G25.2651: Statistical Mechanics

Problem set #7

Due: May 6, 2009

1. Consider a single harmonic degree of freedom q, having a mass m, that obeys the generalized Langevin equation

$$\ddot{q} = -\omega^2 q - \int_0^t d\tau \dot{q}(\tau)\gamma(t-\tau) + f(t)$$

Here ω is the frequency associated with the motion of q, $\gamma(t) = \zeta(t)/m$, and $f(t) = R(t)/m$, where $R(t)$ and $\zeta(t)$ are the random force and friction kernel, respectively. As a crude model of a rapidly decaying friction kernel, consider a $\gamma(t)$ that is constant over a very short time t_0 and then drops suddenly to 0:

$$\gamma(t) = \gamma_0 \theta(t_0 - t)$$

where γ_0 is a constant, $\theta(x)$ is the Heaviside step function, and $t, t_0 \geq 0$.

a. Show that if t_0 is small enough that $\exp(-st_0) \approx 1 - st_0$ for all relevant values of s, then the presence of memory in this system causes the velocity autocorrelation function $C_{vv}(t)$

$$C_{vv}(t) = \frac{\langle \dot{q}(0)\dot{q}(t)\rangle}{\langle \dot{q}^2 \rangle}$$

to oscillate with a frequency less than ω and to decay slowly in time. Determine the decay constant and oscillation frequency of $C_{vv}(t)$.

b. Suppose that we now let t_0 become very large. Show that the velocity autocorrelation no longer decays but oscillates with a frequency different from ω. What is the oscillation frequency of $C_{vv}(t)$?

c. Explain the physical origin of the behavior of the the velocity correlation function in the two limits considered in parts a and b in terms of the response of the bath to the system.

2. Consider the Ising Hamiltonian for which each spin has z neighbors on the lattice. Each spin variable σ_i can take on three values, $-1, 0, 1$. Using mean-field theory, find the transcendental equation for the magnetization, and determine the critical temperature of this model. What are the critical exponents?

3. A simple model of a long polymer chain consists of the following assumptions:

i. The conformational energy E of the chain is determined solely from its backbone dihedral angles.

ii. Each dihedral angle can assume three possible values denoted t for "trans" and g^+ and g^- for the two "gauche" conformations. However, the present model is discrete in the sense that t, g^+ and g^- are the only values the dihedral angles may assume.

iii. Each conformation has an intrinsic energy and is also influenced by the conformations of nearest neighbor dihedral angles only. If the polymer has N atomic sites, then there are $N-3$ dihedral angles numbered $\phi_1, ..., \phi_{N-3}$ by convention. The total energy $E(\phi_1, ..., \phi_{N-3})$ can be written as

$$E(\phi_1, ..., \phi_{N-3}) = \sum_{i=1}^{N-3} \varepsilon_1(\phi_i) + \sum_{i=2}^{N-3} \varepsilon_2(\phi_{i-1}, \phi_i)$$

where each ϕ_i has values t, g^+, or g^-.

iv. The two energy functions ε_1 and ε_2 are assumed to have the following values:

$$\begin{aligned} \varepsilon_1(t) &= 0 \\ \varepsilon_1(g^+) &= \varepsilon(g^-) = \varepsilon \\ \varepsilon_2(g^+, g^-) &= \varepsilon_2(g^-, g^+) = \infty \\ \varepsilon_2(\phi_{i-1}, \phi_i) &= 0 \qquad \text{for all other combinations} \end{aligned}$$

a. Calculate the canonical partition function for this system. You may express your answer in terms of $\sigma \equiv \exp(-\beta\varepsilon)$.

b. Show that, in the limit $N \to \infty$, the partition function behaves as

$$\lim_{N\to\infty} \frac{1}{N} \ln Q = \ln \chi$$

where

$$\chi = \frac{1}{2}\left[(1+\sigma) + \sqrt{1 + 6\sigma + \sigma^2}\right]$$

c. What is the probability, for large N, that all angles will be in the trans conformation?

d. What is the probability, for large N, that the angles will alternate trans, gauche, trans, gauche, ...?