Statistical Physics: Tutorial 5

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Master equation and stochastic processes

A: Core problems

1. **Master equation: 2-state system**

   (a) Show that the conservation of probability, together with Fermi's Golden rule, leads to the quantum master equation,

   $$\frac{dp_i}{dt} = \sum_j \nu_{ij}(p_j - p_i),$$

   where p_i is the probability of occupying state i, and ν_{ij} is the transition rate between a pair of states.

   (b) A system of N atoms, each with energy levels $E = \pm\epsilon$ interacts with a heat bath such that each atom has a transition rate $\nu_\uparrow$ from the lower state to the upper, and $\nu_\downarrow$ in the opposite direction. If there are n_+ and n_- atoms in the two states, obtain the master equation for $n_-(t) - n_+(t)$ and hence derive the relaxation time for the approach of the system to equlibrium.

2. **Master equation: matrix approach**

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

   $$\frac{\partial}{\partial t}\mathbf{p} = \mathbf{M}\cdot\mathbf{p},$$

   where the transition matrix is

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

   (b) Confirm that an equilibrium state is $\mathbf{p} = (1,1,1)/3$; by considering the eigenvalues of M, prove this state is unique.

3. **Langevin overdamped oscillator**

   (a) Consider 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 e.g. by using an integrating factor).

(b) Show further that

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

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

When κ is small enough that $\mu\kappa t \ll 1$, show 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 'fluctuation dissipation theorem'].

B: Further problems

1. **Brownian Motion**

   The Langevin equation for Brownian motion reads

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

   where γ is viscous drag coefficient divided by mass. Show that

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

   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 $D = kT/\gamma$.

2. **Generalised random walk and diffusion limit**

   Consider a particle on a 1D lattice with spacing a. The transition rate between sites depends on position: $\nu_{i\to j} = D_{i,j}/a^2$ with $D_{i,j}$ symmetric, and nonzero only for adjacent i and j.

   (a) Show that the master equation is

   $$a^2\, \dot{p}_i = D_{i,i+1}(p_{i+1} - p_i) - D_{i,i-1}(p_i - p_{i-1})$$

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

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

(b) An alternative argument is to say that there is a hop rate D_i/a^2 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

$$a^2\,\dot{p}_i = D_{i+1}p_{i+1} - D_i p_i - (D_i p_i - D_{i-1}p_{i-1})$$

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 thermal equilibrium with zero potential, and explain why the hopping argument is flawed.