C5.3, Statistical Mechanics
Problem Sheet 4

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March 11, 2021

Question 1 covers aspects of Boltzmann's equation. Question 2 is a revision of calculus of variations to help you with Question 3 (which only needs a very basic form). Question 3 and 4 are intended to help you revise material and methods from the first half of the course. Questions 5-8 will get you thinking about the Ising model, Monte Carlo and Markov chains and encourage you to do play with (and possibly code up) an Ising model.

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1. The Maxwellian distribution $f_0(\mathbf{v}) = e^{\Phi_0}$ is given by the dimensionless relation

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

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 $\mathbf{v}$.

(a) 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

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

(b) The inner product is defined by

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

Calculate the inner products of pairs of $\{1, \mathbf{u}', \tfrac{1}{2}u'^2\}$.

(c) 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 $\mathbf{U} \perp \mathcal{N}$.

(d) 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 $\chi \in \mathcal{N}$.

2. A short review of the calculus of variations: Finding extremals. (You may also want to consult the lecture notes for the Part A short option on calculus of variations.)

   (a) A particle is released from $(x, y) = (0, 0)$ at $t = 0$ and then follows a curve $y = y(x)$ which ends at $(x, y) = (a, h)$, where $h < 0$ is the height lost, and a the horizontal distance traversed. Both values are specified. If g is the gravitational acceleration, the total time it takes for the particle to get from the starting to the end point is

   $$T[y] = \frac{1}{\sqrt{2g}} \int_0^a \frac{\sqrt{1 + y'^2}}{\sqrt{y}} \mathrm{d}x.$$

   To find the $y(x)$ that minimises T, state the Euler-Lagrange equation (ELE); you do not need to solve it. Explain briefly how the ELE is derived.

   (b) (Extremals under integral constraints.) Consider a hanging chain of constant density that falls on a curve $y = y(x)$ with fixed endpoints $y = b$ at $x = \pm a$. It is subject to the constraint that its total length is fixed:

   $$J[y] = \int_{-a}^{a} \sqrt{1 + y'^2} \mathrm{d}x = L,$$

   and minimizes its gravitational potential energy, which is

   $$I[y] = g\rho \int_{-a}^{a} y\sqrt{1 + y'^2} \mathrm{d}x.$$

   State necessary conditions for $y(x)$ and give a complete boundary value problem (with constraints and boundary conditions) for $y(x)$. [You do not have to solve the problem.]

3. Evolution of entropy. The normalised ensemble density is a probability in the phase space $\mathbf{\Gamma}$. This probability has an associated entropy $S(t) = -\int \mathrm{d}\mathbf{\Gamma} \rho(\mathbf{\Gamma}, t) \ln \rho(\mathbf{\Gamma}, t)$. (The notation $\mathbf{\Gamma} = (q_1, \ldots, q_{3N}, p_1, \ldots p_{3N})$ is used a shorthand for vectors in $6N$-dimensional phase space.)

   (a) Show that if $\rho(\mathbf{\Gamma}, t)$ satisfies Liouville's equation for a Hamiltonian $\mathcal{H}$, then $\partial S/\partial t = 0$.

   (b) Using the method of Lagrange multipliers, find the function $\rho_{\max}(\mathbf{\Gamma})$ that maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy, $\langle \mathcal{H} \rangle = \int \mathrm{d}\mathbf{\Gamma} \rho \mathcal{H} = E$.

   (c) Show that the solution to part (b) is stationary, that is $\partial \rho_{\max}/\partial t = 0$.

   (d) How can one reconcile the result in (a) with the observed increase in entropy as the system approaches the equilibrium density in (b)?

4. *Equations of state.* The equation of state constrains the form of internal energy as in the following examples.

   (a) Starting from $\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V$, show that the equation of state $PV = Nk_BT$ in fact implies that E can only depend on T.

   (b) What is the most general equation of state consistent with an internal energy that depends only on temperature?

   (c) Show that for a van der Waals gas, the heat capacity (or specific heat) at constant volume C_V is a function of temperature only. The equation of state for a van der Waals gas is given by

   $$\left[P - a\left(\frac{N}{V}\right)^2\right](V - Nb) = Nk_BT,$$

   where in additional to the usual variables P, V, T, the constant number of particles N and the Boltzmann constant k_B we have two additional parameters a and b.

5. Problem 8.1 in Sethna (not to be handed in).

6. Problem 8.6 in Sethna: *Metropolis*
   [You will need to look at problem 8.5 to help with this problem.]

7. Read chapters 8.2 and 8.3 in Sethna

8. Problem 8.12 in Sethna: *Entropy increases! Markov Chains*

9. Problem 6.11 in Sethna: *Barrier Crossing (Chemistry).*
   [This was marked as option on PS 2 because that sheet was too full.]