

Physics of disordered systems: exercises

October 18, 2022

Contents

1	Colloids	1
1.1	Generalized Langevin equation	1
1.2	Caldeira-Leggett model	2
2	Polymers	4
2.1	Gyration radius	4
2.1.1	Linear polymer	4
2.1.2	Star polymers	4
2.2	Rouse model	5
2.2.1	Rotational dynamics	5
2.2.2	Segmental motion	5
3	Liquids	6
3.1	Short-time dynamics	6
3.2	Memory effects	6
4	Supercooled liquids	8
4.1	Gaussian landscape	8
4.2	Schematic mode-coupling theory	8

1 Colloids

1.1 Generalized Langevin equation

[Sources: R. Zwanzig "Nonequilibrium statistical mechanics", sec. 1.5]

The Langevin equation describes the motion of a colloidal particle in which the friction at time t is proportional to the velocity at the same time. In general, however, we expect that the friction will depend also on the history of the velocity $\dot{x}(s)$ for times s earlier than t . To model such a *memory effect*, we replace the friction coefficient ξ with a memory function $M(t)$ so that the frictional force becomes

$$-\xi\dot{x}(t) \rightarrow -\int_{-\infty}^t F(t-s)\dot{x}(s)$$

This leads to the generalized Langevin equation

$$m\ddot{x}(t) = -m \int_0^t M(t-s)\dot{x}(s)ds + F(t)$$

At this stage the equation is purely phenomenological, but it can be established both from a microscopic model (see the Caldeira-Leggett model below), as well as from the general formalism of the projection operator. Here, we will show that such the generalized Langevin equation also arises also when we eliminate the momentum in the Brownian motion of a harmonic oscillator.

1. Write the Langevin equation of a colloidal particle of mass m in a harmonic external potential $\phi(x) = \frac{1}{2}kx^2$ and determine the equations of motion as a system of two non-linear stochastic differential equations
2. Determine (formally) the momentum $p(t)$, assuming $p(t = -\infty) = 0$
3. Show that the equation of motion for the colloidal particle can be put in the form

$$\frac{dx}{dt} = - \int_{-\infty}^t M(t-s)x(s) + F_x(t)$$

and provide explicit expressions for $M(t)$ and for the new fluctuating force $F_x(t)$.

4. Find the generalized fluctuation-dissipation relation between F_x and M by assuming that the particles is at equilibrium and therefore $\langle x^2 \rangle = k_B T / (m\omega^2)$, where $\omega^2 = k/m$

1.2 Caldeira-Leggett model

[Sources: R. Zwanzig "Nonequilibrium statistical mechanics", sec. 1.6]

We now study the dynamics of a free particle interacting with a large number of independent harmonic oscillators in thermal equilibrium. The model we will present, known as the Caldeira-Leggett model, can be solved exactly and provides a microscopic basis to the Langevin equation, in both its original and generalized form.

Consider a particle of mass m described by its coordinate x and conjugate momentum p . The particle is coupled to a heat bath of N independent harmonic oscillators of masses m_n , described by the coordinates x_i and momenta p_i , with $i = 1, \dots, N$. We assume a bilinear coupling between the particle and each oscillator. The Hamiltonian of the system thus reads

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2} \sum_{i=1}^N \left[\frac{p_i^2}{m_i} + m_i \omega_i^2 \left(x_i - \frac{c_i}{m_i \omega_i^2} x \right)^2 \right]$$

where c_i are coupling constants.

1. Write the equations of motion of the particle and of the harmonic oscillators
2. We now use a trick: we assume that $x(t)$ is known. Show that the equations of motion for the oscillators can then be solved (formally) to give

$$x_i(t) = x_i(0) \cos(\omega_i t) + \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t) + c_i \int_0^t \frac{\sin[\omega_i(t-t')]}{m_i \omega_i} x(t') dt'$$

3. Integrate by parts the integral on the right-hand side and find an expression for $x_i(t) - \frac{c_i}{m_i \omega_i^2} x(t)$.

4. Use the previous results to express the particle's equations of motion in the form of a generalized Langevin equation

$$m\ddot{x}(t) = m \int_0^t M(t-s)\dot{x}(s)ds + F_x(t)$$

and provide the explicit expressions for the memory function $M(t)$ and the random force $F(t)$.

5. Under which conditions does one recover the simple (Markovian) Langevin equation?

2 Polymers

2.1 Gyration radius

We want to determine the gyration radius

$$R_g = \left(\left\langle \frac{1}{N} \sum_{i=1}^N |\vec{R}_i - \vec{R}_{\text{CM}}|^2 \right\rangle \right)^{1/2}$$

of simple models of polymer chains, where $\langle \dots \rangle$ indicates an average over chain conformations and \vec{R}_{CM} is the center of mass of the chain. We will assume that all monomers are identical and that the monomer-monomer distance is b .

First off, show that the gyration radius can be expressed as

$$R_g = \left(\left\langle \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N |\vec{R}_i - \vec{R}_j|^2 \right\rangle \right)^{1/2}$$

which provides a more convenient starting point for the following calculations.

2.1.1 Linear polymer

We first consider an ideal linear chain. Remembering that

$$\sum_{i=1}^N i = \frac{N(N+1)}{2} \quad \sum_{i=1}^N i^2 = \frac{N(N+1)(2N+1)}{6}$$

show that

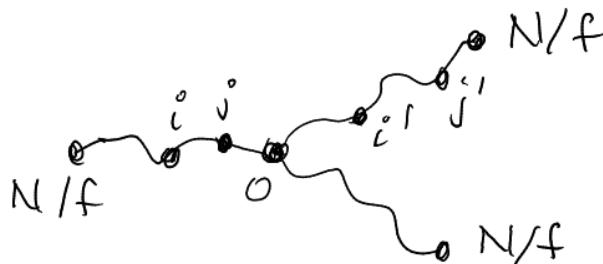
$$R_g^2 = \frac{b^2}{6} \frac{N^2 - 1}{N}$$

Where do the two above expressions come from, by the way?

2.1.2 Star polymers

We now consider a star polymer with "functionality", i.e., the number of arms, f . Each arm α has an equal number N/f of monomers. Since we will consider the limit of a very large number of monomers, it is convenient to recast the sums over monomer index as integrals

$$\sum_{i=1}^N \rightarrow \int_0^N di$$



1. Compute the radius of gyration R_g . *Hint*: consider separately the case in which the monomers belong to the same arm or not.
2. Consider the results for $f = 1, 2$: what do you notice?
3. What is the effect of increasing the functionality at constant N ?
4. How does the gyration radius scale with f in the limit $f \rightarrow \infty$? Establish a link with an effective ideal chain with M monomers.

2.2 Rouse model

[Sources: M. Doi "Introduction to polymer physics", sec. 4.2.2]

2.2.1 Rotational dynamics

We study the rotational motion of a polymer chain of $N + 1$ monomers within the Rouse model. To this end, we consider the time correlation function $\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$ of the end-to-end vector $\vec{R} = \vec{R}_N - \vec{R}_0$.

1. Show that $\vec{R} = -4 \sum_{p=1,3,5,\dots} \vec{X}_p(t)$
2. Use this result to compute the correlation function $\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$
3. Show that the relaxation of $\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$ is dominated by the largest Rouse mode relaxation time, τ_1 .

2.2.2 Segmental motion

We now focus on the internal motion of the polymer segments, always within the Rouse model. We consider the mean square displacement of the n -th monomer after a time t .

$$\Delta R^2(t) = \langle |\vec{R}(n, t) - \vec{R}(n, 0)|^2 \rangle$$

1. Using the correlations between the Rouse vectors $\langle \vec{X}_{p\alpha} \cdot \vec{X}_{q\beta} \rangle$, show that

$$\Delta R^2(t) = 6 \frac{k_B T}{N \xi} t + \frac{4N b^2}{\pi^2} \sum_{p=1}^{\infty} \cos^2 \left(\frac{p\pi n}{N} \right) \frac{1 - \exp(-tp^2/\tau_1)}{p^2}$$

where $\tau_1 = \frac{\xi N^2 b^2}{3\pi^2 k_B T}$ is the largest Rouse mode relaxation time.

1. The behavior of $\Delta R^2(t)$ for $t \gg \tau_1$ is diffusive. What is the physical interpretation of the diffusion coefficient?
2. Show that the behavior of $\Delta R^2(t)$ for $t \ll \tau_1$ is sub-diffusive with an exponent $1/2$. *Hint*: replace the summation in $\Delta R^2(t)$ with an integral over the continuous variable p

3 Liquids

3.1 Short-time dynamics

[Sources: J.-P. Hansen and I. MacDonald "Theory of simple liquids", sec. 7.1 and 7.2]

We want to determine the short-time behavior of the velocity autocorrelation function

$$Z(t) = \frac{1}{3} \langle \vec{v}(t+s) \vec{v}(s) \rangle$$

of a tagged particle of mass m in a liquid.

To this end, it will be useful to establish some general "sum rules" concerning time-dependent correlation functions $C_{AB}(t) = \langle A(s+t)B(s) \rangle$. We will assume that the correlation function is stationary,

$$\frac{dC_{AB}}{ds} = 0$$

1. Show that

$$\langle \dot{A}(t+s)B(s) \rangle = -\langle A(t+s)\dot{B}(s) \rangle$$

2. Show that

$$\langle \ddot{A}(t+s)B(s) \rangle = -\langle \dot{A}(t+s)\dot{B}(s) \rangle$$

3. Consider now the simple but important case in which A and B are the same variable. It can be shown that the correlation function $C_{AA}(t)$ is even in time, if it is stationary. Determine the Taylor expansion of $C_{AA}(t)$ around $t = 0$ up to second order

We now focus on the velocity auto-correlation $Z(t)$. Show that the short time expansion of $Z(t)$ can be put in the form

$$Z(t) = \frac{k_B T}{m} \left(1 - \frac{1}{2} \Omega_0^2 t^2 + \dots \right)$$

where Ω_0 is the so-called Einstein frequency. Assuming that the fluid is at equilibrium at temperature T , express Ω_0 in terms of the average square force $\langle |\vec{F}|^2 \rangle$ acting on the tagged particle.

3.2 Memory effects

[Sources: J.-P. Hansen and I. MacDonald "Theory of simple liquids", sec. 7.3]

We consider a generalized Langevin equation for a tagged particle in a liquid at equilibrium at a temperature T

$$m\dot{\vec{v}}(t) = -m \int_0^t M(t-s) \vec{v}(s) ds + R(t)$$

where $M(t)$ is a memory kernel and $R(t)$ is the random force. This equation is formally exact and can be established using the projector operator formalism. However, an explicit expression for the memory kernel is not available. Here, we will model the memory function $M(t)$ as a simple exponential

$$M(t) = M(0) \exp(-|t|/\tau)$$

1. Show that the velocity autocorrelation function $Z(t)$ obeys the following integro-differential equation

$$\dot{Z}(t) = - \int_0^t M(t-s) Z(s) ds$$

2. By a Laplace transform, show that

$$\tilde{Z}(z) = \frac{k_B T/m}{-iz + \tilde{M}(z)}$$

3. Use the short-time expansion of $Z(t)$ obtained in the previous exercise to show that $M(0) = -\ddot{Z}(0)/Z(0) = \Omega_0^2$ and determine $\tilde{M}(z)$

4. By an inverse Laplace transformation, show that

$$Z(t) = \left(\frac{k_B T/m}{\alpha_- - \alpha_+} \right) [\alpha_+ \exp(-\alpha_- |t|) - \alpha_- \exp(-\alpha_+ |t|)]$$

where α_+ and α_- are the two poles of $\tilde{Z}(z = i\alpha)$.

5. Show that if $\tau < 1/(2\Omega_0)$, $Z(t)$ decays monotonically to zero and with the correct curvature at the origin

6. Show that if $\tau > 1/(2\Omega_0)$, $Z(t)$ displays damped oscillations, with a negative region at intermediate times

Note that the memory relaxation time τ is a free parameter of the model and would have to be determined from experimental or numerical data.

4 Supercooled liquids

4.1 Gaussian landscape

[Sources: S. Sastry, *Nature* 409, 164 (2001)]

We develop a simple model of the potential energy surface of systems with short range interactions and a large number N of interacting particles. The potential energy density of local minima is $u_m = U_m/N$. The two basis hypothesis of the model are

- The density of states of local minima is Gaussian

$$\Omega(U_m) = \exp(\alpha N) \cdot \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(U_0 - U_m)^2}{2\sigma^2}\right]$$

where U_0 is a reference energy and α a combinatorial factor (N -independent). This functional form arises from the idea that for large N and short-range interactions the system can be decomposed into weakly interacting sub-systems. According to the central limit theorem, the distribution of the total potential energy can then be approximated by a Gaussian with $\sigma^2 \sim N$.

- The vibrational free energy is given by the harmonic approximation

$$f_{\text{vib}}(u_m, T) = f_{\text{vib}}(u_0, T) - k_B T b (u_m - u_0)$$

where b is a constant

For a comparison between the model predictions and computer simulation data, see S. Sastry, *Nature* 409, 164 (2001) <http://dx.doi.org/10.1038/35051524>.

1. Compute the average energy density $\langle u_m \rangle$ and plot it as a function of T and $1/T$. Compare with the behavior observed at high and low T in the simulations of Sastry.
2. Compute the configurational entropy S_c as a function of U_m . Find the Kauzmann temperature T_K at which the configurational entropy vanishes. Is T_K finite in the thermodynamic limit?

4.2 Schematic mode-coupling theory

[Sources: Barrat Hansen 12.4; E. Leutheusser *Phys. Rev. A*, 29 2765 (1984)]

The schematic mode-coupling equation

$$\ddot{\phi} + \Omega^2 \phi(t) + \lambda_2 \int_0^t ds \phi^2(t-s) \dot{\phi}(s) = 0$$

provides a simplified description of the time-dependence of a dynamic correlation function $\phi(t)$ in a glass system. The coupling constant λ_2 plays the role of a control parameter, similar to temperature or density in a liquid, while Ω is a constant. This equation can be obtained from the full mode-coupling equations for the (normalized) intermediate scattering function $F(k, t)/S(k)$ by ignoring the coupling between density components and retaining only the contribution to the memory kernel around the main peak of $S(k)$.

Our goal is to determine the asymptotic behavior of $\phi(t)$ for $t \rightarrow \infty$ and discover the existence of an "ideal" glass transition at a finite value of the coupling parameter λ_c . The standard way to tackle this problem is using Laplace transforms [see E. Leutheusser *Phys. Rev. A*, 29 2765 (1984)]. Here we will try to work in the time domain.

1. Let us write $\phi(t) = f + \epsilon(t)$, where $\epsilon \rightarrow 0$ for $t \rightarrow \infty$. By taking the infinite time limit of the schematic mode-coupling equation, show that that $f = \phi(\infty)$ obeys

$$(\Omega^2 - \Omega_0^2)f + \lambda_2 f(f - 1) = 0$$

and provide the expression of Ω_0^2 . In the following, we will assume that Ω_0^2 can be neglected (Is this reasonable? Later on, think about which of the results below would be affected if this were not the case.)

2. Let us determine the solutions of the equation $\Omega^2 f + \lambda_2 f(f - 1) = 0$ as a function of the reduced coupling constant $\lambda = \lambda_2/(4\Omega^2)$. It is clear that $f = 0$ is always a solution and corresponds to an ergodic liquid. Show that for $\lambda > \lambda_c$ the equation admits two additional solutions f_+ , f_- . Determine the critical coupling parameter λ_c .
3. Only the solution f_+ is physically acceptable. Why? *Hint:* analyze how f_- depends on λ . It can also be shown that the solution $f = 0$ becomes unstable for $\lambda > \lambda_c$.
4. Make a first-order Taylor expansion of $f(\lambda)$ close to the transition point λ_c and sketch the behavior of $f(\lambda)$ as a function across the transition. Provide a physical interpretation to the following statement: the system undergoes a transition to an "ideal" glass at λ_c .