}\right], \tag{3.244}$$

where we use (3.237) and (3.180) to define μ and T.

The normalising function Q is known as the *grand partition function*, and is given by

$$Q = \sum_\gamma \exp\left[\frac{(\mu N_\gamma - E_\gamma)}{kT}\right]. \tag{3.245}$$

Just as for the canonical ensemble, we can derive the state variables from Q, thus

$$N = \sum_\gamma p_\gamma N_\gamma = kT\left.\frac{\partial \ln Q}{\partial \mu}\right|_\beta,$$

$$E = \sum_\gamma p_\gamma E_\gamma = \mu N - \left.\frac{\partial \ln Q}{\partial \beta}\right|_\mu ,$$

$$S = -k \sum_\gamma p_\gamma \ln p_\gamma = \frac{E - \mu N + kT \ln Q}{T}. \tag{3.246}$$

By partitioning the sum over the value of N_γ, the grand partition function can be written in the form

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T, N, V), \tag{3.247}$$

where Z is the partition function corresponding to the state with N particles. We can make use of the discrete equivalent of Laplace's method for sums (see also question 3.24), which applies to sums of the form $s = \sum_n s_n$, $s_n = \omega_n e^{-\beta n}$, where ω_n grows rapidly with n, e. g., $\omega_n = n^\Lambda$ for some large Λ. In this case the maximum term occurs for large n, and we have $s \sim \max_n s_n$. This result (which is essentially the central limit theorem) can be applied to (3.247), since (at least for the perfect gas) (3.227) suggests $Z \sim N^{-N}$ at large N. More precisely, the N–th term Q_N of (3.247) is

$$Q_N \sim e^{(\beta\mu+1)N} \left(\frac{V}{N}\right)^N \left(\frac{2\pi kT}{m}\right)^{3N/2}. \tag{3.248}$$

Calculating the value of N for which Q_N is maximum, we then obtain the (ideal gas) estimate

$$\ln Q \sim V e^{\beta\mu} \left(\frac{2\pi kT}{m}\right)^{3/2}. \tag{3.249}$$

Further, the local peaking of the terms in Q is also associated with a peaking of the state probabilities, whence it follows that the mean value $N = \sum_\gamma p_\gamma N_\gamma$ is also the value of N where Q_N is maximal. In particular,

$$Q \sim e^{\beta\mu N} Z = e^{-\beta(F - \mu N)}, \tag{3.250}$$

where (cf. (3.224)) F is the Helmholtz free energy. This leads us to define the *grand potential*

$$\Phi = -kT \ln Q = F - \mu N = E - TS - \mu N, \tag{3.251}$$

which is also consistent with (3.246); from (3.190) and (3.192), we have

$$\Phi = -pV. \tag{3.252}$$

Forming the differential of Φ, we find

$$N = -\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V}, \quad p = -\left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu}, \quad S = -\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu}. \tag{3.253}$$

For the perfect gas, for which Φ is defined via (3.249), use of the definition of N in (3.253) leads to $\Phi = -NkT = -pV$, and thus from (3.251) and the definition of G,

$$G = \mu N, \tag{3.254}$$

as we found earlier.

3.5.2 Ideal solutions

The perfect gas chemical potential is given by (3.241). Since also we have the perfect gas law $p = \dfrac{NkT}{V}$, it follows that we can write

$$\mu = \mu_0(T) + kT \ln\left(\frac{p}{p_0}\right). \tag{3.255}$$

This defines the chemical potential as energy per particle (J pt^{-1}), but it is more common to use a macroscopic definition in which the units are J mol^{-1}, and this is effected by using Avogadro's number $A = 6 \times 10^{23}$ pt mol^{-1}. Multiplying (3.255) by A, we have

$$\mu = \mu_0(T) + RT \ln\left(\frac{p}{p_0}\right), \tag{3.256}$$

where now $R = kA$ is the gas constant, and μ has units J mol^{-1}.

Now let us consider a mixture of gases. If n_i is the number density of gas i, and the particles have mass m_i, then we can define the total number density and average mass per particle as

$$n = \sum_i n_i, \quad m = \frac{\sum_i m_i n_i}{n}, \tag{3.257}$$

and then the internal energy, temperature and pressure are defined by

$$me = \tfrac{3}{2}kT = \frac{\frac{1}{2}\sum_i m_i n_i \overline{u'^2}}{n}, \quad p = \tfrac{1}{3}\sum_i m_i n_i \overline{u'^2}, \tag{3.258}$$

whence we have the perfect gas law in the form

$$p = nkT = \sum_i p_i, \quad p_i = n_i kT. \tag{3.259}$$

This is Dalton's law of partial pressures, which states that the pressure exerted by a mixture of gases is the sum of the pressures which each component would exert were it present on its own; these are known as *partial pressures.* While partial pressures are the commonly used measure of proportion for gases, another such measure is the concentration, which measures the fraction of substance, most commonly in liquids. The *molar* concentration of a substance is its mole fraction. Since a mole contains a fixed number (A) of particles, the mole fraction is also the particle number fraction. Thus for the gas mixture, the molar concentration is

$$c_i = \frac{n_i}{n} = \frac{p_i}{p}. \tag{3.260}$$

It then follows that the molar chemical potential (3.256) of each phase can be written in the form

$$\mu_i = \mu_i^0(T, p) + RT \ln c_i, \tag{3.261}$$

and this relationship (for liquids also) is taken to define an ideal mixture. More generally, one replaces c_i by a_i in this expression, where a_i is called the *activity*, and is a function of the various concentrations.

3.5.3 Chemical reactions

In the (gaseous) reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B, \tag{3.262}$$

the forward net reaction rate according to the law of mass action is

$$r = k_1 A - k_{-1} B; \tag{3.263}$$

this is the rate of formation of B and the rate of loss of A, measured as concentrations. In equilibrium, we thus have

$$\frac{B}{A} = \frac{p_B}{p_A} = K \equiv \frac{k_1}{k_{-1}}. \tag{3.264}$$

For a change $\Delta N = \Delta N_A$ of A particles, we have $\Delta N_B = -\Delta N$, and the change of Gibbs free energy at fixed T and p is

$$\mu_A \Delta N_A + \mu_B \Delta N_B = (\mu_A - \mu_B)\Delta N, \tag{3.265}$$

and at equilibrium this is zero. Using the definition of chemical potential in (3.261), we have

$$\mu_A - \mu_B = \mu_A^0 - \mu_B^0 + RT \ln \frac{p_A}{p_B}, \tag{3.266}$$

and so at equilibrium

$$K = \frac{k_1}{k_{-1}} = \exp\left[-\frac{\Delta G}{RT}\right], \quad \Delta G = \mu_B^0 - \mu_A^0. \tag{3.267}$$

Reaction rates

More generally, one can show that the individual reaction rates satisfy

$$k_{\pm 1} = k_{\pm 1}^0 \exp\left[-\frac{E_\pm}{RT}\right]. \tag{3.268}$$

The quantities $E_\pm$ are called *activation energies*, and the form of (3.268) is known as *Arrhenius kinetics.*

In order to consider why this should be so, we consider the example of bimolecular reactions of the form

$$\mathrm{X} + \mathrm{Y} \overset{k_+}{\to} \mathrm{P}. \tag{3.269}$$

The law of mass action is based on the rate of molecular collisions, as described in section 3.2.1, except now we consider collisions between two different molecules, of diameters d_1 and d_2 and masses m_1 and m_2, with number densities $f_1(\mathbf{r}, \mathbf{v}, t)$ and $f_2(\mathbf{r}, \mathbf{w}, t)$, each of which is a Maxwellian distribution. From (3.26), and consulting figure 3.4, the rate of collisions per unit volume of particles with velocities near $\mathbf{v}$ and $\mathbf{w}$ is

$$f_1(\mathbf{r}, \mathbf{v}, t) f_2(\mathbf{r}, \mathbf{w}, t)\, d\Omega\, d\mathbf{v}\, d\mathbf{w}, \tag{3.270}$$

where now

$$d\Omega = \bar{d}^2\mathbf{k}.\mathbf{V}\,d\omega(\mathbf{k}), \tag{3.271}$$

and $\bar{d} = \frac{1}{2}(d_1 + d_2)$ is the mean diameter.

The simple idea is that when two different molecules collide, they will react providing the energy of impact is sufficiently large. Molecules have atomic bonds, and it requires energy to break them, and in the collisional theory of reaction rates, it is the kinetic energy of impact which provides this energy. When the bonds are broken, there is a possibility that the reaction will proceed to form the product (with new atomic bonds and thus lower energy than the bond-free state). We thus conceive of the molecular chemical states as consisting of local minima in the free energy, with a barrier of height E between them.

It is fairly obvious that it is not the total energy $\frac{1}{2}(m_1v^2 + m_2w^2)$ which is instrumental in enabling the reaction, but the energy associated with the relative velocity. If we define the mass-centred velocity

$$\mathbf{U} = \frac{m_1\mathbf{v} + m_2\mathbf{w}}{m_1 + m_2}, \tag{3.272}$$

then we find that the kinetic energy can be written in the form

$$\tfrac{1}{2}(m_1v^2 + m_2w^2) = \tfrac{1}{2}(m_1 + m_2)U^2 + \tfrac{1}{2}\bar{m}V^2, \tag{3.273}$$

where $\bar{m}$ is the inverse of the sum of the inverse masses,

$$\bar{m} = \frac{m_1m_2}{m_1 + m_2}. \tag{3.274}$$

We then suppose that reactions occur for collisions such that $\frac{1}{2}\bar{m}V^2 > E$, and the frequency r_E of these per unit volume is then

$$r_E = \int\int_{\frac{1}{2}\bar{m}V^2>E} \int_{\Omega_+} f_1(\mathbf{r},\mathbf{v},t)f_2(\mathbf{r},\mathbf{w},t)\,d\Omega\,d\mathbf{v}\,d\mathbf{w}. \tag{3.275}$$

The integration with respect to solid angle over the half-space Ω_+ is simple, and yields a multiplying factor $\pi\bar{d}^2V$. We will assume that the gas is at rest (the mean velocity is zero); then substituting the Maxwellian distributions for f_1 and f_2 into (3.275), the reactive frequency is

$$r_E = \frac{\pi n_1n_2(m_1m_2)^{3/2}\bar{d}^2}{(2\pi kT)^3} \int\int_{\frac{1}{2}\bar{m}V^2>E} \exp\left[-\frac{(m_1v^2 + m_2w^2)}{2kT}\right] V\,d\mathbf{v}\,d\mathbf{w}. \tag{3.276}$$

To evaluate the integral, we change the variables of integration to $\mathbf{U}$ and $\mathbf{V}$. It is straightforward (see question 3.28) to show that the Jacobian of the transformation is one, and thus, bearing in mind (3.273), (3.276) implies

$$r_E = \frac{\pi n_1n_2(m_1m_2)^{3/2}\bar{d}^2}{(2\pi kT)^3} \int\int_{\frac{1}{2}\bar{m}V^2>E} \exp\left[-\frac{\{(m_1 + m_2)U^2 + \bar{m}V^2\}}{2kT}\right] V\,d\mathbf{U}\,d\mathbf{V}. \tag{3.277}$$

Bearing in mind that we are still in six-dimensional space, with an integral only dependent on the 'radii' U and V, we reduce this using $d\mathbf{U} = 4\pi U^2\,dU$, $d\mathbf{V} = 4\pi V^2\,dV$, to the two-dimensional integral

$$r_E = \frac{2n_1n_2(m_1m_2)^{3/2}\bar{d}^2}{(kT)^3}\int_{U,V>0}\int_{\frac{1}{2}\bar{m}V^2>E} \exp\left[-\frac{\{(m_1+m_2)U^2+\bar{m}V^2\}}{2kT}\right] V^3U^2\,dU\,dV. \tag{3.278}$$

Evaluating the integral, we find

$$r_E = n_1n_2\bar{d}^2\left(\frac{8\pi kT}{\bar{m}}\right)^{1/2}\left[1+\frac{E}{kT}\right]\exp\left(-\frac{E}{kT}\right). \tag{3.279}$$

Since the molar concentrations of X, Y and P are just their number densities divided by A, where A is Avogadro's number, this gives us the law of mass action in the form

$$\frac{d[P]}{dt} = r = \frac{r_E}{A} = k_+[X][Y], \quad k_+ = k_0\exp\left(-\frac{E^*}{RT}\right), \tag{3.280}$$

where we also write the activation energy per mole of reactant as $E^* = AE$, and note that $R = Ak$ is the gas constant. The pre-exponential factor is given by

$$k_0 = A\bar{d}^2\left(\frac{8\pi kT}{\bar{m}}\right)^{1/2}\left[1+\frac{E}{kT}\right], \tag{3.281}$$

and is generally taken as a constant, since usually E^* is so large that the temperature variability of (3.281) is obscure. Experimental measurement of E^* then enables k_0 to be calculated. Often this pre-factor differs to that observed by a factor which Lewis called the chemical efficiency, and others call a steric factor. When this is less than one, it can be associated with the proportion of successful (reactive) collisions, the idea being that only correctly aligned collisions will enable the bond-breaking to occur, at least for certain molecules.

3.5.4 Osmotic pressure

Suppose a salt solution is placed in a bath next to a layer of pure solvent,[6] with the two being separated by a semi-permeable membrane, as indicated in figure 3.11. The membrane allows solvent to pass through, but prevents the (larger) solute molecules from passing. As a consequence, the chemical potential of the solvent (only) is continuous across the membrane, and as shown, this causes the solution to draw in solvent, forming an excess pressure head in the solution; this is called the *osmotic pressure*.

Osmotic pressure is very important in living systems. It provides the mechanism whereby living cells maintain an interior pressure, called turgor pressure (in plants). To describe it, we use the language of gas mixtures, although in practice we are

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[6] In a solution, the *solvent* is the liquid into which the *solute* is dissolved. We think of salt dissolving in water, but we could equally think of ice dissolving in molten salt; the distinction is one of convention. Most commonly we have dilute solutions, in which the solute has small concentration.

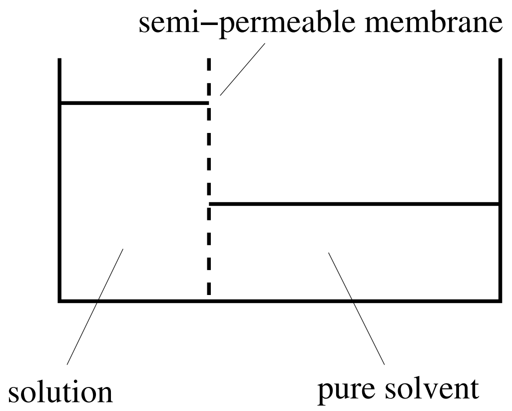

Figure 3.11: Osmotic pressure of a salt solution.

interested in liquid solutions.[7] For the situation shown in figure 3.11, suppose that the pressure on the right is p_0 and that on the left is $p_0+\Pi$; Π is the osmotic pressure. If we denote the concentration of the solute as c, then the solvent concentration $1-c$ in the solution is related to its partial pressure p_s by

$$1-c=\frac{p_s}{p_0+\Pi}. \tag{3.282}$$

The chemical potential of the solvent in solution is thus

$$\mu_s=\mu_s^0+RT\ln\left(\frac{p_s}{p_0}\right)=\mu_s^0+RT\ln\left[\frac{(p_0+\Pi)(1-c)}{p_0}\right], \tag{3.283}$$

while the chemical potential of pure solvent at pressure p_0 is just μ_s^0. Equality of the two implies

$$\Pi=\frac{p_0 c}{1-c}. \tag{3.284}$$

If the number density of the solute is $n_p=\frac{N_p}{V}$, then we have, since $p_0=nkT$ and $c=\frac{n_p}{n}$, and assuming a dilute solution $c\ll 1$,

$$\Pi\approx n_p kT, \tag{3.285}$$

a result known as the van't Hoff formula.

Note that the perturbation of the chemical potential per particle of the solvent due to its concentration (at a fixed pressure) is $\Delta\mu=-kTc$ for a dilute solution, and thus also

$$\Pi=-n\Delta\mu, \tag{3.286}$$

a formula that we will use later.

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[7] There are also solid solutions, and we will mention an example in the section on alloys.

3.5.5 Polymer solution theory

Polymers are long-chain molecules, consisting of a number n_m of *monomers* which are connected together, literally like chains. Examples are proteins and plastics, and their behaviour is decidedly odder than ordinary materials. Polymeric fluids exhibit yield stress, viscoelasticity and gelation, for example.

Polymer solutions are simply solutions of a polymer in a solvent, and we will describe a model to calculate their entropic properties, from which we may for example derive their osmotic pressure. The theory is due to Flory and Huggins and is called *Flory-Huggins theory.* The model consists of two parts, one to calculate the entropy and the other to calculate the internal energy. From these we form the Helmholtz free energy, from which further results may then be derived.

The model visualises the polymer solution as consisting of a lattice of N points, on which N_p polymer molecules sit, each of length n_m monomers, and the remaining $N_s = N - n_m N_p$ sites are occupied by solvent. The number of distinct configurations of the system can be written as

$$W = w_1 w_r, \tag{3.287}$$

where w_1 is the number of ways of placing the first monomer of each polymer, and w_r is the number of ways of placing the remaining $N_p(n_m - 1)$. We should multiply this by the number of ways of placing the solvent molecules, but there is only one distinguishable way, since they fill all the remaining sites. The value of w_1 is simply the number of ways of selecting N_p points from N, and is

$$w_1 = \frac{N!}{N_p!(N - N_p)!}. \tag{3.288}$$

To compute w_r, we allocate the number of ways each monomer can be placed in turn. We define the coordination number z to be the number of nearest neighbours in the lattice. For example, a two-dimensional square lattice allowing only horizontal and vertical connections would have $z = 4$; if also diagonal connections are allowed, $z = 8$. The three-dimensional equivalents are $z = 8$ and $z = 26$. The number of (distinguishable) ways of placing the $(N_p + 1)$-th monomer would thus be z, but this must be multiplied by the fraction of available unoccupied sites, which is $\dfrac{N - N_p}{N}$. Having placed this monomer, the number of ways of placing the next (on the same polymer) is $z-1$ multiplied by the fraction of available sites, $\dfrac{N - N_p - 1}{N}$. Proceeding in this way until all the remaining monomers are placed, we find[8]

$$w_r = \left(\frac{z}{z-1}\right)^{N_p} \left(\frac{z-1}{N}\right)^{N_p(n_m-1)} \frac{(N - N_p)!}{(N - N_p n_m)!}, \tag{3.289}$$

and thus

$$W = \left(\frac{z}{z-1}\right)^{N_p} \left(\frac{z-1}{N}\right)^{N_p(n_m-1)} \frac{N!}{N_p!(N - N_p n_m)!}. \tag{3.290}$$

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[8] Note that if $n_m = 1$ then $w_r = 1$; cf. question 3.31.

Note that this calculation ignores the possibility of (near) self-crossings.

For the pure polymer with $N_s = 0$ and thus $N = N_p n_m$, the corresponding number of states is

$$W_0 = \left(\frac{z}{z-1}\right)^{N_p} \left(\frac{z-1}{N_p n_m}\right)^{N_p(n_m-1)} \frac{(N_p n_m)!}{N_p!}, \tag{3.291}$$

and thus

$$\frac{W}{W_0} = \frac{N!}{(N - n_m N_p)!(N_p n_m)!} \left(\frac{N_p n_m}{N}\right)^{N_p(n_m-1)}. \tag{3.292}$$

We define the entropy relative to the pure polymer to be

$$S - S_0 = k \ln\left(\frac{W}{W_0}\right), \tag{3.293}$$

and applying Stirling's formula to the factorials, we find, after some algebra,

$$S - S_0 = k\left[N_s \ln\left(\frac{N}{N_s}\right) + N_p \ln\left(\frac{N}{n_m N_p}\right)\right], \tag{3.294}$$

and noting that the volume fraction of polymer ϕ satisfies

$$\phi = \frac{n_m N_p}{N}, \quad 1 - \phi = \frac{N_s}{N}, \tag{3.295}$$

it follows that

$$S - S_0 = -kN\left[(1-\phi)\ln(1-\phi) + \frac{1}{n_m}\phi \ln \phi\right]. \tag{3.296}$$

Internal energy

We associate internal energy with mutual interaction of the molecules on a pairwise basis, and there are thus three values of internal energy, e_{pp}, e_{ps} and e_{ss} depending on whether the interaction is polymer-polymer, polymer-solvent, or solvent-solvent. Thus we define the total internal energy to be

$$E = n_{pp}e_{pp} + n_{ps}e_{ps} + n_{ss}e_{ss}, \tag{3.297}$$

where n_{ij} is the number of i–j contacts.

With N sites having coordination number z, there are a total of $\frac{1}{2}zN$ contacts (the factor two arises because we only count pairs once). Now since the number of p–s contacts is n_{ps} and the solvent molecules have a total number of zN_s contacts, the total number of s–s contacts is $\frac{1}{2}(zN_s - n_{ps})$ (again the factor two because each pair is counted once). In the same way the total number of p–p contacts is $\frac{1}{2}(zn_m N_p - n_{ps})$. We define the pure polymer and pure solvent internal energies as

$$E_p = \tfrac{1}{2}zn_m N_p e_{pp}, \quad E_s = \tfrac{1}{2}zN_s e_{ss}, \tag{3.298}$$

and the unmixed internal energy

$$E_0 = E_p + E_s; \tag{3.299}$$

then the internal energy can be written as

$$E = E_0 + n_{ps}\Delta e, \quad \Delta e = e_{ps} - \tfrac{1}{2}(e_{pp} + e_{ss}). \tag{3.300}$$

To estimate n_{ps}, we take a mean field approximation: each of $n_m N_p$ monomers has an average of $\dfrac{zN_s}{N}$ solvent neighbours, and therefore

$$n_{ps} = \frac{n_m N_p z N_s}{N} = zN\phi(1-\phi). \tag{3.301}$$

Hence, denoting the Flory interaction parameter as

$$\chi = \frac{z\Delta e}{kT}, \tag{3.302}$$

we obtain

$$E = E_0 + kT\chi N\phi(1-\phi). \tag{3.303}$$

Finally, the Helmholtz free energy relative to the unmixed state is

$$\Delta F = F - F_0 = kNT\left[\chi\phi(1-\phi) + (1-\phi)\ln(1-\phi) + \frac{1}{n_m}\phi\ln\phi\right]. \tag{3.304}$$

Osmotic pressure

Note that from the Gibbs–Duhem relation (3.186) $F = -pV + \mu_i N_i$, and for a constant volume and temperature system such as we assume here, (3.236) implies

$$\mu_i = \frac{\partial F}{\partial N_i}. \tag{3.305}$$

It follows that the change of chemical potential of the solvent from the unmixed state is

$$\Delta\mu_s = \frac{\partial \Delta F}{\partial N_s}, \tag{3.306}$$

and noting that $N = N_s + n_m N_p$, we find from (3.304) that

$$\Delta\mu_s = kT\left[\chi\phi^2 + \ln(1-\phi) + \left(1 - \frac{1}{n_m}\right)\phi\right], \tag{3.307}$$

and the osmotic pressure is, using (3.286) and noting that $n = \dfrac{N}{V} = \dfrac{1}{V_{\text{site}}}$, where V_{site} is the site volume,

$$\Pi = -E_L\left[\chi\phi^2 + \ln(1-\phi) + \left(1 - \frac{1}{n_m}\right)\phi\right], \tag{3.308}$$

where

$$E_L = \frac{kT}{V_{\text{site}}} \tag{3.309}$$

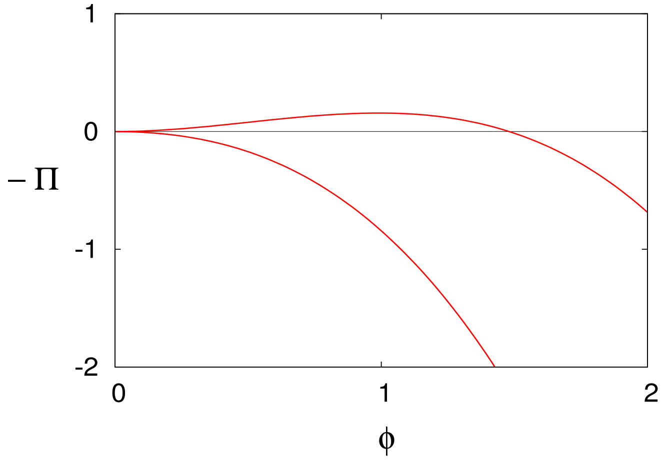

Figure 3.12: The function $-\Pi(\phi)$ given by (3.310) for values $n_m = 100$, $E_L = 1$, and $\chi = 1$ (upper) and $\chi = 0$ (lower). For the case $\chi > \frac{1}{2}$, the polymer swells in contact with solvent until $\phi \approx 3(\chi - \frac{1}{2})$ (for $n_m \gg 1$).

is the energy per site. For a dilute polymer, $\phi \ll 1$, and we can expand (3.308) to give

$$\Pi \approx E_L \left[\frac{1}{n_m}\phi - \left(\chi - \tfrac{1}{2}\right)\phi^2 + \tfrac{1}{3}\phi^3 \ldots \right]. \tag{3.310}$$

This equation demonstrates the distinguishing feature of a polymer solution in the case $\chi > \frac{1}{2}$. For the situation shown in figure 3.11, when the fluid levels are initially the same, solvent flows into the left reservoir if $\Pi > 0$, causing ϕ to decrease, and a simple model describing this is

$$\dot{\phi} = -K\Pi(\phi). \tag{3.311}$$

We thus see that when $\chi < \frac{1}{2}$, $\Pi > 0$ for all ϕ, and the solvent flows in indefinitely. However, when $\chi > \frac{1}{2}$ (the case of a 'poor' solvent), solvent only flows in until an equlibrium is reached when $\Pi = 0$.

3.6 Phase change

One of the more obvious things about matter is that it exists in different states: solid, liquid or gas. Simple observation tells us that the state of matter depends on the temperature. As we raise the temperature, a solid will first melt, and then, at a higher temperature, it will boil. Can we explain this, in the context of our statistical mechanical description of matter?

The answer is yes, to some extent. Our derivation of the perfect gas law (3.175) relied on the solution of the Boltzmann equation, with the collision integral given by its formulation for a dilute hard sphere gas. As the number density of molecules increases, two effects come into play, which we have so far been neglected. The first of these is that the volume of the molecules themselves becomes important, and the second is that the inter-particle potential energy can not be neglected. As we shall see, just these two effects allow us to describe the gas–liquid phase transition.

3.6.1 The virial expansion

We return to the definition of the grand partition expansion for N particles in a box, which from (3.247) is

$$\begin{aligned} Q &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(T,V) \\ &= 1 + e^{\beta\mu} Z_1 + e^{2\beta\mu} Z_2 + \ldots, \end{aligned} \tag{3.312}$$

which is an expansion for $\mu \to -\infty$, i. e., $p \to 0$, i. e., $n \to 0$. Therefore the grand potential $\Phi = -kT \ln Q$ satisfies

$$\Phi = -kT \left[e^{\beta\mu} Z_1 + e^{2\beta\mu} (Z_2 - \tfrac{1}{2} Z_1^2) + \ldots \right], \tag{3.313}$$

so that

$$N = -\frac{\partial \Phi}{\partial \mu} = e^{\beta\mu} Z_1 + 2 e^{2\beta\mu} (Z_2 - \tfrac{1}{2} Z_1^2) + \ldots, \tag{3.314}$$

and inverting this, we have

$$e^{\beta\mu} = \frac{N}{Z_1} - \frac{2(Z_2 - \frac{1}{2} Z_1^2)}{Z_1} e^{2\beta\mu} + \ldots \approx \frac{N}{Z_1} - \frac{2(Z_2 - \frac{1}{2} Z_1^2)}{Z_1} \frac{N^2}{Z_1^2} + \ldots, \tag{3.315}$$

and thus

$$\Phi = -kT \left[N - \frac{(Z_2 - \frac{1}{2} Z_1^2) N^2}{Z_1^2} + \ldots \right], \tag{3.316}$$

and since $\Phi = -pV$ (see (3.252)), it follows that

$$pV = kT \left[N - \frac{(Z_2 - \frac{1}{2} Z_1^2) N^2}{Z_1^2} + \ldots \right], \tag{3.317}$$

and writing this in terms of the number density n, we have the virial expansion

$$p = kT[n + Bn^2 + \ldots], \tag{3.318}$$

where B is known as the second virial coefficient, and is given by

$$B = V \left(\tfrac{1}{2} - \frac{Z_2}{Z_1^2} \right). \tag{3.319}$$

We now wish to calculate B.

To calculate Z_N we define the energy E_γ of a state γ as

$$E_\gamma = \sum_1^N \tfrac{1}{2} m v_i^2 + \sum_{i<j} W(|\mathbf{r}_i - \mathbf{r}_j|), \tag{3.320}$$

where the second sum is over distinct pairs (i, j). Allowing for the Gibbs paradox, the partition function can be defined as (cf. (3.226))

$$Z_N = \frac{m^3}{N!} \int_\Gamma \exp\left[-\beta \left\{ \sum_1^N \tfrac{1}{2} m v_i^2 + \sum_{i<j} W(|\mathbf{r}_i - \mathbf{r}_j|) \right\} \right] d\gamma, \tag{3.321}$$

where the factor m^3 is suggested on account of the relation $\mathbf{p} = m\mathbf{v}$; note that Z_N is not dimensionless (cf. the comment after (3.225)). The integral over velocity space U^N is easily carried out, leaving the expression

$$Z_N = \frac{(2\pi mkT)^{3N/2}}{N!} \int_{V^N : |\mathbf{r}_i - \mathbf{r}_j| > d} \exp\left[-\beta \sum_{i<j} W(|\mathbf{r}_i - \mathbf{r}_j|) \right] d\mathbf{r}_1 \ldots d\mathbf{r}_N. \tag{3.322}$$

In particular,

$$Z_1 = (2\pi mkT)^{3/2} V, \tag{3.323}$$

and

$$Z_2 = \frac{(2\pi mkT)^3}{2} \int_{V^2 : |\mathbf{r}_1 - \mathbf{r}_2| > d} \exp\left[-\beta W(|\mathbf{r}_1 - \mathbf{r}_2|) \right] d\mathbf{r}_1 \, d\mathbf{r}_2. \tag{3.324}$$

To evaluate this, we write the integrand as $1 - (1 - e^{-\beta W})$, and note that the double integral over $V^2 : |\mathbf{r}_1 - \mathbf{r}_2| > d$ is approximately[9] equivalent to integrating with respect to $\mathbf{r}_1$ over $V - \Omega$, where

$$\Omega = \tfrac{4}{3}\pi d^3 \tag{3.325}$$

is the exclusion volume (the volume surrounding $\mathbf{r}_2$ where $\mathbf{r}_1$ cannot be), and then integrating with respect to $\mathbf{r}_2$ over V. The result of this is that the second virial coefficient is

$$B = \tfrac{1}{2}\Omega + \frac{1}{2V} \int_V \int_{V-\Omega} \left\{ 1 - e^{-\beta W(|\mathbf{r}_1 - \mathbf{r}_2|)} \right\} d\mathbf{r}_1 \, d\mathbf{r}_2. \tag{3.326}$$

Again assuming $\Omega \ll V$, this can be approximately written as

$$B = \tfrac{1}{2}\Omega + \frac{1}{2V} \int_V \int_d^\infty 4\pi r^2 \left[1 - e^{-\beta W(r)} \right] dr \, d\mathbf{r}_2, \tag{3.327}$$

and if we suppose

$$W(r) = w(\xi), \quad \xi = \frac{r}{d}, \tag{3.328}$$

then

$$B = \tfrac{1}{2}\Omega + \tfrac{3}{2}\Omega \int_1^\infty \xi^2 \left[1 - e^{-\beta w(\xi)} \right] d\xi. \tag{3.329}$$

As an example, take the Lennard–Jones potential (see figure 3.13), for which

$$W \sim -W_0 \left(\frac{d}{r} \right)^6 \tag{3.330}$$

---

[9] The approximation is associated with inexactness for particles near the boundary. For example, for a particle touching the boundary, its exclusion volume is only $\tfrac{1}{2}\Omega$; the effect is small assuming $\Omega \ll V$, as we do.

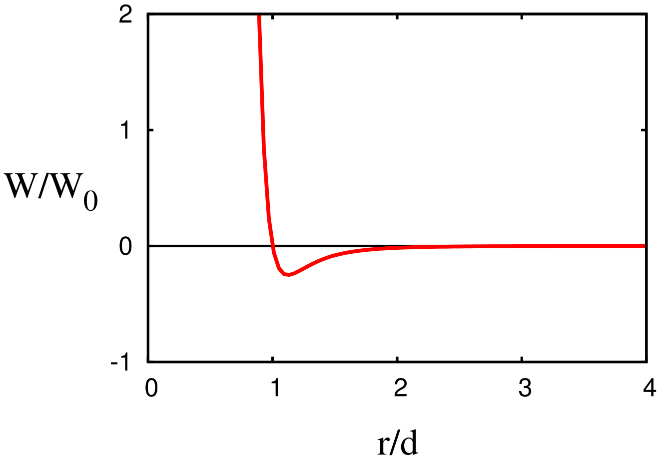

Figure 3.13: The Lennard-Jones potential for inter-particle forces. It is defined as $W = W_0\left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right]$.

at large r; writing $1 - e^{-\beta w} \approx \beta w$ and using (3.330), we find

$$B \approx \tfrac{1}{2}\Omega(1 - \beta W_0). \tag{3.331}$$

We then have

$$p \approx kT\left[n + \tfrac{1}{2}\Omega(1 - \beta W_0)n^2 + \ldots\right], \tag{3.332}$$

or equivalently

$$\frac{p\Omega + \frac{1}{2}W_0(\Omega n)^2}{kT} \approx \Omega n\{1 + \tfrac{1}{2}\Omega n\}. \tag{3.333}$$

The term Ωn is the ratio of the particle exclusion volume to the (mean) volume per particle, and represents the probability of finding a particle at any point in space. The correction term on the right is due to the fact that particles cannot inhabit the same volume, and the factor $\frac{1}{2}$ arises because of double counting of particle exclusion volume. More precisely, this suggests that we could equivalently write

$$\frac{p\Omega + \frac{1}{2}(\Omega n)^2 W_0}{kT} \approx \frac{\Omega n}{1 - \frac{1}{2}\Omega n} \tag{3.334}$$

instead of (3.333), although they are equivalent to the order of approximation given.

If we define

$$a = \tfrac{1}{2}\Omega W_0, \quad b = \tfrac{1}{2}\Omega, \tag{3.335}$$

then this can be written in the form

$$\left(p + \frac{aN^2}{V^2}\right)(V - bN) = NkT, \tag{3.336}$$

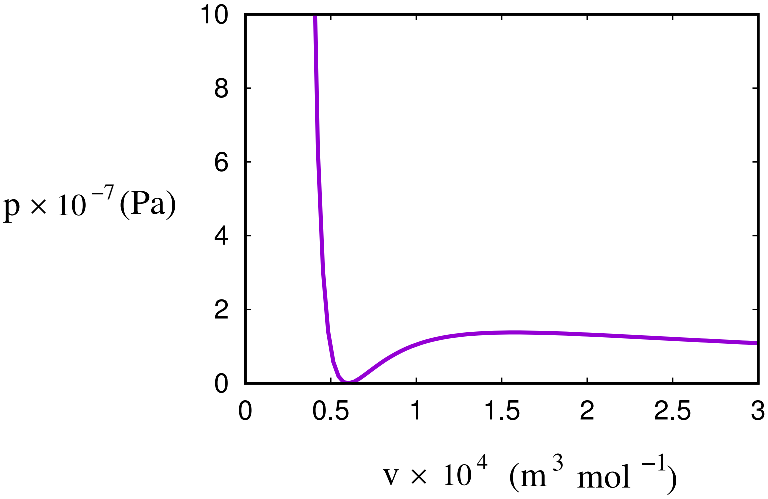

Figure 3.14: Phase transition in the Van der Waals gas. The plot represents p in units of 10^7 Pa as a function of the molar volume v in units of 10^{-4} m^3 mol^{-1} using (3.345), together with (3.344), and the values in (3.343); for these values, the critical value of $\gamma_c = 0.3$. The curve shown is for $\gamma = 0.25$. As γ decreases further, the minimum of the curve becomes negative. Note that the Van der Waals parameters for water, based on the critical point parameters, do not give an accurate estimate of the liquid molar volume: at $T = 100°$ C, $\gamma = 0.3$, and (3.346) would suggest $v_0 = 3.5 \times 10^{-5}$ m^3 mol^{-1}, whereas in fact the molar volume is only about half that.

which is known as the *Van der Waals* equation. As can be seen in figure 3.14, in conditions of prescribed T and p, multiple steady states are possible, and we associate these with phase transitions.

It is common to define the number of particles in terms of the number of *moles* by putting $N = AN_M$, where $A = 6 \times 10^{23}$ is Avogadro's number (particles per mole), and we then define

$$a' = aA^2, \quad b' = bA. \tag{3.337}$$

The units of a' are Pa (m^3 mol^{-1})^2, and those of b' are m^3 mol^{-1}. We also define the *molar volume* as

$$v = \frac{V}{N_M}. \tag{3.338}$$

In terms of these quantities, the Van der Waals equation takes the form

$$p = \frac{g}{v - b'} - \frac{a'}{v^2}, \tag{3.339}$$

where

$$g = RT \tag{3.340}$$

(using the fact that $R = kA$). Evidently we can assume $v > b'$. It is straightforward to show from this (cf. question 3.27) that p is a monotonically decreasing function of

v if $g < g_c$, where

$$g_c = \frac{8a'}{27b'}, \tag{3.341}$$

and this defines a critical temperature T_c. For $T < T_c$, p is non-monotonic, as shown in figure 3.14.

Thus for conditions of fixed pressure, *two* equilibrium molar volumes are possible. The lower one corresponds to the liquid state where $v = v_L$, and the upper corresponds to the gaseous state $v = v_G$. Typically $v_G \gg v_L$. As T approaches T_c, the liquid and gas densities approach each other, and become equal at $T = T_c$ and at a critical pressure

$$p_c = \frac{g_c}{8b'}; \tag{3.342}$$

at this *critical point*, the liquid–gas phase transition disappears. The definition of the critical point is where $p'(v) = p''(v) = 0$, and it is this which determines (3.341). Since the critical temperature and pressure can be experimentally determined, this allows us to determine a' and b'. For water, we have $T_c = 647$ K and $p_c = 221$ bars $= 2.21 \times 10^7$ Pa, and this leads to

$$a' = 0.55 \text{ Pa } (\text{m}^3 \text{ mol}^{-1})^2, \quad b' = 0.3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1},$$

$$g_c = 0.54 \times 10^4 \text{ Pa } (\text{m}^3 \text{ mol}^{-1}). \tag{3.343}$$

It is convenient to define

$$v = b'w, \quad g = \frac{a'\gamma}{b'}, \quad p = \frac{a'\Pi}{b'^2}, \tag{3.344}$$

so that w, γ and Π are dimensionless, and

$$\Pi = \frac{\gamma}{w-1} - \frac{1}{w^2}, \tag{3.345}$$

and this is used in plotting figure 3.14. At large w, $\Pi \approx \dfrac{\gamma}{w}$, and this is the perfect gas law. For small $w \approx 1$, we find

$$v \approx v_0(1 - \beta p), \quad v_0 = b'(1+\gamma), \quad \beta = \frac{\gamma b'^2}{a'(1+\gamma)}, \tag{3.346}$$

which represents the weakly compressible liquid.

At a fixed pressure, reduction of temperature eventually leads to the possibility of multiple steady states, and condensation occurs at a value of T determined by Maxwell's equal-area rule

$$\int_{v_L}^{v_G} p\, dv = p_{\text{sat}}(v_G - v_L), \tag{3.347}$$

which follows from the condition that when both phases are present, their chemical potentials must be equal. We have the result (e. g., by a Maxwell relation-type derivation from the grand potential relations (3.253))

$$\left.\frac{\partial \mu}{\partial p}\right|_{v,T} = v, \tag{3.348}$$

where μ is the molar chemical potential (cf. (3.256)), whence, integrating slightly illegally[10] from v_G to v_L,

$$\mu_L = \mu_G + \int_G^L \frac{v\,dp}{N}, \tag{3.349}$$

and we obtain (3.347) on integrating by parts.

3.6.2 Condensation

Having illustrated the mechanism of phase transition via the classical statistical mechanical approach, it is now of interest to see whether the Boltzmann equation can be used to infer the same result. The answer to this is: to some extent. We now describe how this is done.

First we return to the Boltzmann equation, but now we allow for a non-zero intermolecular attraction between the particles. The idea is that this term provides a mechanism for spatial instability, since it facilitates a tendency for particles to cluster together. Consulting (3.16), we now define the collision integral as the sum of two terms $Q_{\rm C}$ and $Q_{\rm LR}$, where $Q_{\rm C}$ is the usual collisional form given by (3.39), and $Q_{\rm LR}$ is given by (3.16). The Boltzmann equation, now sometimes called the Boltzmann–Vlasov equation with the extra term, takes the form

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla} f + \mathbf{A}.\boldsymbol{\nabla}_{\mathbf{v}} f = Q_{\rm C}, \tag{3.350}$$

where we ignore any external potential, and from (3.16),

$$\mathbf{A} = -\int_V \frac{a(\xi)\boldsymbol{\xi}}{\xi} n(\mathbf{r}-\boldsymbol{\xi},t)\,d\boldsymbol{\xi}, \tag{3.351}$$

in which

$$a(\xi) = \frac{W'(\xi)}{m} \tag{3.352}$$

is the inter-particle acceleration associated with the attractive part of the potential W. For the Lennard–Jones potential defined by

$$W = W_0\left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right], \tag{3.353}$$

we would take

$$a(\xi) = \frac{6W_0 d^6}{mr^7}, \quad r > d. \tag{3.354}$$

Next we non-dimensionalise the variables. We define the thermal velocity scale

$$v_0 = \sqrt{\frac{kT_0}{m}}, \tag{3.355}$$

---

[10] It is not the integration which is illegal, but the assumption that the passage from G to L proceeds along the equilibrium Van der Waals curve. It is particularly illegal when the equilibrium curve dips to negative pressures!

an acceleration scale

$$a_0 = \frac{W_0}{md}, \tag{3.356}$$

and a mean inter-molecular distance

$$l = \frac{1}{n_0^{1/3}}, \tag{3.357}$$

where n_0 is a typical value of the number density. We then scale the variables as

$$\begin{gathered} n \sim n_0, \quad f \sim \frac{n_0}{v_0^3}, \quad \mathbf{r} \sim l, \quad a = a_0 a^* \left(\frac{\xi}{d} \right), \\ v \sim v_0, \quad t \sim \frac{l}{v_0}, \quad \mathbf{A} \sim \frac{a_0 d^4}{l^4}, \quad Q_{\mathrm{C}} = \frac{n_0^2 d^2}{v_0^2} Q, \end{gathered} \tag{3.358}$$

and this leads us to the non-dimensional form of the equation,

$$\begin{aligned} & \frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla} f + \beta \mathbf{A}.\boldsymbol{\nabla}_{\mathbf{v}} f = \nu^2 Q, \\ Q \quad &= \quad \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)] \, d\Omega \, d\mathbf{w}, \\ \mathbf{A} \quad &= \quad -\frac{1}{\nu} \int_V \frac{a(\xi) \boldsymbol{\xi}}{\xi} n(\mathbf{r} - \nu \boldsymbol{\xi}, t) \, d\boldsymbol{\xi}, \end{aligned} \tag{3.359}$$

in which all the variables are dimensionless (in particular $d\Omega = dS/V$), we have dropped the asterisk from a^*, and the dimensionless parameters are defined by

$$\beta = \frac{a_0 d^4}{v_0^2 l^3}, \quad \nu = \frac{d}{l}. \tag{3.360}$$

In the absence of any spatial variation, $\mathbf{A} = \mathbf{0}$ and the left hand side of the equation is simply $\partial f / \partial t$. Thus the steady state is still given by the Maxwellian distribution, which in its dimensionless form is

$$f = f_0(v) = \frac{1}{(2\pi)^{3/2}} e^{-\frac{1}{2} v^2}, \tag{3.361}$$

where for convenience we will assume that the mean velocity is zero. We now examine the stability of this state to spatial perturbations.

As we did in the Chapman–Enskog method, we write $f = e^{\Phi}$, the Maxwellian is

$$\Phi_0 = -\tfrac{1}{2} v^2 - \tfrac{3}{2} \ln(2\pi), \tag{3.362}$$

and we linearise the equation about the steady state by writing

$$\Phi = \Phi_0 + \phi, \tag{3.363}$$

and neglecting nonlinear terms; the linearised form of $(3.359)_1$ is

$$\phi_t + \mathbf{v}.\boldsymbol{\nabla} \phi - \beta \mathbf{A}.\mathbf{v} = \nu^2 \mathcal{L} \phi, \tag{3.364}$$

where the linearised form of $\mathbf{A}$ is

$$\mathbf{A} = -\frac{1}{\nu}\int_P \frac{a(\xi)\boldsymbol{\xi}}{\xi} f_0(v)\phi(\mathbf{r}-\nu\boldsymbol{\xi},\mathbf{v},t)\,d\mathbf{v}\,d\boldsymbol{\xi}, \tag{3.365}$$

and the linearised collision operator is

$$\mathcal{L}\phi = \int_U \int_{\Omega_+} f_0(w)\Delta\phi\,d\Omega\,d\mathbf{w}. \tag{3.366}$$

We now seek normal mode solutions to this equation of the form

$$\phi = \psi(\mathbf{v})e^{i\mathbf{k}.\mathbf{r}+\sigma t}, \tag{3.367}$$

where $\mathbf{k}$ is the wave vector. This leads to the eigenvalue problem for $\psi(\mathbf{v})$ in the form

$$(\sigma + i\mathbf{k}.\mathbf{v})\psi - \beta\mathbf{B}.\mathbf{v} = \nu^2\mathcal{L}\psi, \tag{3.368}$$

where

$$\mathbf{B} = -\frac{1}{\nu}\int_V \frac{a(\xi)\boldsymbol{\xi}}{\xi} e^{-i\nu\mathbf{k}.\boldsymbol{\xi}}\,d\boldsymbol{\xi}, \tag{3.369}$$

and we have assumed a normalisation in which

$$\int_U f_0(v)\psi(\mathbf{v})\,d\mathbf{v} = 1. \tag{3.370}$$

To evaluate $\mathbf{B}$, we take Cartesian coordinates in $V = \mathbf{R}^3$ with the z axis in the $\mathbf{k}$ direction. By symmetry, the x and y components are zero, and therefore we can write

$$\mathbf{B} = iC(\nu k)\mathbf{k}, \tag{3.371}$$

and by changing to spherical polar coordinates, we find that (writing $K = \nu k$)

$$C(K) = \frac{4\pi}{K^2}\int_1^\infty ra(r)\left[\frac{\sin Kr}{Kr} - \cos Kr\right]dr; \tag{3.372}$$

see question 3.29. The function $C(K)$ is plotted in figure 3.15; its asymptotic limits for small and large K are (taking $a = 6/r^7$, corresponding to (3.354), and with a_0 given in (3.356))

$$\begin{aligned} C &\sim \tfrac{8}{3}\pi - \tfrac{4}{5}\pi K^2 + \ldots, \qquad K \to 0,\\ C &\sim \frac{24\pi\sin K}{K^3} + \ldots, \qquad K \to \infty. \end{aligned} \tag{3.373}$$

As a consequence of (3.371), (3.368) is

$$(\sigma + i\mathbf{k}.\mathbf{v})\psi - i\beta C\mathbf{k}.\mathbf{v} = \nu^2\mathcal{L}\psi. \tag{3.374}$$

Our aim is to solve this equation to determine $\sigma(\mathbf{k})$. Eigenfunctions ψ for which $\operatorname{Re}\sigma > 0$ are unstable.

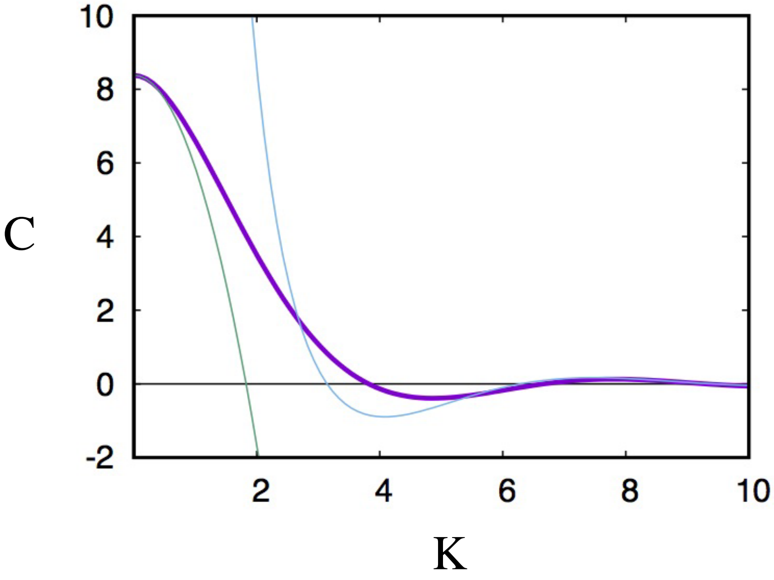

Figure 3.15: The function $C(\nu k) = C(K)$ defined by (3.372). The thin lines give the asymptotic limits from (3.373).

The limit $\nu \to 0$

The difficulty in solving (3.374) lies with the linearised collision operator $\mathcal{L}$. We are able to sidestep this difficulty by using the fact that $\nu \ll 1$. On this basis we neglect the collision term (and it can be shown that this is a regular perturbation), and then we simply have

$$\psi = \frac{i\beta C\mathbf{k}.\mathbf{v}}{\sigma + i\mathbf{k}.\mathbf{v}}, \tag{3.375}$$

and the normalisation condition (3.370) implies

$$i\beta C \int_U \frac{f_0(v)\mathbf{k}.\mathbf{v}\,d\mathbf{v}}{\sigma + i\mathbf{k}.\mathbf{v}} = 1, \tag{3.376}$$

and it is this which determines σ.

To evaluate (3.376), we take the z axis in the direction of $\mathbf{k}$, so that $\mathbf{k}.\mathbf{v} = kz$. Carrying out the integrals in x and y, this leads to

$$\frac{i\beta C}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{kz\, e^{-\frac{1}{2}z^2}\, dz}{\sigma + ikz} = 1. \tag{3.377}$$

Defining

$$\sigma = \sqrt{2}k\eta, \tag{3.378}$$

this can be manipulated to the form

$$\frac{1}{\beta C} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{te^{-t^2}\, dt}{t - i\eta}, \tag{3.379}$$

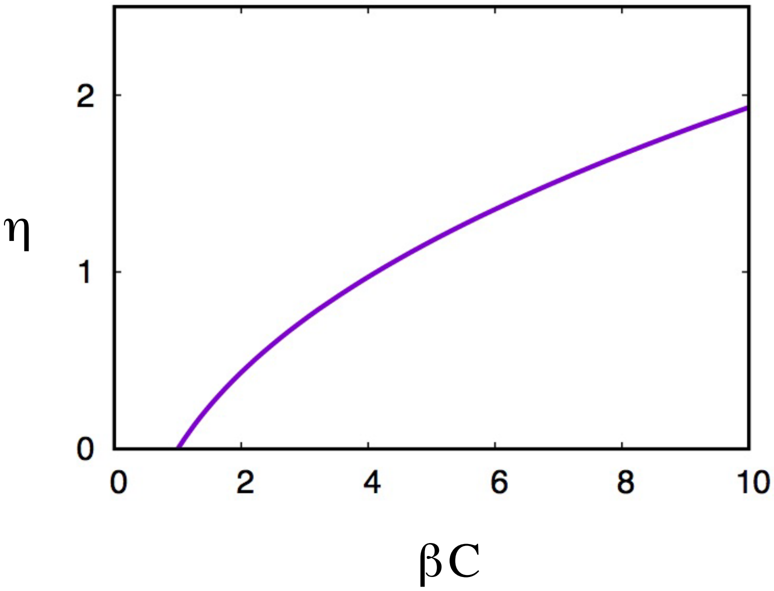

Figure 3.16: The scaled growth rate $\eta = \dfrac{\sigma}{\sqrt{2}k}$ as a function of βC, given by (3.382).

and then

$$1 - \frac{1}{\beta C} = \frac{\eta}{i\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-t^2}\,dt}{t - i\eta} = \frac{2\eta^2}{\sqrt{\pi}} \int_0^{\infty} \frac{e^{-t^2}\,dt}{t^2 + \eta^2}; \tag{3.380}$$

see also question 3.30. This integral is related to a form of the 'plasma dispersion function'. Specifically, if we define

$$w(i\eta) \equiv W(\eta) = e^{\eta^2} \operatorname{erfc} \eta, \tag{3.381}$$

then, providing $\operatorname{Re}\eta > 0$, the integral in (3.380) is proportional to $W(\eta)$, and

$$1 - \frac{1}{\beta C} = \sqrt{\pi}\eta W(\eta) = \sqrt{\pi}\eta\, e^{\eta^2} \operatorname{erfc} \eta. \tag{3.382}$$

If η is a root of (3.379), then so is $-\bar{\eta}$ (by taking the complex conjugate of the first integral) and $\bar{\eta}$ (by taking the complex conjugate of the second integral); and thus also $-\eta$: it follows that we can take $\operatorname{Re}\eta \geq 0$ without loss of generality, since for $\operatorname{Re}\eta < 0$, we simply consider $-\eta$. By taking the imaginary part of the second integral in (3.380), it follows that in fact either η is real or purely imaginary. The latter case corresponds to neutral stability, and is discussed below. For real η, we can then suppose $\eta > 0$. In this case, (3.380) shows that a root only exists if $\beta C > 1$, and this is shown in figure 3.16.

The basic result is that the uniform steady state is unstable to spatial fluctuations if $\beta C > 1$, and this first occurs when $\beta > \frac{3}{8\pi}$, which thus gives the critical value for condensation to occur. Near this value, we can expand C for small K (from (3.373)) and βC for small η, and this leads to the approximate result, when $\beta \approx \frac{3}{8\pi}$, that

$$\sigma \approx \sqrt{\frac{2}{\pi}}k\left[\left(\tfrac{8}{3}\beta\pi - 1\right) - \tfrac{3}{10}\nu^2k^2\right]. \tag{3.383}$$

The case $\beta C < 1$

What happens if $\beta C < 1$? It appears that in this case, the only possibility is a pure wave motion in which $\sigma = -i\omega$, and in that case the defining equation for ψ, (3.374), can be written as

$$(\mathbf{k}.\mathbf{v} - \omega)\psi - \beta C\mathbf{k}.\mathbf{v} = -i\nu^2\mathcal{L}\psi. \tag{3.384}$$

Again we neglect the collision term on the basis that ν is small. Now because of the singularity of (3.384), solutions take the approximate form

$$\psi = \frac{\beta C\mathbf{k}.\mathbf{v}}{\mathbf{k}.\mathbf{v} - \omega} + \sqrt{2\pi}A\,\delta\Big(z - \frac{\omega}{k}\Big), \tag{3.385}$$

where we take the z coordinate in U in the direction of $\mathbf{k}$.

The normalisation condition now leads, after some algebra, to

$$\frac{\beta C\Omega}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{e^{-t^2}dt}{t-\Omega} + Ae^{-\Omega^2} = (1-\beta C), \tag{3.386}$$

where we have defined

$$\omega = \sqrt{2}k\Omega, \tag{3.387}$$

and using the Plemelj formulae together with the definition of $w(z)$ in (3.380) and (3.381), this leads to the definition of A as

$$A = 2\beta C\Omega\int_0^{\Omega} e^{t^2}\,dt + (1-\beta C)e^{\Omega^2}. \tag{3.388}$$

It may be noted that if $\beta C < 1$, the possibility of $A = 0$ is not available. In view of (3.387), the wave speed is $\sqrt{2}\Omega$.

The instability we have identified is associated with condensation. It is natural to enquire whether the Boltzmann theory can be pushed further into the nonlinear limit. It seems so: the asymptotic approximation of $(3.359)_1$ as

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla} f + \beta\mathbf{A}.\boldsymbol{\nabla}_{\mathbf{v}} f = 0 \tag{3.389}$$

remains valid until $f \sim 1/\nu^3$ and $r \sim \nu$, at which point nucleation occurs; until that point, (3.389) applies, and the suggestion is that nucleation occurs through a finite time blow-up of f, this only being eventually capped by the entrance of the collision integral when molecular spacing is of $O(d)$; however, this remains as conjecture.

3.6.3 Surface energy

Consider a situation in which two fluids are separated by an interface. We might have two liquids such as oil and water, or a gas and a liquid such as air and water, or even a solid-liquid interface such as ice and water. We think of the latter as representing a phase change, whereas we think of an air/water interface as being an interface between two different substances, but in fact the difference is one of degree. Place water in a container with vacuum above and the water will immediately begin to evaporate, so that the space above the water becomes filled with water vapour; this is a simple change of phase. The only difference when air fills the space above is that the gas phase is now a mixture of different gases (including water vapour), and equally the water phase is a mixture of water with dissolved gases from the air. Both situations represent phase change, with the difference simply being that the air/water interface represents phase change of a mixture, which in other terms is simply an alloy.

Interfaces possess energy. In order to create a surface in a fluid (or solid), molecular bonds must be cut: effectively molecules must be pulled apart and this requires work to be done, which is manifested as an excess energy of the surface. Suppose the surface energy of an interface of area A between two fluids, as shown in figure 3.17, is γ. If we perturb the interface, so that the area becomes $A + dA$, then the increment of the Helmholtz free energy (at constant T, V) is

$$dF = \sum_i (-p\,dV - S\,dT) + \gamma\,dA = 0, \tag{3.390}$$

and since $dV_1 = -dV_2 = dV$, say, we derive the interfacial jump condition

$$p_1 - p_2 = \gamma \frac{\partial A}{\partial V} = 2\gamma\kappa = \gamma \boldsymbol{\nabla}.\,\mathbf{n}. \tag{3.391}$$

The quantity κ in (3.391) is defined to be the mean curvature, and the fact that $\dfrac{\partial A}{\partial V} = \boldsymbol{\nabla}.\,\mathbf{n}$ is a result of differential geometry which can be understood by reference to figure 3.18. In perturbing the surface, we may suppose each point of the surface moves along the normal $\mathbf{n}$, thus tracing out an incremented volume, whose normal $\hat{\mathbf{n}}$

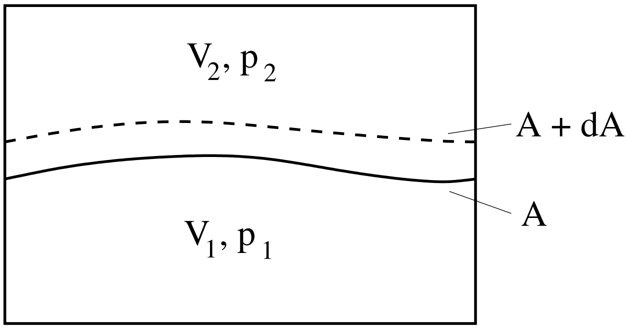

Figure 3.17: Two fluids of volumes V_1 and V_2 and pressures p_1 and p_2 are separated by an interface of area A.

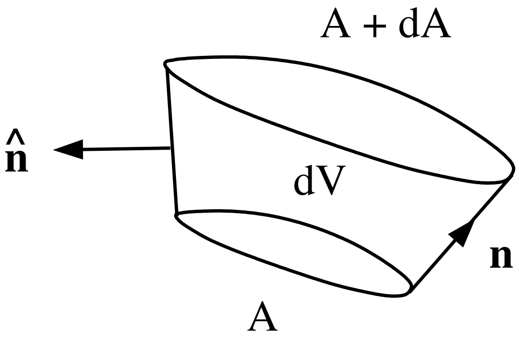

Figure 3.18: Calculation of surface curvature.

is equal to $\mathbf{n}$ on A and $A + dA$, but orthogonal to it on the interconnecting surface. Evidently, then

$$dA = \int_{\partial(dV)} \mathbf{n}.\hat{\mathbf{n}}\,dS = \int_{dV} \boldsymbol{\nabla}.\,\mathbf{n}\,dV, \tag{3.392}$$

whence

$$\frac{\partial A}{\partial V} = \boldsymbol{\nabla}.\,\mathbf{n}. \tag{3.393}$$

In practice, if the surface is given by $z = \eta(x, y)$, then

$$\boldsymbol{\nabla}.\,\mathbf{n} = -\boldsymbol{\nabla}.\left[\frac{\boldsymbol{\nabla}\eta}{(1 + |\boldsymbol{\nabla}\eta|^2)^{1/2}}\right], \tag{3.394}$$

and for small values of the curvature we have the commonly used approximation

$$2\kappa = -\nabla^2\eta. \tag{3.395}$$

3.6.4 The Clapeyron equation

The saturation temperature at which phase change occurs depends on pressure. It is for example well known that the boiling point of water decreases as pressure decreases. This is certainly familiar to mountain climbers. And as mentioned in the preceding section, boiling effectively begins immediately in a vacuum. The dependence of melting or boiling temperature on pressure is determined by the *Clapeyron equation*, (sometimes the Clausius–Clapeyron equation), which is derived as follows.

At equilibrium between two phases, let us say solid and liquid, of a pure (single component) material, the specific Gibbs free energies[11] are equal, $g_s = g_l$, for given temperature and pressure. Now suppose the pressure (and consequently also the (melting) temperature) is changed. Then for each phase

$$\Delta g = v\Delta p - s\Delta T, \tag{3.396}$$

---

[11] Which are the chemical potentials.

where v is specific volume and s is specific entropy, but since we remain in equilibrium, the change must be the same for each phase; it follows that

$$\Delta s \Delta T = \Delta v \Delta p, \tag{3.397}$$

where

$$\Delta s = s_l - s_s, \quad \Delta v = v_l - v_s. \tag{3.398}$$

The latent heat is defined as $L = T_M \Delta s = \Delta h$, where T_M is the melting temperature, and thus (3.397) can be written in the form

$$\frac{\Delta T}{T_M} = \frac{\Delta v}{L} \Delta p, \tag{3.399}$$

and this is the Clapeyron equation. Normally $\rho_s > \rho_l$, i. e., $\Delta v > 0$, so that T_M increases with pressure. The melting point of ice is a rare exception (since ice floats on water); silicon is another.

The Gibbs–Thomson effect

If in addition we allow the interface to be curved, that is, we consider also surface energy, then an additional correction to the Clapeyron equation ensues; this is called the Gibbs–Thomson effect. (3.396) still applies, but now $\Delta p_s \neq \Delta p_l$; the consequent generalisation of (3.399) is

$$\frac{L \Delta T}{T_M} = \Delta v \Delta p_l + v_s (p_s - p_l), \tag{3.400}$$

assuming a reference state of zero curvature. This is the generalised Clapeyron equation. The term in $p_s - p_l$ represents the effect of surface energy.

3.6.5 Alloys

Next we consider the solidification of alloys, which are mixtures of two or more substances. We will frame our discussion in terms of freezing liquids, but the reader should be aware that there is no real distinction between the processes of melting and freezing, evaporation and condensation, dissolution and precipitation, and indeed chemical reaction. They all involve a change of state, where matter in one macroscopic form is transformed to another, and the same basic principles describe them all.

At a solid-liquid interface the chemical potentials of each component are equal:

$$\mu_i^L = \mu_i^S \tag{3.401}$$

for components $i = 1, 2, \ldots$. For two components A and B, say, we let c be the concentration (as mole fraction) of B. For an ideal solution we have

$$\mu_A = \mu_A^0 + RT \ln(1 - c), \quad \mu_B = \mu_B^0 + RT \ln c \tag{3.402}$$

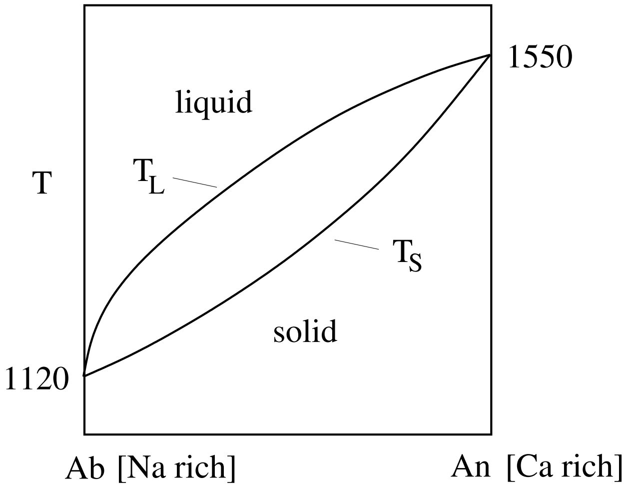

Figure 3.19: The phase diagram for the solid solution albite (Ab)–anorthite (An), which can be found on page 106 of McBirney (1984). T_L is the liquidus and T_S the solidus. The rock is called plagioclase, and is a solid solution of the general form $(\mathrm{NaSi})_x(\mathrm{CaAl})_{1-x}\mathrm{AlSi_2O_8}$.

in each phase, and the specific Gibbs free energy in each phase has the form

$$g = \mu_A(1-c) + \mu_B c. \tag{3.403}$$

The condition of equilibrium between the two phases can then be shown (see question 3.33) to be determined by the values of c_S in the solid phase and c_L in the liquidus phase which mark the locations of tangency of a straight line to the functions $g_S(c)$ and $g_L(c)$. This gives two distinct values of concentration of A in solid and liquid for an ideal solution, and a typical such phase diagram is shown in figure 3.19, for the crystalline rock plagioclase, which forms from the solidification of certain magmas.

The plagioclase phase diagram represents the situation where an ideal mixture forms a 'solid solution'. The mixture is ideal in that the two components are miscible: there is no energetic penalty for mixing the molecules, and the solid solution represents the solid phase equivalent. In plagioclase, we can simply replace the combination Na-Si with Ca-Al, without energetic penalty. It is more commonly the case that the solid phases, at least, are immiscible, and this modifies the form of the chemical potentials in (3.403), for example as suggested in question 3.33. The consequence of this is the typical eutectic phase diagram shown in figure 3.20.

3.6.6 Nucleation and crystal growth

When a solid is precipitated from a solution, or freezes from a liquid, nucleation occurs, in which a small nucleus of finite radius is created, and subsequently grows. If this occurs spontaneously within the liquid, the process is called homogeneous nucleation; if it occurs on an impurity (typically a pre-existing solid particle, but any solid surface will do), it is called heterogeneous nucleation. In practice, unless

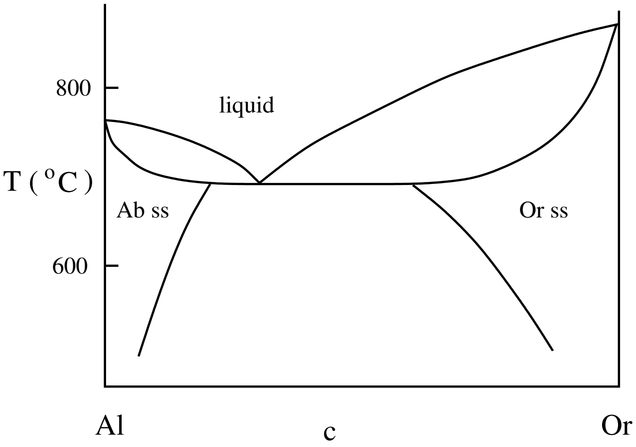

Figure 3.20: A phase diagram representing eutectic solidification. This is for the system albite ($NaAlSi_3O_8$)—orthoclase ($KAlSi_3O_8$) (McBirney 1984, p. 110). The albite and orthoclase solid solution (ss) fields are indicated.

great care is taken, heterogeneous nucleation is the norm. Nucleation can be easily observed in a saucepan of boiling water. As the temperature increases, sub-cooled boiling occurs as small bubbles rapidly grow and then collapse from sites on the base of the pan. Only as the boiling temperature is approached does the bubble nucleation become regular and continuous.

Consider now nucleation of an almost pure solid A from a (uniform) liquid solution of A in B. In the absence of any solid, we suppose that the chemical potential of A in the liquid is μ_A^L, and N molecules of A will thus have a Gibbs free energy $\mu_A^L N$. If these same N molecules form a solid nucleus, then there is a corresponding free energy $\mu_A^S N$, but in addition the surface has an additional surface area $4\pi\gamma r^2$, where γ is surface energy and r is nucleus radius. Therefore the change of free energy in creating the nucleus is

$$\Delta G = 4\pi\gamma r^2 - N\Delta\mu_A^\infty, \tag{3.404}$$

where $\Delta\mu_A^\infty = \mu_A^L - \mu_A^S$. We relate N to r as follows. If the solid molecules have mass m and molecular volume v, then the solid density is $\rho_s = \dfrac{m}{v}$, and additionally $mN = \frac{4}{3}\pi r^3 \rho_s$ for a spherical nucleus, whence (3.404) gives

$$\Delta G = 8\pi\gamma \left[\tfrac{1}{2}r^2 - \frac{r^3}{3r_c}\right], \tag{3.405}$$

where the critical radius is

$$r_c = \frac{2\gamma v}{\Delta\mu_A^\infty}. \tag{3.406}$$

Figure 3.21 shows the variation of ΔG with r. It increases to a maximum when $r = r_c$ and then decreases. The maximum value is an equilibrium, and thus gives (analogously to determination of the liquidus temperature) the dependence of the

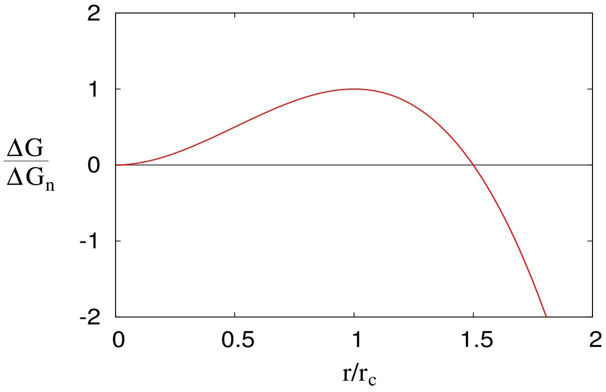

Figure 3.21: The variation of free energy with nucleus radius.

equilibrium concentration on nucleus radius. The maximum value at r_c,

$$\Delta G_n = \frac{16\pi\gamma^3 v^2}{3(\Delta\mu_A^\infty)^2}, \tag{3.407}$$

represents an explicit energy barrier which needs to be overcome if a viable nucleus is to form. The mechanism to do this is analogous to the way in which chemical reactions occur, and is due to statistical fluctuations in the molecular motions.

Lifshitz-Slyozov theory

To understand the implication of figure 3.21, we need to consider a supersaturated liquid in which the chemical potential $\mu_A^L > \mu_A^S$. The point is that equilibrium at the surface requires $\mu_A^L = \mu_A^S$ there, so that a supersaturated liquid is one where in the far field $\mu_A^L > \mu_A^S$. If $\Delta\mu_A^\infty = 0$, nucleation is impossible.

Suppose then that we have a spherical nucleus in a liquid with concentration (mole fraction) c. If the solution is ideal, we have

$$\mu_A^L = \mu_A^S + kT \ln\left(\frac{c}{c_s}\right), \tag{3.408}$$

where c_s is the saturation concentration where liquid and solid are in equilibrium (for a planar interface). (We use k rather than R as we have defined μ as energy per particle.) Lifshitz-Slyozov theory considers the situation where the far field is supersaturated, thus $c \to c_s + \Delta c$ as the spherical polar radius $\xi \to \infty$, but $\Delta\mu_A = \mu_A^L - \mu_A^S$ is spatially varying (and so $\Delta\mu_A^\infty$ denotes the far field value). On the other hand, we suppose that the chemical potential is at equilibrium *at the interface*, thus

$$\Delta\mu_A = \frac{2\gamma v}{r} \quad \text{at} \quad \xi = r \tag{3.409}$$

(this follows from the remark after (3.406)). For small supersaturations,

$$\Delta\mu_A \approx \frac{kT(c - c_s)}{c_s}, \tag{3.410}$$

and therefore the concentration field in the liquid satisfies

$$\begin{aligned} c &\to c_s + \Delta c \quad \text{as} \quad \xi \to \infty, \\ c &= c_s + \frac{\alpha}{r} \quad \text{on} \quad \xi = r, \end{aligned} \tag{3.411}$$

where

$$\alpha = \frac{2\gamma v c_s}{kT}. \tag{3.412}$$

The excess chemical potential in the far field is

$$\Delta\mu_A^\infty \approx \frac{kT\Delta c}{c_s}. \tag{3.413}$$

If we assume that crystal growth rate $V = \dot{r}$ is slow compared to diffusion in the liquid (this will be the case if $rV \ll D$, where D is the solute diffusion coefficient), then we can take the concentration field to be in equilibrium, and thus

$$c = c_s + \Delta c + \frac{\alpha - r\Delta c}{\xi}. \tag{3.414}$$

The growth rate is equal to the diffusive flux at the interface, and thus

$$\dot{r} = V = \frac{D}{r}\left(\Delta c - \frac{\alpha}{r}\right). \tag{3.415}$$

This explicitly shows that the equilibrium at $r_c = \dfrac{\alpha}{\Delta c}$ is unstable, and nuclei below this threshold size will collapse. Also, the assumption $r\dot{r} \ll D$ which allows the quasi-static approximation to be made is seen to require the supersaturation to be small, $\Delta c \ll 1$.

The Lifshits–Slyozov theory can be used to study coarsening, or Ostwald ripening, which is the process whereby larger crystals grow at the expense of smaller ones. The physical mechanism for this is that the concentration at the surface of small crystals is higher than at the surface of large crystals, so there is a tendency for solute to flow from small to large. In a supersaturated medium, all supercritical crystals will grow, but as they do the supersaturation decreases, and the smallest crystals eventually become subcritical and disappear.

To analyse this, we need to define a grain size distribution $\phi(r,t)$, such that $\phi\,dr$ is the number density per unit volume of the medium of crystals with radius in $(r, r+dr)$. Conservation of crystals then gives the equation

$$\phi_t + (V\phi)_r = 0, \tag{3.416}$$

where in a mean field approximation based on small crystal volume fraction, the growth rate $V(r,t)$ is given by (3.415); V depends on t because Δc varies with time. Specifically, the volume fraction of crystals is

$$\Phi = \int_0^\infty \tfrac{4}{3}\pi r^3 \phi\, dr; \tag{3.417}$$

then if Δc_0 is the initial supersaturation, conservation of solute implies

$$\Delta c = \frac{\Delta c_0 - \Phi}{1 - \Phi} \approx \Delta c_0 - \Phi \tag{3.418}$$

for the weak supersaturation limit $\Delta c_0 \ll 1$. Thus V is given by

$$V = D\left[\frac{\Delta c_0 - \Phi}{r} - \frac{\alpha}{r^2}\right], \tag{3.419}$$

and by integrating (3.416) from 0 to ∞ and using integration by parts, we find

$$\dot{\Phi} = 4\pi D\left[(\Delta c_0 - \Phi)\bar{r} - \alpha N\right], \tag{3.420}$$

where $\bar{r}$ and N are the mean radius per unit volume and the number density of particles,

$$\bar{r} = \int_0^\infty r\phi\,dr, \quad N = \int_0^\infty \phi\,dr. \tag{3.421}$$

(3.416) is a hyperbolic equation for which the characteristics are

$$\begin{aligned}\dot{r} &= D\left(\frac{\Delta c - \Phi}{r} - \frac{\alpha}{r^2}\right),\\ \dot{\phi} &= D\left(\frac{\Delta c - \Phi}{r^2} - \frac{2\alpha}{r^3}\right)\phi,\\ \dot{\Phi} &= 4\pi D\left[(\Delta c_0 - \Phi)\bar{r} - \alpha N\right],\end{aligned} \tag{3.422}$$

and in general numerical solution is necessary, subject to initial conditions for ϕ at $t = 0$. (No conditions are necessary at $r = 0$ since for $\alpha > 0$ all characteristics arrive at $r = 0$ from $t = 0$.)

It is clear from $(3.422)_3$ that $\Phi \to \Delta c_0$ at large time, and a local similarity solution describing this approach is available. We define

$$\phi = \frac{1}{t^{4/3}}\psi(s,t), \quad s = \frac{r}{t^{1/3}}, \tag{3.423}$$

from which it follows that

$$\Phi = \int_0^\infty \tfrac{4}{3}\pi s^3\psi\,ds, \quad \bar{r} = \frac{\bar{s}}{t^{2/3}}, \quad N = \frac{\bar{N}}{t}, \tag{3.424}$$

where

$$\bar{s} = \int_0^\infty s\psi\,ds, \quad \bar{N} = \int_0^\infty \psi\,ds. \tag{3.425}$$

Equation (3.416) then takes the form

$$-\tfrac{4}{3}\psi + t\psi_t + \frac{\partial}{\partial s}\left[D\left\{\frac{t^{1/3}(\Delta c_0 - \Psi)}{s} - \frac{\alpha}{s^2}\right\}\psi\right] = 0, \tag{3.426}$$

of which we seek a solution

$$\psi \sim \psi_0(s) + \frac{\psi_1(s)}{t^{1/3}} + \ldots, \qquad \Phi \sim \Phi_0 - \frac{\Phi_1}{t^{1/3}} + \ldots, \tag{3.427}$$

and equating inverse powers of t then requires

$$\begin{aligned}
\Phi_0 &= \int_0^\infty \tfrac{4}{3}\pi s^3 \psi_0 \, ds = \Delta c_0, \\
\Phi_1 &= \frac{\alpha \bar{N}_0}{\bar{s}_0}, \quad \bar{s}_0 = \int_0^\infty s\psi_0 \, ds, \quad \bar{N}_0 = \int_0^\infty \psi_0 \, ds,
\end{aligned} \tag{3.428}$$

and the solution for ψ_0 is

$$\psi_0 = \frac{Bs^2}{(\Phi_1 s + \alpha)^\nu} \exp\left[\frac{\alpha s}{\Phi_1^2} - \frac{s^2}{2\Phi_1}\right], \quad \nu = 1 + \frac{\alpha^2}{\Phi_1^3}, \tag{3.429}$$

where B is determined by satisfying $(3.428)_1$. These results are consistent with the famous coarsening law $r \sim t^{1/3}$.

Becker–Döring theory

We now turn to the fundamental problem of homogeneous nucleation, which is to describe the mechanism of creation of supercritical nuclei. The deterministic Lifshits–Slyozov theory clearly implies that subcritical nuclei simply disappear, so in order to enable supercritical nucleus formation, we must revert to a stochastic description.

In the Becker–Döring theory, we consider nuclei to be clusters of particles, and we let N_n be the number density per unit volume of the fluid of clusters having n particles. In particular, N_1 is just the solute concentration of the liquid. The cluster numbers are governed by the reversible reaction

$$N_n + N_1 \underset{k_n^-}{\overset{k_n^+}{\rightleftharpoons}} N_{n+1}, \quad n \geq 1. \tag{3.430}$$

The overall reaction rates are

$$R_n = k_n^+ N_1 N_n - k_n^- N_{n+1}, \tag{3.431}$$

and the equations are then

$$\begin{aligned}
\dot{N}_n &= R_{n-1} - R_n, \quad n \geq 2, \\
\dot{N}_1 &= -2R_1 - \sum_2^\infty R_n,
\end{aligned} \tag{3.432}$$

where the factor two in the equation for N_1 arises because two N_1 molecules are involved in the R_1 reaction. It follows from these that particle number is conserved, as it should be:

$$\sum_1^\infty n N_n = C. \tag{3.433}$$

The system has a possible steady state, in which $R_n = 0$, and this implies

$$N_n = L_n N_1^n, \tag{3.434}$$

where

$$L_n = \prod_1^{n-1} K_i, \quad L_1 = 1, \quad K_i = \frac{k_i^+}{k_i^-}; \tag{3.435}$$

N_1 is determined from

$$\sum_1^\infty n L_n N_1^n = C, \tag{3.436}$$

providing this series converges; as we shall see, this is only the case when the solution is not supersaturated.

The system has a Lyapounov function, analogous to Boltzmann's H-function, given by

$$H = \sum_1^\infty N_n \left[\ln \left(\frac{N_n}{L_n} \right) - 1 \right], \tag{3.437}$$

from which it follows (noting that $L_{n+1} = K_n L_n$) that

$$\dot{H} = -\sum_1^\infty k_n^- N_{n+1} \left[\frac{L_{n+1} N_1 N_n}{L_n N_{n+1}} - 1 \right] \ln \left(\frac{L_{n+1} N_1 N_n}{L_n N_{n+1}} \right) \leq 0, \tag{3.438}$$

with equality ($\dot{H} = 0$) only at the steady state, where H is a minimum, and

$$H = H_0 = C \ln N_1 - \sum_1^\infty L_n N_1^n. \tag{3.439}$$

If the steady state exists, it is thus globally stable.

The question now arises, does the steady solution exist? It does if the series (3.436) converges. This depends on the definition of L_n and thus K_n, and thus we need to make some assumption about the forward and backward rate coefficients $k_n^\pm$. Before we do this, we derive the continuum limit of the model, which yields a Fokker–Planck equation for N. We can write $(3.432)_1$ and (3.431) in the form

$$\begin{aligned} \dot{N}_n &= R_{n-1} - R_n, \\ R_n &= V_n N_n - k_n^- (N_{n+1} - N_n), \end{aligned} \tag{3.440}$$

where

$$V_n = k_n^+ N_1 - k_n^-. \tag{3.441}$$

Replacing differences by derivatives, we find

$$\begin{aligned} \frac{\partial N}{\partial t} + \frac{\partial R}{\partial n} &= 0, \\ R &= VN - D^* \frac{\partial N}{\partial n}, \end{aligned} \tag{3.442}$$

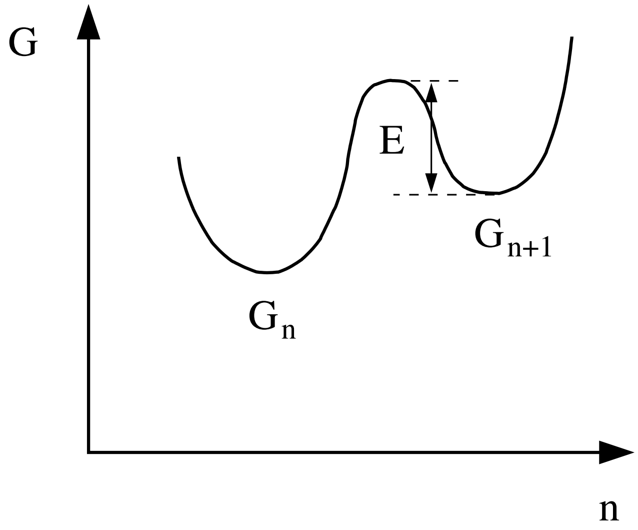

Figure 3.22: Schematic illustration of the neighbouring potential wells of n- and $(n+1)$-clusters.

where $V = V_n$, $D^* = k_n^-$; this approximation is valid when the variables are slowly varying, which in turn is the case when n is large. We see that (3.442) is analogous to the Lifshits–Slyozov theory, with the growth rate being V, but with the crucial extra diffusive term, which arises through the stochasticity of the process.[12] It is this which enables nucleation to occur. In order to compare the two theories, we need to compare the respective growth rates V. The Lifshits–Slyozov growth rate is given by (3.415). Using the definitions of α in (3.412) and Δc from (3.413), and relating particle number to radius via

$$n = \frac{4\pi r^3}{3v}, \tag{3.443}$$

where v is particle (molecular) volume, we find that the Lifshitz–Slyozov cluster growth rate (in terms of n, i. e., $\dfrac{dn}{dt}$), is

$$V^{LS} = \frac{8\pi\gamma Dc}{kT}\left[\left(\frac{n}{n_c}\right)^{1/3} - 1\right], \tag{3.444}$$

where n_c is the critical cluster particle number, corresponding to r_c in (3.405) using (3.443). We now compare this to the Becker-Döring growth rate in (3.441).

We conceptualise the rate coefficients $k_n^{\pm}$ as being associated with a jump over an energy barrier, as discussed in section 3.5.3, and illustrated in figure 3.22. It is thus

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[12] It is tempting to try and derive the Becker–Döring equations by means of a random walk model, where $p_n(t) = \dfrac{N_n}{\sum_1^\infty N_n}$ is the probability that a cluster is of size n. It seems difficult to do this, because the total number of clusters is not conserved during the process. See also question 3.35.

natural to suppose that

$$k_n^+ = k_+ \exp\left[-\frac{(G_{n+1} - G_n + E)}{kT}\right], \quad k_n^- = k_- \exp\left[-\frac{E}{kT}\right], \tag{3.445}$$

and we will arbitrarily suppose that the detachment activation energy E is constant. In the continuum limit, $G_{n+1} - G_n \approx \Delta G_{n+1} - \Delta G_n \approx G'$, where we take $G(n)$ to be determined by (3.405). Translating this, we find

$$-G' \approx \frac{kT\Delta c}{c}\left[1 - \left(\frac{n_c}{n}\right)^{1/3}\right]. \tag{3.446}$$

The Becker–Döring growth rate is thus

$$V^{BD} = k_n^- \left[KN_1 \exp\left\{\frac{\Delta c}{c}\left[1 - \left(\frac{n_c}{n}\right)^{1/3}\right]\right\} - 1\right], \tag{3.447}$$

where

$$K = \frac{k_+}{k_-}. \tag{3.448}$$

Since we assume small supersaturation, we can expand (3.447) to find

$$V^{BD} = k_n^- \left[KN_1 - 1 + KN_s\Delta c\left\{1 - \left(\frac{n_c}{n}\right)^{1/3}\right\}\right], \tag{3.449}$$

where since c is mole fraction and N_1 is solute molecules per unit volume, $N_1 = N_s c$, N_s being the (approximately constant) solvent molecule number per unit volume. (3.447) or (3.449) can be compared to (3.444). Despite the obvious differences, the behaviour of each expression has similar behaviour, being negative for small n, and monotonically increasing with n. The only significant difference is that the Becker–Döring threshold nucleus number depends on solute concentration, unless $N_1 = \dfrac{1}{K}$. More generally, N_1 will decrease during crystallisation, implying that nucleation becomes more and more difficult as growth proceeds. That there is a difference is unsurprising insofar as the Becker–Döring theory ignores spatial variability in the solute field.

Heterogeneous nucleation

The Becker–Döring theory provides a rational description for the homogeneous nucleation of crystals, but in reality, unless extreme experimental care is taken, nucleation occurs heterogeneously, on pre-existing impurities in the liquid. To understand how this occurs, consider an area A of a solid impurity in contact with a liquid solution, where the chemical potential of A is μ_A^L. If the area forms a nucleus of precipitate consisting of N molecules with chemical potential μ_A^S, then the change in free energy is $-(\mu_A^L - \mu_A^S)N = -\Delta\mu_A N$, but the corresponding change of surface energy is $(\gamma_{SI} + \gamma_{SL} - \gamma_{LI})A = \Delta\gamma A$, where γ_{jk} is the surface energy at the interface between phase j and phase k (S, L, I indicate solid, liquid, impurity). If the nucleated solid phase is (initially) a monolayer, then $N = \dfrac{A}{d^2}$, where d is particle diameter, and thus the total free energy change is

$$\Delta G = \left(\Delta\gamma - \frac{\Delta\mu_A}{d^2} \right) A. \tag{3.450}$$

We thus see that heterogeneous nucleation occurs ‘spontaneously’ if $\Delta\mu_A > d^2\Delta\gamma$, and there is no energy barrier to nucleation. In this case, a Becker–Döring type theory is unnecessary (it would be associated with two-dimensional spreading of the monolayer across the surface), and growth will occur as soon as the nucleation threshold (3.450) is achieved. Note that $\Delta\gamma$ may be negative; in this case sub-critical nucleation occurs, but is not maintained as the crystals grow and become spherical. An example of this is observed in sub-cooled boiling, for example in a saucepan of water, where small bubbles are nucleated in crevices, rapidly grow to become spherical before collapsing.

We can adapt Lifshits–Slyozov theory to this case also. Assuming equilibrium at the interface of a spherical crystal of radius r, where $\Delta G = 0$ in (3.450), we find the crystal growth rate is, using (3.410),

$$V = \frac{D}{r} \left[\Delta c - \frac{c_s d^2 \Delta\gamma}{kT} \right]_+, \tag{3.451}$$

where $[x]_+ = \max(x, 0)$, and growth begins from the assumed known impurity grain size.

3.7 Notes and references

There are, of course, a large number of books on statistical mechanics, and they trace their way through the subject in various ways. Commonly, there is introductory review material on probability, and sometimes on thermodynamics, enunciated as a set of rules. Almost inevitably, however, one comes to a point in any of these books where some result appears by magic, and you are left with the idea that at some point, they are making it up. The present exposition aims to select a path through the material which avoids this habit.

The subject is not helped by the fact that its texts are almost inevitably opaque. Possibly the best example is the book by Chapman and Cowling (1970), which a colleague describes as like chewing glass. An illustration of its convolution is in its Byzantine equation numbering system, which finds its mirror in the inexplicable decision for modern scientific journals to abandon page numbering. Despite these comments, the book gives a thorough exposition, if one can make one’s way through the tangled prose, and is in fact the basic reference for the particle-based approach to statistical mechanics. Much of the material presented here can be interpreted as a translation, or exegesis of Chapman and Cowling’s seminal work.

Tolman (1938) Landau and Lifshitz (1980) Truesdell (1969) E (2011) Chisholm and de Borde (1958) Uhlenbeck and Ford (1963) Woods (1996) Chandler (1987) Kardar (2007) Schwabl (2006) Sethna (2006) Grad (1958)

Fluid mechanics (Yih 1977) Batchelor (1967)

3.7.1 Boltzmann equation

The Boltzmann equation is derived directly by Chapman and Cowling (1970) in the form

$$\frac{Df}{Dt} \equiv \frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = Q, \tag{3.452}$$

that is to say, they propose that f changes at a rate Q as we follow the fluid. This can be reconciled with (3.18) by realising that the partial derivatives are taken with either $\mathbf{r}$ or $\mathbf{v}$ (or, in the case of $\partial/\partial t$, both) fixed; thus, since we suppose $\mathbf{g} = \mathbf{g}(\mathbf{r})$, we have

$$\mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f = \boldsymbol{\nabla}_{\mathbf{r}}.(f\mathbf{v}), \quad \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = \boldsymbol{\nabla}_{\mathbf{v}}.(f\mathbf{g}). \tag{3.453}$$

The conservation form (3.18) is given by Drew and Passman (1999).

The derivation of the Boltzmann equation from the Liouville equation via the BBGKY hierarchy is described, tersely but lucidly, by Kardar (2007). The initials stand for the authors, Bogoliubov, Born, Green, Kirkwood and Yvon, who independently derived the equations just before the second world war. As suggested in question 3.5, the relation between the BBGKY equations and the Boltzmann equation involves a conceptual jump, not the least because we go from a reversible to an irreversible system.

Grad (1949)

3.7.2 Chapman–Enskog method

The derivation of values of the viscosity and the thermal conductivity is usually associated with the names of Chapman and Enskog. The exposition of this in the book by Chapman and Cowling (1970) is a model of opacity, and in any case the Chapman-Enskog expansion is queried by Cercignani (1988), and barely mentioned by Sone (2002): Cercignani favours the Hilbert expansion, although the approximations appear to coincide at leading order. Apparently, the difference between the methods lies in the way in which higher order terms are computed. In the Chapman–Enskog method, higher approximations lead to higher derivatives, much as if one was approximating a delay-differential equation by expanding in terms of the delay, and this is a dubious procedure.

One might suppose that later authors would do a better job at exposition than Chapman and Cowling; unfortunately, it is not the case. The approximation procedure, which as it turns out is actually quite straightforward, is retold in variously confusing ways by everybody who contrives to write on the subject. The expositions by Schwabl (2006) and Sone (2002), for example, are very muddled.

One wonders why this should be so. One reason is that the various authors appear to have no understanding of scaling. They do have the idea that the derivative term $\dot{f}$ in the Boltzmann equation is small, but they seem to have little idea how to then place the problem in its correct asymptotic context. The ingredients are all there, but are all mixed up. It is in fact Chapman and Cowling who provide a lucid path, but even they render the material more intransigent than a Guardian crossword. As an example, we come across expressions for thermal conductivity and viscosity on pages 125 and 126, but it is not until page 168 that we find an expression which is interpretable in terms of units.

3.7.3 Chemical reaction rates

As discussed by Laidler and King (1983), there are a number of ways of deriving the Arrhenius dependence of reaction rate on temperature, $k \propto \exp(-E/RT)$. The statistical mechanical view is presented by Eyring (1935), but the collisional theory presented here is associated with the names of Lewis (1918) and Trautz (1916), though Lewis does not actually provide the calculation. This is done by Chapman and Cowling (1970, p. 89).

3.7.4 Flory–Huggins theory

The theory was announced in two brief notes by Flory (1941) and Huggins (1941), with a longer exposition by Flory (1942); see also Flory (1953, pp. 497 ff.).

3.7.5 Phase change

One of the more puzzling aspects of statistical mechanics is the confrontation of the statement that entropy increases with the reality of phase change. The simplest interpretation of phase change associates it with a double well energy potential, and molecular fluctuations can drive a system from one state to another. Explicit examples of this are in the collisional theory of chemical reaction rates, and in the nucleation of crystals. On the other hand, the Boltzmann H-function (see (3.74)) appears to be a Lyapounov function with a unique minimum given by the Maxwellian distribution.

The reality is that if interparticle forces and particle volume are included in the particle description, thus promoting phase change, any equivalent of H must have multiple minima, corresponding to the different phases. An implication of this is that any corresponding definition of the entropy will allow transient states in which a decrease is possible.

Nucleation

An explicit example of this is given in the discussion of nucleation, where the energy barrier separating the two separate stable states is determined in terms of surface energy. The deterministic growth or decay rate of an already existing nucleus is given by Lifshitz and Slyozov (1961), who were largely concerned with coarsening, or Ostwald ripening, for which also see Voorhees (1985).

The Lifshitz–Slyozov theory does not attempt to describe the process of nucleation itself, which relies on statistical fluctuations to create nuclei larger than the critical size. It is through this process that the Arrhenius nucleation rate arises, and the kinetic theory of nucleation is given by Becker and Döring (1935), and ably expounded by Neu and Bonilla (2003); Ball *et al.* (1986) and Penrose (1997) analyse a particular version of the Becker–Döring theory and are able to obtain asymptotic results; but their choice of the rate constants is not consistent with the discussion here. Both Neu and Bonilla (2003) and Velázquez (1998) give the continuum limit as a Fokker–Planck equation. A useful review of both nucleation and crystal growth is the paper by Dowty (1980).

Fragmentation

The large time similarity solution which describes Ostwald ripening is just one of a number of processes, many of them in the geosciences, which indicate scale-invariant and thus self-similar behaviour (Turcotte 1997). Fragmentation processes invariably lead to power-law distributions, and numerous examples of such grain size distributions exist, for example in broken coal, asteroid size, earthquake fault gouge and soils (Turcotte 1997, p. 44). The basic model to describe such distributions is the master equation, and examples of this applied to fragmentation, aggregation and many other processes are described by Krapivsky *et al.* (2010).

Exercises

3.1 *Billiard in a circular enclosure.*[13]

A particle moves with constant speed v in a circular arena with radius length 1, and bounces perfectly off the walls. Write down a Hamiltonian in terms of the cylindrical coordinates r and θ which approximates this behaviour. Is it unique?

Let θ denote the angular position of impact and let $\phi = \frac{1}{2}(\pi - \alpha)$ be the (positive) angle between the trajectory and the radius. Show that ϕ is constant, and write down a difference equation relating sucessive values θ_n of θ.

Find values of ϕ such that the sequence $\{\theta_n\}$ has a

period two cycle $\{\theta_1, \theta_2, \theta_1, \theta_2, \ldots\}$;

period three cycle $\{\theta_1, \theta_2, \theta_3, \theta_1, \theta_2, \theta_3, \ldots\}$;

period n cycle $\{\theta_1, \theta_2, \ldots, \theta_n, \theta_1, \ldots\}$.

How many such orbits are there?

For the next part you will need the basic ideas of measure theory. Roughly speaking, the measure of a set $I \in \mathbf{R}$ is $m(I) = \int_{\mathbf{R}} f(x)\,dx$, where $f(x) = 1$ for $x \in I$, $f(x) = 0$ otherwise. We speak of a set of measure zero, and say that something is true for almost all $x \in J$ if the set of values I in J for which it is *not* true has measure zero. The type example of a set of measure zero is the set of rational numbers, essentially as they are countable. Definition of the integral of everywhere discontinuous functions needs the apparatus of Lebesgue theory,

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[13] Thanks to Roger Dodd for this exercise.

but the essence is encapsulated in the following argument. We can count all positive rationals in $(0,1)$ as

$$\frac{1}{2},\frac{1}{3},\frac{2}{3},\frac{1}{4},\frac{2}{4},\frac{3}{4},\ldots,$$

(here with some overcounting). For each rational p/q define a neighbourhood I_{pq} of width $\varepsilon/2^q$, and then define $I=\bigcup\limits_{p,q} I_{pq}$, and $f(x)=1$ on I, and zero otherwise. Because I contains all the rationals in (0,1) (denote them as $\mathbf{Q}_{(0,1)}$), it is self-evident that the integral of f over I is larger than the measure of $\mathbf{Q}_{(0,1)}$. But clearly

$$\int_I f(x)\,dx<\varepsilon\sum_1^\infty\frac{q}{2^q}=2\varepsilon,$$

and letting $\varepsilon\to 0$, we see that that the rationals have measure zero.

Show that for almost all choices of α, the trajectory approaches arbitrarily closely any point in a certain annulus. How is this result altered if there is also an inner circle with the same centre?

[*It may help to take $\theta=2\pi\psi$ and $\alpha=2\pi\beta$, and consider the shift map $\psi\to\psi+\beta$ when β is rational. This takes us towards the subject of chaos, which after all is at the heart of the assumption of ergodicity in mechanical systems. See also section 1.5.2.*]

3.2 *The BBGKY hierarchy.*

N particles have positions $\mathbf{q}(\mathbf{t})\in V$ and momenta $\mathbf{p}(\mathbf{t})\in U$ and are considered to form a trajectory in the $6N$–dimensional space $\Gamma=V^N\times U^N$. Denoting $\gamma_i=(\mathbf{q}_i,\mathbf{p}_i)$ and $\gamma=(\gamma_1,\ldots,\gamma_N)$, explain why an ensemble of trajectories of $\gamma(t)$ in Γ has a density ρ which is invariant under permutations of the elements of γ.

The s–particle distribution function is defined by

$$f_s(\gamma_1,\ldots,\gamma_s)=\frac{N!}{(N-s)!}\rho_s(\gamma_1,\ldots,\gamma_s),$$

where the s–particle density is

$$\rho_s=\int_{\Gamma_{s+1}}\rho\,d\Gamma_{s+1},\quad d\Gamma_{s+1}=\prod_{s+1}^{N}d\gamma_k,\quad d\gamma_k=d\mathbf{q}_k\,d\mathbf{p}_k.$$

Assuming Liouville's theorem, show that

$$\frac{\partial\rho_s}{\partial t}=-\int\{\rho,H\}\,d\Gamma_{s+1},$$

where you should also define the Poisson bracket $\{\rho,H\}$.

Assume that the Hamiltonian

$$H = \sum_1^N \left[\frac{p_i^2}{2m} + V(\mathbf{q}_i)\right] + \sum_{\substack{(i,j)\\ \text{pairs}}} W_{ij}, \quad W_{ij} = W(|\mathbf{q}_i - \mathbf{q}_j|),$$

where V is a global potential, and W is the potential of pair interactions, and partition

$$H = H_s + H_{N-s} + H',$$

where the terms represent respectively sums over $i, j \le s$, $i, j > s$, and the remainder.

Show successively that

$$\int \{\rho, H_s\}\, d\Gamma_{s+1} = \{\rho_s, H_s\},$$

$$\int \{\rho, H_{N-s}\}\, d\Gamma_{s+1} = 0,$$

assuming $\rho \to 0$ as $\gamma_k \to \infty$, and

$$-\int \{\rho, H'\}\, d\Gamma_{s+1} = \sum_{j=s+1}^{N} \sum_{i=1}^{s} \int_{P_j} \frac{\partial \rho_{s+1}(\gamma_1, \dots, \gamma_s, \gamma_j)}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{ij}}{\partial \mathbf{q}_i}\, d\gamma_j,$$

where P_j is the space spanned by γ_j.

Explain why the integral is independent of j, and hence derive the BBGKY hierarchy equations

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int_{\Gamma_{s+1}} \sum_{i=1}^{s} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i}\, d\gamma_{s+1}.$$

3.3 Write down the Liouville equation describing the evolution of an ensemble of Hamiltonian trajectories in a $6N$–dimensional phase space Γ described by a probability density ρ, and comment on the symmetries of the density which may be assumed.

Show that the Liouville equation is time-reversible, in a sense you should define.

The s–particle probability density is defined by

$$\rho_s = \int_{\Gamma_{s+1}} \rho\, d\Gamma_{s+1}, \quad d\Gamma_{s+1} = \prod_{s+1}^{N} d\gamma_k, \quad d\gamma_k = d\mathbf{q}_k\, d\mathbf{p}_k,$$

and satisfies the BBGKY hierarchy equation, for each s,

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int_{\Gamma_{s+1}} \sum_{i=1}^{s} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i}\, d\gamma_{s+1},$$

where $W_{ij} = W(|\mathbf{q}_i - \mathbf{q}_j|)$ is the inter-particle potential.

Show that under a suitable time reversal transformation, the BBGKY equations are reversible, in a sense you should define in the context of a set of trajectories in Γ.

3.4 A particle undergoes a random walk on the integers $\mathbf{Z}$, and the probability of being at position $x = n\Delta x$ at step $t = j\Delta t$ is $p_{n,j}$. Suppose the events move left, move right, remain stationary, have probabilities l, r and $1-l-r$ respectively. By using conditional probabilities, show that

$$p_{n,j} = lp_{n+1,j-1} + (1-l-r)p_{n,j-1} + rp_{n-1,j-1}.$$

Assuming that the time and space steps are small, show that $p(x,t)$ satisfies approximately the partial differential equation

$$p_t + vp_x = Dp_{xx},$$

and give expressions for v and D.

By transforming to a moving reference frame and seeking a similarity solution, find the solution assuming the particle starts at $x = 0$, and hence the mean drift velocity of the particle.

3.5 The BBGKY hierarchy of equations is given by

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int_{\Gamma_{s+1}} \sum_{i=1}^{s} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i}\, d\gamma_{s+1},$$

where $\{f, H\}$ is the Poisson bracket, and $W_{ij} = W(|\mathbf{r}_i - \mathbf{r}_j|)$ is the inter-particle potential. Defining the inter-particle acceleration as $\mathbf{a}_{ij} = -\frac{1}{m}\boldsymbol{\nabla}_{\mathbf{r}_i} W_{ij}$, where m is particle mass, and the external force per unit mass acting on particle i to be $\mathbf{g}$, show that the BBGKY equations take the form

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^{s} \left[\mathbf{v}_i.\boldsymbol{\nabla}_{\mathbf{r}_i} f_s + \left\{ \mathbf{g} + \sum_{j=1}^{s} \mathbf{a}_{ij} \right\}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_s \right] = -\int_{\Gamma_{s+1}} \mathbf{a}_{i,s+1}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_{s+1}\, d\gamma_{s+1}.$$

In particular, show that the one-particle velocity distribution function $f_1 = f(\mathbf{r}, \mathbf{v}, t)$ satisfies

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = -\int_P \mathbf{a}(\mathbf{r} - \mathbf{s}).\boldsymbol{\nabla}_{\mathbf{v}} f_2(\mathbf{r}, \mathbf{v}; \mathbf{s}, \mathbf{w}, t)\, d\mathbf{s}\, d\mathbf{w},$$

where $P = V \times U$ is the space spanned by $\mathbf{s}$ and $\mathbf{w}$.

Explain the basis for assuming

$$f_2(\mathbf{r}, \mathbf{v}; \mathbf{s}, \mathbf{w}, t) = f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{s}, \mathbf{w}, t),$$

and show that f then satisfies the Boltzmann equation in the form

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + (\mathbf{g} + \mathbf{A}).\boldsymbol{\nabla}_{\mathbf{v}} f = 0,$$

where

$$\mathbf{A} = \int_P \mathbf{a}(\boldsymbol{\xi}) f(\mathbf{r} - \boldsymbol{\xi}, \mathbf{w}, t)\, d\boldsymbol{\xi}\, d\mathbf{w}.$$

Show that in this form, the equation is time-reversible.

Show that the assumption of a conservative attractive interparticle force, $\mathbf{a} = -\boldsymbol{\nabla} W(\xi)$, implies

$$\mathbf{a} = -\frac{a(\xi)\boldsymbol{\xi}}{\xi}, \quad a > 0,$$

and show [*hint: Taylor expand* f] that if a is a rapidly decreasing function of ξ over a distance small compared to the variation of f, an approximate expression for $\mathbf{A}$ is

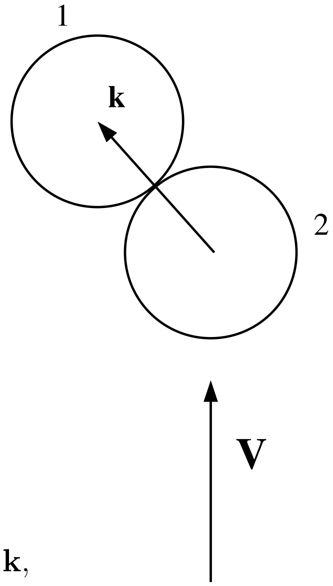
$$\mathbf{A} = K\boldsymbol{\nabla} n, \quad n = \int_U f\, d\mathbf{w}, \quad K = \int_0^\infty \frac{4\pi}{3}\xi^3 a(\xi)\, d\xi.$$

What does this imply physically?

3.6 The Boltzmann equation for a set of N particles in a volume V is given by

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = Q.$$

Explain the meaning of the terms in this equation, and give a concise summary of the way in which it is derived.



Derive a form for the collision term by considering the particles to consist of perfectly elastic spheres, and writing Q as the difference between a production term and a removal term,

$$Q = Q_+ - Q_-.$$

Consider first collisions between particles 1 and 2 with velocities $\mathbf{v}$ and $\mathbf{w}$, with relative velocity

$$\mathbf{V} = \mathbf{w} - \mathbf{v},$$

as shown in the figure. Show that the velocities after collision are

$$\begin{aligned} \mathbf{v}' &= \mathbf{v} + (\mathbf{V}.\mathbf{k})\mathbf{k}, \\ \mathbf{w}' &= \mathbf{w} - (\mathbf{V}.\mathbf{k})\mathbf{k}, \end{aligned}$$

where $\mathbf{k}$ is the unit vector along the line of centres at impact.

Hence show that, if d is particle diameter,

$$Q_- \, d\mathbf{r}\, d\mathbf{v}\, dt \approx f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{w},t)\, d\Omega\, d\mathbf{w}\, d\mathbf{r}\, d\mathbf{v}\, dt,$$

where $d\Omega = d^2\mathbf{V}.\mathbf{k}\, d\omega$, explaining in terms of the diagram what the solid angle ω represents.

By considering the reversed time collision (in which particles with velocities $\mathbf{v}'$ and $\mathbf{w}'$ collide to produce velocities $\mathbf{v}$ and $\mathbf{w}$), show that

$$Q_+ \, d\mathbf{r}\, d\mathbf{v}\, dt = f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{w}',t)\, a^2\mathbf{k}'.\mathbf{V}'\, d\omega(\mathbf{k}')\, d\mathbf{w}'\, d\mathbf{r}\, d\mathbf{v}'\, dt,$$

where $\mathbf{V}' = \mathbf{w}' - \mathbf{v}'$ and $\mathbf{V}'.\mathbf{k}' > 0$. Hence deduce, assuming that

$$d\mathbf{v}'\, d\mathbf{w}' = d\mathbf{v}\, d\mathbf{w},$$

that

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{w}',t) - f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{w},t)]\, d\Omega\, d\mathbf{w}.$$

Under a time reversal transformation, show that Q is invariant, and thus that the Boltzmann equation is not time-reversible.

3.7 The collision integral for the Boltzmann equation is given by

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{v}')f(\mathbf{w}') - f(\mathbf{v})f(\mathbf{w})]\, d^2\mathbf{V}.\mathbf{k}\, d\omega(\mathbf{k})\, d\mathbf{w},$$

where we write $f(\mathbf{v}) \equiv f(\mathbf{r}, \mathbf{v}, t)$. Describe the meaning of the construction of this integral.

Show that

$$2\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = \int_\Sigma \Delta(\psi) f(\mathbf{v}) f(\mathbf{w})\, d\Sigma,$$

where

$$\Delta(\psi) = \psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w}).$$

Deduce that

$$\int_U \psi(\mathbf{v}) Q\, d\mathbf{v} = 0$$

if and only if ψ is conserved during a collision.

The post-collision velocities are given by

$$\begin{aligned} \mathbf{v}' &= \mathbf{v} + (\mathbf{V}.\mathbf{k})\mathbf{k}, \\ \mathbf{w}' &= \mathbf{w} - (\mathbf{V}.\mathbf{k})\mathbf{k}, \\ \mathbf{V} &= \mathbf{w} - \mathbf{v}; \end{aligned}$$

show that the quantities $\psi = 1$, $\mathbf{v}$ and $\frac{1}{2}v^2$ are conserved, and show that these are the only such quantities. What do they correspond to physically?

3.8 Write down the Boltzmann equation for the evolution of the one-particle velocity distribution function describing the molecular motion of a fluid. (The form of the collision integral Q need not be written explicitly.)

If the number density is defined by

$$n = \int_U f\, d\mathbf{v},$$

and the average $\bar{\phi}$ of a quantity ϕ is defined by

$$n\bar{\phi} = \int_U f\phi\, d\mathbf{v},$$

write down definitions for the density ρ, velocity $\mathbf{u}$ and internal energy e of the fluid.

Use the Boltzmann equation to show that the average of a quantity ψ satisfies the evolution equation

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \boldsymbol{\nabla}.(\rho\bar{\psi}\mathbf{u}) + \boldsymbol{\nabla}.\mathbf{J}_\psi = \rho\left[\overline{\psi_t + \mathbf{v}.\boldsymbol{\nabla}\psi + \mathbf{g}.\boldsymbol{\nabla}_\mathbf{v}\psi}\right],$$

providing (collisional conservation of ψ)

$$\int_U \psi Q \, d\mathbf{v} = 0.$$

What is the definition of $\mathbf{J}_\psi$?

Assuming $\psi = 1, \mathbf{v}, \frac{1}{2}v^2$ are conserved in collisions, derive equations of conservation of mass, momentum and energy for the fluid, and show in particular that the energy equation can be reduced to the form

$$\rho \frac{de}{dt} = \boldsymbol{\sigma} : \boldsymbol{\nabla} \mathbf{u} - \boldsymbol{\nabla} . \, \mathbf{q},$$

where we have used the tensor double scalar product $\mathbf{a} : \mathbf{b} = a_{ij} b_{ij}$ (summed), and you should define $\boldsymbol{\sigma}$ and $\mathbf{q}$. What do they represent physically?

3.9 Let $U_K \subset U$ be that part of velocity space on which the distribution function $f < e^{-Kv^2}$, where $K > 0$ is arbitrary. Let $\mathbf{v} \in A \subset U_K$ if $v < \dfrac{1}{\sqrt{K}}$, and let B be the complement of A in U_K.

Show that

$$\int_A f \ln f \, d\mathbf{v} > -\frac{a}{K^{3/2}}, \quad \int_B f \ln f \, d\mathbf{v} > -\frac{b}{K^{3/2}}$$

(where you should determine values of $a, b > 0$).

If U'_K denotes the complement of U_K in U, and the energy integral satisfies

$$\int_U v^2 f \, d\mathbf{v} < E,$$

show that

$$\int_{U'_K} f \ln f \, d\mathbf{v} > -EK.$$

Hence show that

$$H = \int_U f \ln f \, d\mathbf{v} > -\left[\frac{(a+b)}{K^{3/2}} + EK \right],$$

and deduce that

$$H > -5 \left(\frac{a+b}{2} \right)^{2/5} \left(\frac{E}{3} \right)^{3/5}.$$

3.10 Suppose that the one particle distribution function f is independent of position, and that there is no external body force. Show that the Boltzmann equation takes the form

$$\frac{\partial f}{\partial t} = Q.$$

Suppose that

$$\int_U \psi(\mathbf{v}) Q \, d\mathbf{v} = \tfrac{1}{2} \int_\Sigma \Delta(\psi) f(\mathbf{v}) f(\mathbf{w}) \, d\Sigma,$$

where

$$\Delta(\psi) = \psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w}).$$

Show that

$$\int_U \psi(\mathbf{v}) Q \, d\mathbf{v} = \tfrac{1}{4} \int_\Sigma \Delta(\psi) [f(\mathbf{v}) f(\mathbf{w}) - f(\mathbf{v}') f(\mathbf{w}')] \, d\Sigma,$$

and deduce that if

$$H = \int_U f \ln f \, d\mathbf{v},$$

then

$$\dot{H} = \tfrac{1}{4} \int_\Sigma \Delta(\psi) f(\mathbf{v}) f(\mathbf{w}) (1 - \zeta) \ln \zeta \, d\Sigma,$$

where

$$\zeta = \frac{f(\mathbf{v}') f(\mathbf{w}')}{f(\mathbf{v}) f(\mathbf{w})}.$$

Deduce that $\dot{H} \leq 0$, that H is bounded below, and therefore that $\dot{H} \to 0$ as $t \to \infty$. Assuming that $\psi = 1, \mathbf{v}, \frac{1}{2} v^2$ are the only independent solutions of $\Delta\psi = 0$, deduce that in the resulting equilibrium

$$f = A \exp\left[-\tfrac{1}{2} C |\mathbf{v} - \hat{\mathbf{v}}|^2\right],$$

and find A, C and $\hat{\mathbf{v}}$ in terms of the number density n, mean velocity $\mathbf{u}$ and temperature T, defined by

$$n = \int_U f \, d\mathbf{v}, \quad n\mathbf{u} = \int_U f \mathbf{v} \, d\mathbf{v}, \quad \frac{nkT}{m} = \int_U f |\mathbf{v} - \mathbf{u}|^2 \, d\mathbf{v}.$$

What are the units of f? Show that the definition of H is not dimensionally consistent. Defining instead

$$H = \int_U f \ln(f/f_0) \, d\mathbf{v},$$

where f_0 is a suitable dimensional constant, show that the preceding results are not altered.

3.11 The Maxwellian distribution $f_0(\mathbf{v}) = e^{\Phi_0}$ is given by the dimensionless relation

$$\Phi_0 = A - \tfrac{1}{2} C u'^2,$$

where

$$A = \ln\left[\frac{n^*}{(2\pi T^*)^{3/2}}\right], \quad C = \frac{1}{T^*}, \quad \mathbf{u}' = \mathbf{v} - \mathbf{u},$$

and A, C and $\mathbf{u}$ are functions of $\mathbf{r}$ and t but not $\mathbf{v}$. Use the definition

$$\dot{\Phi}_0 = \frac{\partial \Phi_0}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}\Phi_0 + \frac{\mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}}\Phi_0}{F^2}$$

to show that

$$\dot{\Phi}_0 = \frac{dA}{dt} + \mathbf{u}'.\left[\boldsymbol{\nabla}A - \frac{C\mathbf{g}}{F^2} + C\frac{d\mathbf{u}}{dt} - \tfrac{5}{2}T^*\boldsymbol{\nabla}C\right] + \tfrac{1}{2}u'^2\left[\tfrac{2}{3}C\boldsymbol{\nabla}.\,\mathbf{u} - \frac{dC}{dt}\right]$$
$$-\mathbf{W}.\boldsymbol{\nabla}C + CU_{ij}\frac{\partial u_i}{\partial x_j},$$

where $\dfrac{d}{dt} = \dfrac{\partial}{\partial t} + \mathbf{u}\,.\boldsymbol{\nabla}$, and

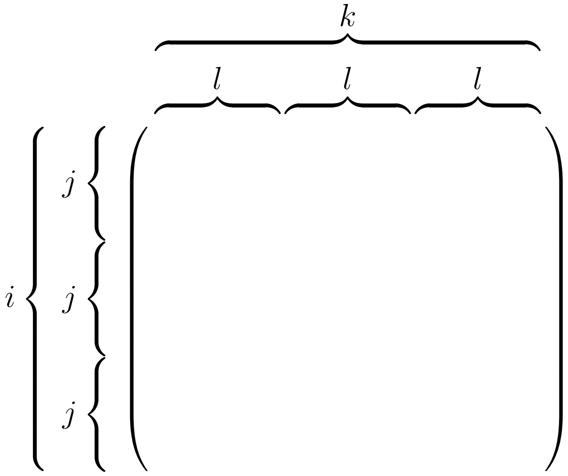
$$\mathbf{W} = \left(\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*\right)\mathbf{u}', \quad U_{ij} = u'_i u'_j - \tfrac{1}{3}u'^2\delta_{ij}.$$

The inner product is defined by

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v})\phi(\mathbf{v})\psi(\mathbf{v})\,d\mathbf{v};$$

show that if $\mathcal{N}$ is the space spanned by $\{1, \mathbf{u}', \frac{1}{2}u'^2\}$, then $\mathbf{W} \perp \mathcal{N}$ and $\mathbf{U} \perp \mathcal{N}$. Calculate the inner products of pairs of $\{1, \mathbf{u}', \frac{1}{2}u'^2\}$, and deduce three equations which must be satisfied by A, C and $\mathbf{u}$, if the constraint $\langle \dot{\Phi}_0, \chi \rangle = 0$ is satisfied for each $\chi \in \mathcal{N}$.

3.12 The 9×9 matrix $\mathcal{R}$ has elements $\mathcal{R}_{ijkl}$, where the suffixes range from 1 to 3, and the matrix elements are labelled as indicated below:



Thus the third element in the fourth row has suffixes 2113, and so on.

Explain why matrix multiplication gives

$$(\mathcal{RS})_{ijkl} = \mathcal{R}_{ijpq}\mathcal{S}_{pqkl},$$

why the identity matrix has

$$\mathcal{I}_{ijkl} = \delta_{ik}\delta_{jl},$$

and why

$$\mathcal{R}^T_{ijkl} = \mathcal{R}_{klij}.$$

Hence show that if R is an orthogonal 3×3 matrix, and $\mathcal{R}_{ijkl} = R_{ik}R_{jl}$, then $\mathcal{R}\mathcal{R}^T = \mathcal{I}$, so that $\mathcal{R}$ is orthogonal.

3.13 A general symmetric tensor in the orthogonal complement of $\mathbf{vv}$ in U^2 can be written in the form

$$\mathbf{W} = A\mathbf{uu} + B\mathbf{ww} + L(\mathbf{uv} + \mathbf{vu}) + M(\mathbf{uw} + \mathbf{wu}) + N(\mathbf{vw} + \mathbf{wv}).$$

By using the fact that for the tensor $\mathcal{R}$ defined by $\mathcal{R}_{ijkl} = R_{ik}R_{jl}$, where R is any orthogonal matrix leaving $\mathbf{v}$ invariant,

$$\mathcal{R}\,\mathbf{uu} = R\mathbf{u}\,R\mathbf{u},$$

etc., and that

$$\begin{aligned} R\mathbf{w} &= \mathbf{w}\cos\theta + \mathbf{u}\sin\theta, \\ R\mathbf{u} &= -\mathbf{w}\sin\theta + \mathbf{u}\cos\theta, \end{aligned}$$

where θ is non-zero, show that $\mathcal{R}\mathbf{W} = \mathbf{W}$ if and only if $A = B$ and $L = M = N = 0$.

3.14 The linear operator $\mathcal{L}$ is defined on a function $\phi(\mathbf{v})$ by

$$\mathcal{L}\phi = \int_U \int_{\Omega_+} f_0(\mathbf{v})\Delta\phi(\mathbf{v}, \mathbf{w})\, d\Omega\, d\mathbf{w},$$

where the Maxwellian is

$$f_0(\mathbf{v}) = \frac{n^*}{(2\pi T^*)^{3/2}} \exp\left(-\frac{u'^2}{2T^*}\right),$$

$\mathbf{u}' = \mathbf{v} - \mathbf{u}$, $d\Omega = \mathbf{V}.\mathbf{k}\, d\omega(\mathbf{k})$, and the quantities n^*, T^* and $\mathbf{u}$ are independent of $\mathbf{v}$. Show that under the scaling transformation $\mathbf{v} = \sqrt{T^*}\mathbf{v}^*$,

$$\mathcal{L}\phi = n^* T^{*1/2} \mathcal{L}^*\phi,$$

where

$$\mathcal{L}^*\phi = \frac{1}{(2\pi)^{3/2}} \int_{U^*} \int_{\Omega^*_+} \exp\left(-\tfrac{1}{2}u'^{*2}\right) \Delta\phi\, d\Omega^*\, d\mathbf{w}^*.$$

Hence show that the solution of the equation

$$-\mathcal{L}[F(u')\mathbf{u}'] = \mathbf{W} = (\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*)\mathbf{u}'$$

has the form

$$F(u') = \frac{T^{*1/2} F^*(u'^*)}{n^*},$$

where

$$-\mathcal{L}^*[F^*(u'^*)\mathbf{u}'^*] = \mathbf{W}^* = (\tfrac{1}{2}u'^{*2} - \tfrac{5}{2})\mathbf{u}'^*.$$

Similarly, show that the solution of

$$-\mathcal{L}[G(u')\mathbf{U}] = \mathbf{U}, \quad U_{ij} = u'_i u'_j - \tfrac{1}{3}u'^2\delta_{ij},$$

is

$$G(u') = \frac{G^*(u'^*)}{n^* T^{*1/2}},$$

where

$$-\mathcal{L}^*[G^*(u'^*)\mathbf{U}^*] = \mathbf{U}^*, \quad U^*_{ij} = u'^*_i u'^*_j - \tfrac{1}{3}u'^{*2}\delta_{ij}.$$

3.15 The dimensionless functions

$$A = \ln\left[\frac{n^*}{(2\pi T^*)^{3/2}}\right], \quad C = \frac{1}{T^*},$$

are found, from the solvability conditions for the perturbed Boltzmann equation, to satisfy the equations

$$\frac{dA}{dt^*} = 0, \quad \frac{dC}{dt^*} = \tfrac{2}{3}C\boldsymbol{\nabla}^*.\mathbf{u}^*,$$

$$C\frac{d\mathbf{u}^*}{dt^*} = -\boldsymbol{\nabla}^*A + \tfrac{5}{2}T^*\boldsymbol{\nabla}^*C + \frac{C\mathbf{g}^*}{F^2},$$

where the dimensional variables are related to their dimensionless (starred) equivalents via

$$n = n_0 n^*, \quad T = T_0 T^*, \quad \mathbf{u} = v_0\mathbf{u}^*, \quad t = \frac{L}{v_0}t^*, \quad \boldsymbol{\nabla} = \frac{1}{L}\boldsymbol{\nabla}^*, \quad \mathbf{g} = g_0\mathbf{g}^*,$$

and

$$v_0 = \sqrt{\frac{kT_0}{m}}, \quad F^2 = \frac{v_0^2}{g_0 L}.$$

Write the equations for A, C and $\mathbf{u}^*$ as dimensional equations for n, T and $\mathbf{u}$, and show that with the assumptions

$$p = nkT, \quad e = \frac{3kT}{2m},$$

they can be rearranged to the Euler equations in the form

$$\rho\frac{d\mathbf{u}}{dt} = -\boldsymbol{\nabla}p + \rho\mathbf{g},$$

$$\frac{d\rho}{dt} + \rho \boldsymbol{\nabla} . \mathbf{u} = 0,$$

$$\frac{de}{dt} + p\frac{dv}{dt} = 0,$$

where

$$\rho = mn, \quad v = \frac{1}{\rho}.$$

3.16 Define the particle-weighted average $\bar{\phi}$ of a function ϕ in terms of the one-particle velocity distribution function $f(\mathbf{r}, \mathbf{v}, t)$.

Show that if f is given by the Maxwellian distribution

$$f = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{mu'^2}{2kT}\right],$$

then the Boltzmann specific entropy $s = -\frac{k}{m}\overline{\ln f}$ is given by

$$s = \frac{k}{m}\left[\tfrac{3}{2} - \ln\left\{n\left(\frac{m}{2\pi kT}\right)^{3/2}\right\}\right].$$

Assuming $e = \dfrac{3kT}{2m}$, show that if n is constant, then

$$T\,ds = de.$$

3.17 In thermodynamic equilibrium, the specific entropy s satisfies

$$T\,ds = de + p\,dv.$$

Explain the meaning of the terms in this equation.

Define the specific enthalpy h, the specific Gibbs free energy g, and the specific Helmholtz free energy f, and show that

$$dh = T\,ds + v\,dp.$$

$$dg = v\,dp - s\,dT,$$

$$df = -p\,dv - s\,dT.$$

By forming mixed second derivatives in two ways, derive the Maxwell relations

$$\begin{aligned}
\left(\frac{\partial p}{\partial s}\right)_v &= -\left(\frac{\partial T}{\partial v}\right)_s, \\
\left(\frac{\partial v}{\partial s}\right)_p &= \left(\frac{\partial T}{\partial p}\right)_s, \\
\left(\frac{\partial v}{\partial T}\right)_p &= -\left(\frac{\partial s}{\partial p}\right)_T, \\
\left(\frac{\partial p}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T.
\end{aligned}$$

Four partial derivatives are associated with specifically named quantities, which can be measured. These are the coefficient of thermal expansion

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p ,$$

the coefficient of isothermal compressibility

$$\xi = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T ,$$

the specific heat at constant pressure,

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p ,$$

and the specific heat at constant volume,

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v .$$

With these definitions, show that

$$T\,ds = de + p\,dv = c_p\,dT - \beta v T\,dp,$$

3.18 The density ρ, velocity $\mathbf{u}$ and internal energy e of a fluid are given by the conservation laws

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}.\,(\rho\mathbf{u}) &= 0,\\ \frac{\partial(\rho\mathbf{u})}{\partial t} + \boldsymbol{\nabla}.\,(\rho\mathbf{u}\mathbf{u}) &= \boldsymbol{\nabla}.\,\boldsymbol{\sigma} + \rho\mathbf{F}\\ \frac{\partial}{\partial t}\left[\tfrac{1}{2}\rho u^2 + \rho e + \rho V\right] + \boldsymbol{\nabla}.\,\left[\{\tfrac{1}{2}\rho u^2 + \rho e + \rho V\}\mathbf{u}\right] &= \boldsymbol{\nabla}.\,(\boldsymbol{\sigma}.\mathbf{u}) - \boldsymbol{\nabla}.\,\mathbf{q},\end{aligned}$$

where $\boldsymbol{\sigma}_i$ is the stress tensor, $\mathbf{q}$ is the heat flux, and the conservative body force $\mathbf{F}$ is defined by

$$\mathbf{F} = -\boldsymbol{\nabla} V,$$

where V is the potential.

Show that the momentum equation can be written in the form

$$\rho\left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}.\boldsymbol{\nabla}\,)\mathbf{u}\right] = \boldsymbol{\nabla}.\,\boldsymbol{\sigma} + \rho\mathbf{F},$$

and that the energy equation can be reduced to

$$\rho\left[\frac{de}{dt} + p\frac{dv}{dt}\right] = \tau_{ij}\dot{\varepsilon}_{ij} - \boldsymbol{\nabla}.\,\mathbf{q},$$

where

$$\sigma_{ij} = -p\delta_{ij} + \tau_{ij}, \quad v = \frac{1}{\rho}.$$

Deduce that for a Maxwellian velocity distribution, $\dot{e} + p\dot{v} = 0$.

3.19 The gamma function is defined by

$$\Gamma(s) = \int_0^\infty t^{s-1} e^{-t}\, dt.$$

Show by induction or otherwise that $\Gamma(n+1) = n!$ if n is a positive integer.

If s is large and positive, find an approximation for $\Gamma(s)$. [*Hint: put $t = s\xi$ in the integrand, and expand the integrand locally about its maximum.*]

Hence deduce Stirling's approximation,

$$n! \sim n^n e^{-n} \sqrt{2\pi n}$$

as $n \to \infty$.

3.20 The volume of an M-dimensional hypersphere of radius R is

$$V_M(R) = \frac{\pi^{M/2} R^M}{(M/2)!}.$$

Derive this result in three ways: by direct calculation, using induction on M; by calculation of

$$I_M(\alpha) = \int_{\mathbf{R}^M} e^{-\alpha r^2}\, dV$$

and use of the Laplace transform; and by reduction (show that $f'_M(\xi) = \pi f_{M-2}(\xi)$, where $V_M(R) = f_M(R^2)$).

3.21 The entropy of a microcanonical ensemble for the hard sphere gas is defined by

$$S = \ln \left[\frac{3N}{2E} \frac{V^N (2\pi m E)^{3N/2}}{N!(3N/2)!} \right],$$

where the number of particles N is very large. Use Stirling's approximation to show that

$$S \approx kN \left[\tfrac{5}{2} + 3 \ln m - \ln \left(\frac{N}{V} \right) + \tfrac{3}{2} \ln \left(\frac{4\pi E}{3mN} \right) \right],$$

and explain why this definition is extensive.

If the factorial $N!$ were omitted from the definition of the entropy, show that Gibbs's paradox would ensue, insofar as the resulting 'entropy' would not be extensive.

3.22 A canonical ensemble consists of N particles in a volume V at temperature T. Define the partition function Z, assuming a state space of Ω equiprobable states, and hence deduce expressions for the energy and entropy of the system.

Show that the Helmholtz free energy F satisfies

$$Z = e^{-\beta F},$$

where you should define β. Show also that

$$p = -\left.\frac{\partial F}{\partial V}\right|_T,$$

and hence deduce that

$$G = kT\left[-\ln Z + \frac{V}{Z}\left.\frac{\partial Z}{\partial V}\right|_T\right].$$

3.23 What are the two postulates which underlie classical statistical mechanics?

A two level system consists of N atoms which can exist in two states: a ground state with energy zero, and an excited state with energy E^*. Define the state of the i–th atom to be n_i, where $n_i = 0$ if in the ground state and $n = 1$ if in the excited state. Assuming a suitable Hamiltonian dynamics for the system, write down the Hamiltonian, and deduce the probability p_γ of the state $\gamma = (n_1, n_2, \ldots, n_N)$. Hence show that the partition function is given by

$$Z = (1 + e^{-\beta E^*})^N,$$

where $\beta = \dfrac{1}{kT}$.

Show from the definition of the entropy S that

$$S = \frac{E}{T} + k\ln Z,$$

and deduce that the Helmholtz free energy $F = E - TS$ is given by $F = -kT\ln Z$. Hence write down expressions for S and F for this two-level system.

3.24 Suppose that

$$Z(E) = \sum_{n=0}^{\infty} Z_n(E),$$

where $Z_n = cE^\Lambda e^{-\beta E}$, $E = nE^*$, and Λ is large. By mimicking the application of Laplace's method for integrals, show that Z can be approximated by an integral, and hence show that

$$Z \approx \frac{\sqrt{2\pi\Lambda}}{\beta E^*} Z_{\max},$$

where $Z_{\max} = \max_n Z_n$.

3.25 The chemical potential is defined as

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}.$$

Deduce that also

$$\mu = -T \left.\frac{\partial S}{\partial N}\right|_{E,V}.$$

Use the definition of the Gibbs free energy $G = E + pV - TS$ to show that

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{p,T}.$$

For the perfect gas

$$\ln Z = N\left[1 - \ln\left(\frac{N}{V}\right) + \tfrac{3}{2}\ln\left(\frac{2\pi kT}{m}\right)\right], \quad E = \tfrac{3}{2}NkT.$$

Use the definition

$$S = \frac{E}{T} + k\ln Z$$

to calculate μ and G, and hence show that $G = \mu N$ for the perfect gas.

3.26 The grand potential is defined by

$$\Phi = E - TS - \mu N.$$

Using the differential expression for dE, show that

$$N = -\left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V}, \quad p = -\left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu}, \quad S = -\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu}.$$

For the perfect gas, the grand potential is defined by

$$\Phi = -kTVe^{\beta\mu}\left(\frac{2\pi kT}{m}\right)^{3/2}.$$

Using this, show that $G = \mu N$.

3.27 The grand partition function Q for a number of particles in a box of volume V is defined as

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(T,V),$$

where Z_N is the partition function for N particles, and $\beta = 1/kT$. By expanding for small N to second order, find an expression for the grand potential $\Phi = -kT\ln Q = -pV$, and hence deduce that the equation of state takes the form

$$p = kT[n + Bn^2 + \ldots], \quad (*)$$

where $n = N/V$, and

$$B = V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right).$$

Assuming that

$$Z_N = \frac{(2\pi mkT)^{3N/2}}{N!} \int_{V^N:|\mathbf{r}_i - \mathbf{r}_j|>d} \exp\left[-\beta \sum_{i<j} W(|\mathbf{r}_i - \mathbf{r}_j|)\right] d\mathbf{r}_1 \ldots d\mathbf{r}_N,$$

where the inter-molecular potential $W(r)$ is defined for $r > d$ and is small, derive approximations for Z_1 and Z_2. Show that Z_2/Z_1^2 is dimensionless, and that

$$B = b - a\beta,$$

where

$$b = \tfrac{1}{2}\Omega, \quad a \approx -\tfrac{3}{2}\Omega \int_1^\infty \xi^2 w(\xi)\, d\xi,$$

where $w(\xi) = W(d\xi)$ and $\Omega = \frac{4}{3}\pi d^3$.

Hence show that the equation of state can be written in the equivalent asymptotic form

$$p + an^2 = \frac{nkT}{1 - bn}.$$

Why might this be a better expression that $(*)$?

By considering the graph of p versus n at fixed T, show that multiple steady states occur if

$$T < T_c = \frac{8a}{27kb}.$$

3.28 The velocity variables $\mathbf{v}$, $\mathbf{w}$ of two particles are related to the centre of mass velocity $\mathbf{U} = \alpha_1\mathbf{v} + \alpha_2\mathbf{w}$ and the relative velocity $\mathbf{V} = \mathbf{w} - \mathbf{v}$, where $\alpha_1 = \dfrac{m_1}{m_1 + m_2}$, m_1 and m_2 being the masses of the particles, and $\alpha_2 = 1 - \alpha_1$. Show that the transformation from $\mathbf{v}$, $\mathbf{w}$ to $\mathbf{U}$, $\mathbf{V}$ has Jacobian equal to one.

3.29 The function $\mathbf{B}(\mathbf{k})$ is defined by

$$\mathbf{B} = -\frac{1}{\nu} \int_V \frac{a(\xi)\boldsymbol{\xi}}{\xi} e^{-i\nu\mathbf{k}.\boldsymbol{\xi}}\, d\boldsymbol{\xi},$$

where $V = \mathbf{R}^3$, and the function $a(\xi) = 0$ for $\xi < 1$. Show that

$$\mathbf{B} = iC(\nu k)\mathbf{k},$$

and by changing to spherical polar coordinates, show that (writing $K = \nu k$)

$$C(K) = \frac{4\pi}{K^2} \int_1^\infty ra(r) \left[\frac{\sin Kr}{Kr} - \cos Kr\right] dr.$$

Now suppose that $a(r) = 6/r^7$. Derive the asymptotic limits

$$C \sim \tfrac{8}{3}\pi - \tfrac{4}{5}\pi K^2 + \ldots, \quad K \to 0,$$

$$C \sim \frac{24\pi \sin K}{K^3} + \dots, \qquad K \to \infty,$$

by expanding the integral as a Taylor series, and by integration by parts, respectively.

What limits the extension of the small K result beyond $O(K^2)$? Use successive integration by parts to show that

$$C(K) = \left[\frac{4}{K^2} + 1 - \frac{K^2}{6}\right] \frac{\sin K}{K} + \left[-\frac{4}{K^2} - \frac{1}{3} + \frac{K^2}{6}\right] \cos K + \frac{\pi K^3}{12} - \mathrm{Si}(K),$$

where

$$\mathrm{Si}(K) = \int_0^K \frac{\sin s \, ds}{s},$$

and hence find the next term in the expansion.

3.30 An equation to determine σ in terms of a real parameter γ is

$$i \int_U \frac{f_0(v)\mathbf{k}.\mathbf{v} \, d\mathbf{v}}{\sigma + i\mathbf{k}.\mathbf{v}} = \gamma,$$

where

$$f_0(v) = \frac{1}{(2\pi)^{3/2}} e^{-\frac{1}{2}v^2}$$

is the (dimensionless) Maxwellian. By taking the z axis in the direction of $\mathbf{k}$, show that

$$\frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{kz \, e^{-\frac{1}{2}z^2} \, dz}{\sigma + ikz} = \gamma,$$

and show further that if

$$\sigma = \sqrt{2}k\eta,$$

this can be manipulated to the form

$$\gamma = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{te^{-t^2} \, dt}{t - i\eta},$$

and then

$$1 - \gamma = \frac{2\eta^2}{\sqrt{\pi}} \int_0^{\infty} \frac{e^{-t^2} \, dt}{t^2 + \eta^2}.$$

Assuming that $\eta > 0$, show that η is a monotonically decreasing function of γ for $0 < \gamma < 1$, and that there is no real solution for $\gamma > 1$. Sketch the graph of $\eta(\gamma)$.

Show that

$$1 - \gamma = \sqrt{\pi}\eta \, e^{\eta^2} \operatorname{erfc} \eta, \qquad \operatorname{erfc} \eta = \frac{2}{\sqrt{\pi}} \int_{\eta}^{\infty} e^{-s^2} \, ds.$$

[*Hint: consider the integral*

$$J(\alpha) = \int_0^{\infty} \frac{e^{-\alpha(t^2+\eta^2)} \, dt}{(t^2 + \eta^2)}.]$$

3.31 In liquid lattice theory, the molecules of the liquid are conceived to lie on the points of a lattice. If the liquid is a mixture of molecules A and B, with the molar concentration of B being c, then if the lattice has N sites, there are $N_A = (1-c)N$ molecules of A and $N_B = cN$ molecules of B. Let z be the coordination number of the sites; by consideration of the number W of distinguishable states, show that the entropy of mixing is

$$S = -kN \ln\left[(1-c)\ln(1-c) + c\ln c\right].$$

Now suppose that the internal energy is determined as

$$E = n_{AA}e_{AA} + n_{AB}e_{AB} + n_{BB}e_{BB},$$

where n_{ij} is the number of i–j contacts, and e_{ij} is the corresponding internal energy. Show that

$$n_{AA} = \tfrac{1}{2}(zN_A - n_{AB}), \quad n_{BB} = \tfrac{1}{2}(zN_B - n_{AB}),$$

and explain why we can take

$$n_{AB} = \frac{zN_AN_B}{N}.$$

Deduce that if $e_{AA} = e_{BB} = e_0$,

$$E = zN\left[\tfrac{1}{2}e_0 + c(1-c)\Delta e\right],$$

where

$$\Delta e = e_{AB} - e_0.$$

Deduce that the Helmholtz free energy is

$$F = N\left[\tfrac{1}{2}ze_0 + kT\{\chi c(1-c) + (1-c)\ln(1-c) + c\ln c\}\right],$$

where the interaction parameter is

$$\chi = \frac{z\Delta e}{kT}.$$

Suppose a system is subject to constant temperature and pressure, and that the molecular volumes of both A and B are the same, and equal to v_m. Show that the chemical potentials of A and B are

$$\mu_A = \mu_0 + kT\{\ln(1-c) + \chi c^2\},$$

$$\mu_B = \mu_0 + kT\{\ln c + \chi(1-c)^2\},$$

where

$$\mu_0 = \tfrac{1}{2}ze_0 + pv_m.$$

Draw graphs of the specific Gibbs free energy $g = \dfrac{G}{N}$ as a function of concentration c, and show that phase separation will occur if $\chi > 2$.

3.32 In the Earth, solid rock begins to melt as it rises (convectively) towards the surface at mid-ocean ridges, or beneath volcanic island chains such as Hawaii. The melting temperature depends on pressure as

$$T_M(p) = T_0 + \Gamma p,$$

where $\Gamma > 0$. It then forms a partially molten solid-liquid mixture, in which the liquid forms a network of veins interlaced through the grains of the now porous solid. Denoting average solid pressure as p_s and liquid pressure p_l within the mixture, why may we take the temperature in the mixed phase region to be $T_M(p_l)$? [*Hint: think of the time scales over which solid and liquid stresses relax.*]

Now we wish to calculate a thermodynamic boundary condition at the interface between the partially molten region (m) and the surrounding cold solid (c) mantle rocks. We assume that temperature is continuous,

$$[T]_c^m = 0,$$

where the square brackets denote the jump at the interface, there is a normal force balance

$$[\phi p_l + (1-\phi)p_s]_c^m = 0,$$

where the liquid volume fraction (porosity) is denoted by ϕ, and the specific Gibbs free energy is continuous:

$$[\phi g_l + (1-\phi)g_s]_c^m = 0.$$

Noting that $g_s = g_l$ on the partially molten side, show that these conditions imply

$$\phi(p_s - p_l) = 0$$

at the boundary.

3.33 A liquid binary alloy consists of a solvent A and a solute B of which the latter has concentration c, and the liquid is in thermodynamic equilibrium with its solid phase. The specific Gibbs free energies of solid and liquid phases are denoted by g_S and g_L, and their dependence on concentration is given by

$$g = \mu_A(1-c) + \mu_B c,$$

for coefficients μ_A^S and μ_B^S, and μ_A^L and μ_B^L, respectively, which are defined by

$$\mu_A = \mu_A^0 + kT\ln(1-c),$$

$$\mu_B = \mu_B^0 + kT\ln c,$$

with similar additional superscripting S, L of the coefficients μ_A^0 and μ_B^0.

Show that the equilibrium conditions $\mu_A^L = \mu_A^S$ and $\mu_B^L = \mu_B^S$ are solved by liquid and solid values of the concentration c_L, c_S which satisfy

$$g_S'(c_S) = g_L'(c_L) = \frac{g_S(c_S) - g_L(c_L)}{c_S - c_L},$$

and illustrate the procedure graphically.

Show that if

$$\Delta\mu_A = \mu_A^{0L} - \mu_A^{0S}, \quad \Delta\mu_B = \mu_B^{0L} - \mu_B^{0S},$$

then at the melting points T_A and T_B of pure A and pure B, $\Delta\mu_A = 0$ and $\Delta\mu_B = 0$ respectively.

Suppose that for $T \neq T_A, T_B$, $\Delta\mu_A < 0$ and $\Delta\mu_B > 0$. Show that $c_S > c_L$, and draw the phase diagram for the solidus and liquidus temperatures.

Now suppose that the solids are immiscible, in the sense that

$$\mu_A^S = \mu_A^{0S} + kT\{\ln(1-c) + \chi c^2\},$$

$$\mu_B^S = \mu_B^{0S} + kT\{\ln c + \chi(1-c)^2\}$$

(cf. question 3.31), where χ is positive. Draw typical forms for g_S and g_L, and describe the consequent form of the phase diagram. [*This gives the typical eutectic phase diagram.*]

3.34 The grain size distribution ϕ of a population of growing crystals is given by the evolution equation

$$\phi_t + (V\phi)_r = 0,$$

where the crystal growth rate V is given by

$$V = D\left[\frac{\psi}{r} - \frac{\alpha}{r^2}\right],$$

where r is grain radius and

$$\psi = \Delta c_0 - \int_0^\infty \tfrac{4}{3}\pi r^3 \phi \, dr,$$

and is initially positive.

Suppose that α is small and can be neglected. By solving the resulting problem, show that if the initial grain size distribution is $\phi_0(r)$, then at later times

$$\phi = \frac{r}{\{r^2 - z(t)\}^{1/2}}\phi_0[\{r^2 - z(t)\}^{1/2}],$$

where z is given by

$$\dot{z} = 2D\left[\Delta c_0 - \int_0^\infty \tfrac{4}{3}\pi(z+\xi^2)^{3/2}\phi_0(\xi)\, d\xi\right],$$

with $z(0) = 0$.

Deduce that z increases and approaches a constant at large t. For the particular case where $\phi_0(r) = K\delta(r - r_0)$, where K is such that $\int_0^\infty \frac{4}{3}\pi r^3 \phi_0(r)\,dr = f\Delta c_0$, $f < 1$, derive an ordinary differential equation for $\zeta = \dfrac{z}{r_0^2}$ in terms of $\tau = \dfrac{2D\Delta c_0 t}{r_0^2}$, and deduce that $\zeta \to \dfrac{1}{f^{2/3}} - 1$ as $\tau \to \infty$.

3.35 Consider the evolution of particle cluster size as a random walk on the integers $n \geq 1$, where n is the cluster number. If $p_n(t)$ is the probability that a cluster has n particles at time t, $q_n\,dt$ is the probability of adding a particle to an n-cluster in time dt, $r_n\,dt$ is the probability of removing one, and $M(t)$ is the total number of clusters, give an argument why the incremented probability at $t + dt$ is

$$p_n(t + dt) = q_{n-1}p_{n-1}\,dt + r_n p_{n+1}\,dt + p_n\left[1 - q_n\,dt - r_{n-1}\,dt - \frac{dM}{M}\right], \quad n \geq 2,$$

and deduce that in this case

$$\dot{p}_n = S_{n-1} - S_n - \frac{\dot{M}p_n}{M}, \quad n \geq 2,$$

where

$$S_n = q_n p_n - r_n p_{n+1}, \quad n \geq 1.$$

Hence show that

$$\dot{p}_1 = \frac{\dot{M}}{M}(1 - p_1) - S_1.$$

Defining a generating function

$$G(s,t) = \sum_1^\infty p_n s^n,$$

explain why G must be a monotonically increasing function of s with $G = 1$ at $s = 1$. Show that if $q_n = q$ and $r_n = r$ are constant, then

$$\frac{\partial G}{\partial t} = (s - 1)\left[qG - r\left(\frac{G}{s} - p_1\right)\right] + \frac{\dot{M}}{M}(s - G),$$

and deduce that if $q < r$, there is a steady state in which

$$G = \frac{(r - q)s}{r - qs},$$

and calculate the resulting probability density.

Equivalently, show that if $q > r$, a steady state is not possible. What do you think happens in this case?

Show that, by identifying $N_n = Mp_n$, this model is equivalent to the Becker–Döring model.

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