Problem Set 5

Advanced Statistical Mechanics

Deadline: Friday, 14 Khordad, 23:59

1 Stochastic Processes

1.1 Generalized Langevin Equation (GLE)

For a one dimensional system, by incorporating the effects of the fluid in Newton's second law one may write a Langevin equation of motion for the position $x(t)$ of a particle of mass m as a second order stochastic differential equation,

$$m\ddot{x}(t) = -\gamma\dot{x}(t) + F(x,t) + \xi(t) \tag{1}$$

The random force is generated by a Gaussian white noise $\xi(t)$, with average $\langle\xi(t)\rangle = 0$ and correlation $\langle\xi(t')\xi(x'')\rangle = 2\gamma k_B T\delta(t' - t'')$. The prefactor of the dirac delta ensures thermodynamic consistency according to the (second) fluctuation-dissipation theorem, linking the drag coefficient γ of the dissipative term $-\gamma\dot{x}$ to the strength of the noisy term. As a deterministic force due to the fluid we focus on the case $F(x,t) = \partial_x U(x,t)$ with a time-dependent potential energy $U(x,t)$.

If the particle is immersed in a solution containing fro example long and complex polymers, the above-mentioned separation of time scales in no longer possible and memory effects occur. One may then consider a generalized Langevin equation with constant diffusion coefficient. For $t \geq 0$ this equation reads

$$m\ddot{x}(t) = -\int_{t_m}^{t} dt'\Gamma(t - t')\dot{x}(t') - \partial_x U(x,t) + \eta(t) \tag{2}$$

where $\Gamma(t)$ is the memory kernel, $t_m \leq 0$ is the time to which the memory effects extend and $\eta(t)$ is a colored Gaussian noise obeying $\langle\eta(t)\rangle = 0$. The fluctuation-dissipation relation is still valid in the more general form $\langle\eta(t')\eta(t'')\rangle = k_B T\Gamma(|t' - t''|)$: thermodynamic equilibrium is present in the medium if its two effects (dissipation and noise) are proportional at all times.

The aim of this problem is to solve the GLE with a parabolic confinement potential $U(x,t) = \frac{\kappa}{2}(x - \lambda(t))^2$, then

$$m\ddot{x}(t) = -\int_{t_m}^{t} dt'\Gamma(t - t')\dot{x}(t') - \kappa(x(t) - \lambda(t)) + \eta(t) \tag{3}$$

Moreover, we will restrict ourselves to the case of a non-divergent time dependent effective friction coefficient $\hat{\gamma}(t)$, i.e. such that $\hat{\gamma} = \lim_{t\to\infty} \hat{\gamma}(t) = \lim_{t\to\infty} \int_0^t dt'\Gamma(t') < \infty$, which is a sensible physical requirement.

One of the analytical solutions for the GLE is obtained with constant κ. Through this approach, one may use Laplace transform. Our way to tackle this problem is to introduce a modified Laplace transform with an arbitrary initial time $t_m \leq 0$ that acts on a given function $g(t)$ as follows

$$\hat{g}(k) = \mathcal{L}_k(g(t)) = \int_{t_m}^{\infty} dt e^{-kt} g(t) \tag{4}$$

i) Show that the action of the modified Laplace transform on integrals is equal to the action of the standard transform, namely

$$\mathcal{L}_k\left(\int_{t_m}^t dt' g(t')\right) = \frac{\hat{g}(k)}{k} \tag{5}$$

ii) By applying the Laplace transform to the GLE and by using the above result, calculate the following equation

$$\mathcal{L}_k(m\ddot{x}(t)) = \mathcal{L}_k\left(-\int_{t_m}^t dt'\Gamma(t-t')\dot{x}(t') - \kappa(x(t) - \lambda(t)) + \eta(t)\right) \tag{6}$$

Now, we introduced the "position susceptibility" $\mathcal{X}_x(t)$, defined via its Laplace transform

$$\mathcal{X}_x(k) = (mk^2 + k\hat{\Gamma}(k) + \kappa)^{-1} \tag{7}$$

By defining the inverse of the modified Laplace transform through the usual Bromwich integral

$$g(t) = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} dk e^{kt} \hat{g}(s) \tag{8}$$

where α is such that the chosen vertical contour in the complex plane has all the singularities of $g(s)$ on its left side, we see that $\mathcal{L}_k^{-1}(e^{-kt_m}) = 2\delta(t - t_m)$ and $\mathcal{L}_k^{-1}(\frac{e^{-kt_m}}{k}) = \theta(t - t_m)$, where $\theta(t)$ is the Heaviside step function.

iii) By transforming back equation that you have calculated in the previous part to real time, show that for $t > 0 \geq t_m$,

$$x(t) = x_{t_m}(1 - \kappa\mathcal{X}(t - t_m)) + mv_{t_m}\mathcal{X}_x(t - t_m) + \int_{t_m}^t dt'\mathcal{X}_x(t - t')(\kappa\lambda(t') + \eta(t')) \tag{9}$$

Another important quantity we are interested in is the variance of the position at time t. Given that system started at time t_m with position x_{t_m} and velocity v_{t_m}, we have that

$$\langle\Delta^2 x\rangle_{t_m,t} = \left\langle (x(t) - \langle x\rangle_{t_m,t})^2 \right\rangle_{t_m,t} \tag{10}$$

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iv) By using the previously obtained expression for the position and defining

$$\phi(t) = \int_{t_m}^{t} \mathcal{X}_x(t - t')\eta(t')dt' \tag{11}$$

obtain an expression for $\left\langle \Delta^2 x \right\rangle_{t_m,t}$

Hint: See arXiv:2005.04012 [cond-mat.stat-mech]

2 The Partition Function

2.1 Boltzmann Distribution

In this problem we try to review the Boltzmann's 1877 paper which for the first time established the probabilistic basis of entropy.

Suppose we have n molecules. Each of them is capable of having kinetic energies

$$0, \epsilon, 2\epsilon, \cdots, p\epsilon \tag{12}$$

and suppose these energies are distributed in all possible ways among the n molecules, such that the total energy is a constant $\lambda\epsilon = L$. Any such distribution, in which the first molecule may have a kinetic energy of e.g., 2ϵ, the second may have 6ϵ, and so on, up to the last molecule, we call a complexion. We seek the number $\mathcal{P}$ of complexions where w_0 molecules have kinetic energy 0, w_1 molecules have kinetic energy ϵ, ω_2 have kinetic energy 2ϵ, up to the w_p which have kinetic energy $p\epsilon$. Dividing the number $\mathcal{P}$ by the number of all possible complexions, we get the probability of the state distribution.

The first task is to determine the permutation number, $\mathcal{P}$, for any state distribution. It must be understood that

$$w_0 + w_1 + w_2 + \cdots + w_p = n \tag{13}$$

$$w_1 + 2w_2 + 3w_3 + \cdots + pw_p = \lambda \tag{14}$$

i) Calculate the total number of permutations and show that it equals to

$$\mathcal{P} = \frac{n!}{w_0!w_1!\cdots} \tag{15}$$

The most likely state distribution with be for those w_i values for which $\mathcal{P}$ is a maximum. Since the denominator of $\mathcal{P}$ is a product, it is easiest to determine the minimum of its logarithm, that is the minimum of

$$M = \ln(w_0!) + \ln(w_1!) + \cdots \tag{16}$$

It is a natural in our problem that only integer values of w_i are meaningful. However to apply differential calculus, we will allow non-integer values, and so find the minimum of the expression

$$M = \ln \Gamma(w_0 + 1) + \ln \Gamma(w_1 + 1) + \cdots \tag{17}$$

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ii) By using Lagrange multipliers and the constraint equations show that

$$
\begin{aligned}
& \frac{\mathrm{d}\ln\Gamma(w_1+1)}{\mathrm{d}w_1} - \frac{\mathrm{d}\ln\Gamma(w_0+1)}{\mathrm{d}w_0} \\
&= \frac{\mathrm{d}\ln\Gamma(w_2+1)}{\mathrm{d}w_2} - \frac{\mathrm{d}\ln\Gamma(w_1+1)}{\mathrm{d}w_1} \\
&= \frac{\mathrm{d}\ln\Gamma(w_3+1)}{\mathrm{d}w_3} - \frac{\mathrm{d}\ln\Gamma(w_2+1)}{\mathrm{d}w_2}
\end{aligned}
\tag{18}
$$

Exact solution of the problem through evaluation of the gamma function integral is very difficult; fortunately the general solution for arbitrary finite values of p and n does not interest us here, but only the solution for the limiting case of larger and larger number of molecules. Then the numbers w_i become larger and larger, so we introduce the function

$$
\phi(x) = \ln\Gamma(x+1) - x(\ln x - 1) - \frac{1}{2}\ln 2\pi
\tag{19}
$$

ii) Show that we have

$$
\ln w_1 + \frac{\mathrm{d}\phi(w_1)}{\mathrm{d}w_1} - \ln w_0 - \frac{\mathrm{d}\phi(w_0)}{\mathrm{d}w_0} = \ln w_2 + \frac{\mathrm{d}\phi(w_2)}{\mathrm{d}w_2} - \ln w_1 - \frac{\mathrm{d}\phi(w_1)}{\mathrm{d}w_1}
\tag{20}
$$

and similarly for the other indexes. It is also well known that

$$
\phi(x) = -\frac{1}{2}\ln x + \frac{1}{12x} + \cdots
\tag{21}
$$

This series is not valid for $x = 0$, but here $x!$ and $\sqrt{2\pi}(x/e)^x$ should have the same value, and $\phi(x) = 0$.

Therefore the problem of finding the minimum of $\prod_i w_i!$ is replaced by the easier problem of finding the minimum of

$$
\prod_i \sqrt{2\pi}\left(\frac{w_i}{e}\right)^{w_i}
\tag{22}
$$

providing w is not zero, even at moderately large values of p and n both problems have matching solutions.

iii) Show that

$$
\frac{w_2}{w_1} = \frac{w_3}{w_2} = \frac{w_4}{w_3} = \cdots
\tag{23}
$$

One sees immediately that the minimum of the denominator of

$$
\frac{\sqrt{2\pi}\left(\frac{n}{e}\right)^n}{\prod_i \sqrt{2\pi}\left(\frac{w_i}{e}\right)^{w_i}}
\tag{24}
$$

is found instead of the minimum of the denominator of $\mathcal{P}$.

If we denote the common values of the quotient (23) by x we obtain

$$
w_1 = w_0 x, \quad w_2 = w_0 x^2, \quad w_3 = w_0 x^3, \quad \cdots
\tag{25}
$$

The two equation (13) and (14) become

$$w_0(1 + x + x^2 + \cdots + x^p) = n \tag{26}$$

$$w_0(x + 2x^2 + 3x^3 + \cdots + px^p) = \lambda \tag{27}$$

iv) By solving the above equation, show that we can obtain

$$w_0 = \frac{n^2}{n + \lambda}, \quad w_1 = \frac{n^2\lambda}{(n + \lambda)^2}, \quad w_3 = \frac{n^2\lambda^2}{(n + \lambda)^3}, \quad \cdots \tag{28}$$

v) With some approximations, prove that

$$w_s \approx \frac{n\epsilon}{\mu}e^{-\frac{\epsilon s}{\mu}} \tag{29}$$

where $\mu = \frac{\lambda\epsilon}{n}$ is equal to the average kinetic energy of a molecule.

Thus we obtain the Boltzmann' distribution for a discrete case.

vi) Until now, the calculations are just for the discrete case. Do all of these procedures for the continuous case.

2.2 General Properties of The Partition Function

Write an essay and summarize the 9th chapter of Huang's book. (At least 5 pages)

2.3 Ideal Bose Gas

Derive with the help of the saddle point integration method a formula for the partition function for an ideal Bose gas of N particles.

2.4 The Lee-Yang Theorem in Electrostatics

Show that the equation of state

$$\begin{aligned}
\frac{P}{k_BT} &= \int_0^\pi d\theta g(\theta) \log(1 - 2z\cos\theta + z^2) \\
\frac{1}{v} &= 2z \int_0^\pi d\theta g(\theta) \frac{z - \cos\theta}{1 - 2z\cos\theta + z^2}
\end{aligned} \tag{30}$$

of the Lee-Yang lattice gas has the following electrostatic analog:

i) Consider a circular cylinder of unit radius perpendicular to the complex z plane, cutting it at the unit circle. Suppose the cylinder is charged with a surface charge density that depends only on the angle θ around the unit circle (with $\theta = 0$ corresponding to $z = 1$). The charge density (per unit area) is equal to $g(\theta)$, with $g(\theta) = g(-\theta)$. Let $\phi(z)$ and $E(z)$ be, respectively, the electrostatic potential and the electric field at a point z on the real axis. Then

$$\begin{aligned}
\frac{P}{k_BT} &= -\frac{1}{2}\phi(z) \\
n &= \frac{1}{2}zE(z)
\end{aligned} \tag{31}$$

where $n = \frac{1}{v}$ is the density.

ii) Assume $g(0) \neq 0$. Show by electrostatic argument that P is continuous at $z = 1$, but n jumps discontinuously. This shows that there is a first-order phase transition. Using Gauss's theorem in electrostatics, show the discontinuity in density is given by

$$\Delta n = 2\pi g(0) \tag{32}$$

2.5 About the Grand Partition Function

Consider the grand partition function

$$\mathcal{Z}(z, V) = (1 + z)^V (1 + z^{\alpha V}) \tag{33}$$

where α is a positive constant.

i) Write down the equation of state in a parametric form, eliminate z graphically, and show that there is a first-order transition. Find the specific volumes of the two phases.

ii) Find the roots of $\mathcal{Z}(z, V) = 0$ in the complex z plane, at fixed V. Show that as $V \to \infty$ the roots converge toward the real axis at $z = 1$.

iii) Find the equation the phase-transition density fails to show any sign of the transition. This will demonstrate that the order of the operation $z\frac{\partial}{\partial z}$ and $V \to \infty$ can be interchanged only within a single-phase region.