STATISTICAL PHYSICS

Classical Dynamics, Time's Arrow, Stochastic Dynamics **Tutorial Sheet 8**

The questions that follow on this and succeeding sheets are an integral part of this course. The code beside each question has the following significance:

- **K**: key question – explores core material
- **R**: review question – an invitation to consolidate
- **C**: challenge question – going beyond the basic framework of the course
- **S**: standard question – general fitness training!

8.1 Liouville's equation for an Hamiltonian assembly [R]

(i) If $u(q_i, p_i, t)$ is any well-behaved function of the canonical variables specifying a Hamiltonian assembly, show that its total time derivative

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + \sum_i \left(\frac{\partial q_i}{\partial t}\frac{\partial u}{\partial q_i} + \frac{\partial p_i}{\partial t}\frac{\partial u}{\partial p_i} \right)$$

is given by

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + [u, H]$$

where the Poisson bracket is defined by

$$[F, G] = \sum_i \left(\frac{\partial F}{\partial q_i}\frac{\partial G}{\partial p_i} - \frac{\partial F}{\partial p_i}\frac{\partial G}{\partial q_i} \right) .$$

What is the total time derivative of the Hamiltonian H ?

(ii) Review the derivation of Liouville's equation, for the phase space density ρ given in lectures. Show that Liouville's equation may be written as

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

Show that two ways to have a stationary ensemble, i.e.

$$\frac{\partial \rho}{\partial t} = 0 ,$$

are $\rho=$ constant or $\rho = \rho(H)$.

Can you relate these cases to familiar ensembles?

(iii) Show using Liouville's equation and the result $\underline{\nabla} \cdot \underline{V} = 0$ that

$$\frac{\partial f(\rho)}{\partial t} = -\underline{\nabla} \cdot (f\underline{V})$$

where $f(\rho)$ is any function of phase space density ρ.

Hence show by using the divergence theorem that

$$\frac{\partial S}{\partial t} = -k\frac{\partial}{\partial t}\int \rho \ln \rho \; d\Gamma = 0$$

8.2 **Concavity [K]** Show that the function $s(\rho) = -k\rho \ln \rho$ is concave i.e.

$$\frac{\mathrm{d}^2 s}{\mathrm{d}\rho^2} \leq 0$$

Show by a sketch that this implies

$$s(x\rho_1 + (1-x)\rho_2) \geq xs(\rho_1) + (1-x)s(\rho_2)$$

where $0 \leq x \leq 1$

Deduce

$$s(\overline{\rho}) \geq \overline{s(\rho)}$$

8.3 **Detailed Balance [K]**

(i) Starting from the principle of detailed balance for an isolated system, show that for two groups of states within it A and B, the overall rate of transitions from group A to group B is balanced, in equilibrium, by those from B to A:

$$\nu_{A\to B}\, p_A^{eq} = \nu_{B\to A}\, p_B^{eq}$$

(ii) Deduce that the principle applies to microstates in the canonical ensemble, and hence that the jump rates between states of a subsystem (of fixed number of particles) connected to a heat bath *must* obey

$$\frac{\nu_{i\to j}}{\nu_{j\to i}} = e^{\beta(E_j - E_i)}$$

8.4 **Generalised Random Walk and Diffusion limit [S]**

Consider a particle on a one dimensional lattice of sites $i = 1...L$. The particle does not experience an external potential, but its diffusivity depends on position: $\nu_{i\to j} = D_{i,j}$ with $D_{i,j}$ symmetric, and nonvanishing only for adjacent i and j. (This can be achieved e.g. by having an activation barrier of various heights between each pair of neighbouring sites, with the sites themselves all having the same potential energy $V = 0$.)

(i) Show that the master equation is

$$\dot{p}_i = D_{i,i+1}(p_{i+1} - p_i) - D_{i,i-1}(p_i - p_{i-1})$$

and thereby obtain the continuum diffusion equation for a particle of spatially varying diffusivity $D(x)$:

$$\dot{p}(x) = \frac{\partial}{\partial x}\left(D(x)\frac{\partial p(x)}{\partial x}\right)$$

(ii) A certain student asserts that an equally good master equation for a particle whose diffusivity depends on position can be found by having a hop rate D_i at each site i (so that the particle has the same rate for hops to the left and to the right from site i). Show that this gives

$$\dot{p}_i = D_{i+1}p_{i+1} - D_i p_i - (D_i p_i - D_{i-1}p_{i-1})$$

and hence leads to the continuum 'diffusion equation'

$$\dot{p}(x) = \frac{\partial^2}{\partial x^2}\left(D(x)p(x)\right)$$

Show that the steady state solution of this equation fails to describe the thermal equilibrium state of a particle in zero external potential.

Explain carefully where the student's mistake lies. Can you think of a different physical situation which this equation *does* describe?

8.5 A Langevin Equation [S]

(i) For the Langevin equation

$$\dot{x} = -\mu\kappa x + \mu f$$

for an overdamped harmonic particle subject to a random force f, show that the following is a solution (describing a particle released from $x = 0$ at $t = 0$):

$$x(t) = \mu \int_0^t f(t') \exp[-\mu\kappa(t - t')]dt'$$

(A proof by substitution is adequate, but it would be better to construct the solution by using an integrating factor for example.)

(ii) Show further that

$$\langle x^2(t)\rangle = \mu^2 \exp[-2\mu\kappa t] \int_0^t \int_0^t g(t' - t'') \exp[\mu\kappa(t' + t'')]dt'\, dt''$$

where $g(t' - t'') = \langle f(t')f(t'')\rangle$. Assuming this quantity is so sharply peaked about the origin that it may be approximated as $g\delta(t' - t'')$ where $g = \int_{-\infty}^{\infty} g(u)du$, recover the result that

$$\langle x^2(t)\rangle = \frac{\mu g}{2\kappa}\left(1 - \exp(-2\mu\kappa t)\right)$$

Sketch this function.

Show, when κ is small enough that $\mu\kappa t \ll 1$, that the particle behaves diffusively with $\langle x^2\rangle = \mu^2 g t$. Hence deduce a relation between g and the mobility μ.

Explain why the amount of damping in the system (as set by μ^{-1}) also determines the amount of noise (as set by g). [The result is called the 'fluctuation dissipation theorem'.]

8.6 Brownian Motion [S]

For the Langevin equation far damped Brownian motion

$$\frac{dv}{dt} = -\gamma v + \eta \quad \text{with} \quad \langle \eta(t)\eta(t')\rangle = \Gamma\delta(t - t')$$

Show that

$$\langle v(t_1)v(t_2)\rangle = (v(0)^2 - \frac{\Gamma}{2\gamma})\mathrm{e}^{-\gamma(t_1+t_2)} + \frac{\Gamma}{2\gamma}\mathrm{e}^{-\gamma|t_1-t_2|}$$

and identify $\Gamma = 2\gamma kT$.

Obtain the mean-square displacement

$$\langle [x(t) - x(0)]^2 \rangle = \frac{\Gamma t}{\gamma^2} - \frac{\Gamma}{\gamma^3}\left[1 - \mathrm{e}^{-\gamma t}\right] + \left(\frac{v(0)^2}{\gamma^2} - \frac{\Gamma}{2\gamma^3}\right)\left[1 - \mathrm{e}^{-\gamma t}\right]^2$$

and deduce Einstein's relation $D = 2kT/\gamma$

8.7 **Master Equation** [S]

An isolated system can occupy three possible states of the same energy. The kinetics are such that it can jump between states 1 and 2 and between states 2 and 3 but not directly between states 1 and 3:

Per unit time, there is a probability ν_o that the system makes a jump, from the state it is in, into (each of) the other state(s) it can reach.

(a) Show that the occupancy probabilities $\mathbf{p} = (p_1, p_2, p_3)$ of the three states obey the master equation

$$\dot{\mathbf{p}} = \mathbf{M}.\mathbf{p}$$

where the transition matrix is

$$\mathbf{M} = \nu_0 \begin{pmatrix} -1 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -1 \end{pmatrix}$$

(b) Confirm that an equilibrium state is $\mathbf{p} = (1, 1, 1)/3$.

(c) Prove this equilibrium state is unique.
[Hint: For part (c), consider the eigenvalues of M.]

8.8 **Eigenvectors of the Markov matrix** [C] This is a continuation of previous question: harder, but worth it...

Find the eigenvectors $\mathbf{u}_i$ and eigenvalues λ_i of $\mathbf{M}$.

Show that an initial state $\mathbf{p}(t = 0) = A\mathbf{u}_i$ evolves according to

$$\mathbf{p}(t) = A\mathbf{u}_i e^{\lambda_i t}$$

An ensemble of these systems are prepared, all initially in state 1. By decomposing the initial probability vector $\mathbf{p} = (1, 0, 0)$ into eigenvectors of $\mathbf{M}$, or otherwise, find the proportion of systems in each state, as a function of time.

[Answers: $p_1 = 1/3 + e^{-\nu_o t}/2 + e^{-3\nu_o t}/6$; $p_2 = 1/3 - e^{-3\nu_o t}/3$; $p_3 = 1/3 - e^{-\nu_o t}/2 + e^{-3\nu_o t}/6$.]