C5.3, Statistical Mechanics

Problem Sheet 3

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1. *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 $\Gamma = V^N \times U^N$, and denote $\gamma_i = (\mathbf{q}_i, \mathbf{p}_i)$ and $\gamma = (\gamma_1, \ldots, \gamma_N)$.

   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

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

   (a) 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.

   (b) 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 $\{\rho, H\}$.

   (c) 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 distinct $i, j \le s$, $i, j > s$, and the remainder, respectively.

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

$$-\int \{\rho, H'\}\, d\Gamma_{s+1} = \sum_{j=s+1}^{N} \sum_{i=1}^{s} \int_{P_j} \frac{\partial \rho_{s+1}(\gamma_1, \ldots, \gamma_s, \gamma_j)}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{ij}}{\partial \mathbf{q}_i}\, d\gamma_j,$$

where P_j $(= P = V \times U)$ is the space spanned by γ_j.

(d) Explain why the integral is independent of j, and hence derive the BBGKY hierarchy equations

$$\frac{\partial f_s}{\partial t} + \{f_s, H\} = \int_{\Gamma_{s+1}} \sum_{i=1}^{s} \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i}\, d\gamma_{s+1}.$$

2. The Boltzmann equation for a set of N particles in a volume V is given by

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g} \cdot \boldsymbol{\nabla}_{\mathbf{v}} f = Q.$$

(a) Explain the meaning of the terms in this equation, and give a concise summary of the way in which it is derived.

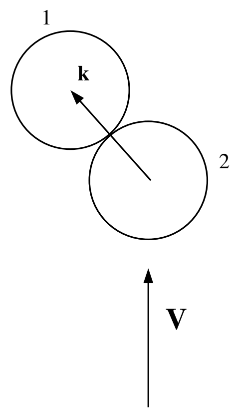
(b) Derive a form for the collision term by considering the particles to consist of perfectly elastic spheres, and writing Q as the difference between a production term and a removal term,

$$Q = Q_+ - Q_-.$$

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



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

where $\mathbf{k}$ is the unit vector along the line of centres at impact.

(c) Hence show that, if d is particle diameter,

$$Q_- \, d\mathbf{r}\, d\mathbf{v}\, dt \approx f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{w},t)\, d^2\mathbf{k}\cdot\mathbf{V}\, d\omega(\mathbf{k})\, d\mathbf{w}\, d\mathbf{r}\, d\mathbf{v}\, dt,$$

explaining in terms of the diagram what the solid angle ω represents.

(d) 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

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

where $\mathbf{V}' = \mathbf{w}' - \mathbf{v}'$ and $\mathbf{V}'\cdot\mathbf{k}' > 0$. Hence deduce, assuming that

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

that

$$Q = \int_U \int_{\mathbf{V}\cdot\mathbf{k}>0} [f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{w}',t) - f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{w},t)]\, d^2\mathbf{k}\cdot\mathbf{V}\, d\omega(\mathbf{k})\, d\mathbf{w}.$$

(e) Under a time reversal transformation, show that Q is invariant, and thus that the Boltzmann equation is not time-reversible.

3. (a) 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.)

(b) 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.

(c) Use the Boltzmann equation to show that the average of a quantity ψ satisfies the evolution equation

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\bar{\psi}\mathbf{u}) + \boldsymbol{\nabla}\cdot\mathbf{J}_\psi = \rho\,\left[\overline{\psi_t + \mathbf{v}\cdot\boldsymbol{\nabla}\psi + \mathbf{g}\cdot\boldsymbol{\nabla}_\mathbf{v}\psi}\right],$$

provided (collisional conservation of ψ)

$$\int_U \psi Q\, d\mathbf{v} = 0.$$

What is the definition of $\mathbf{J}_\psi$?

(d) 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

$$\rho \frac{de}{dt} = \boldsymbol{\sigma} : \boldsymbol{\nabla} \mathbf{u} - \boldsymbol{\nabla} \cdot \mathbf{q},$$

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?

4. 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. Define the inter-particle acceleration as $\mathbf{a}_{ij} = -(1/m) \boldsymbol{\nabla}_{\mathbf{r}_i} W_{ij}$, where m is particle mass, and the external force per unit mass acting on particle i to be $\mathbf{g}$.

(a) Show that the BBGKY equations take the form

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

In particular, show that the one-particle velocity distribution function $f_1 = f(\mathbf{r}, \mathbf{v}, t)$ satisfies

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g} . \boldsymbol{\nabla}_{\mathbf{v}} f = - \int_P \mathbf{a}(\mathbf{r} - \mathbf{s}) \cdot \boldsymbol{\nabla}_{\mathbf{v}} f_2(\mathbf{r}, \mathbf{v}; \mathbf{s}, \mathbf{w}, t) \, d\mathbf{s} \, d\mathbf{w},$$

where $P = V \times U$ is the space spanned by $\mathbf{s}$ and $\mathbf{w}$.

(b) 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

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}_{\mathbf{r}} f + (\mathbf{g} + \mathbf{A}) . \boldsymbol{\nabla}_{\mathbf{v}} f = 0,$$

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.

(c) 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?