Fisica dei sistemi disordinati

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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

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

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 establised 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 $\langle x^2\rangle = k_BT/(m\omega^2)$, 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 $i = 1, \ldots, N$. 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

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

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 explict 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 Non-equilibrium thermodynamics

2.1 Onsager reciprocity relations

[Sources: Callen 14-4; Laundau & Lifshitz vol.5 120]

We consider the out-of-equilibrium evolution of an observable X_j, defined in a macroscopic subsystem in local equilibrium conditions at time t and at point $\vec{r}$. Physical examples are $X_k = E$ or $X_k = N$. For small deviations from equilibrium, the currents of X_j are expressed as linear combinations of the thermodynamic forces, that is $\sum_i L_{ij} \nabla Y_i$, where Y_i is the variable conjugated to X_i, $F_i = \nabla Y_i$ is the associated thermodynamic force and L_{ij} are the kinetic coefficients.

At equilibrium, the equilibrium average value of X is $\langle X \rangle$, while the time-dependent correlation function evaluated from the fluctuations is $\langle \delta X_k(t) \delta X_j(0) \rangle$. Our goal is to establish the famous symmetry property $L_{ij} = L_{ji}$, known as Onsager reciprocity relation.

1. Assume that the microscopic equations of motion are invariant under time reversal. Discuss the conditions of validity of the equation $\langle \delta X_k(t) \delta X_j(0) \rangle = \langle \delta X_k(-t) \delta X_j(0) \rangle$. We will assume these conditions are met in the next equations.
2. From consideration of the limit $t \to 0$ for the correlation function, show that $\langle \delta \dot{X}_k \delta X_j \rangle = \langle \delta \dot{X}_j \delta X_k \rangle$
3. Assuming that the decay of a fluctuation δX_k is governed by the same linear dynamic equations as in a macroscopic transport process, show that

$$\sum_i L_{ik} \langle \delta X_j \delta F_i \rangle = \sum_i L_{ij} \langle \delta X_k \delta F_i \rangle$$

4. Using thermodynamic fluctuations theory, show that $\langle \delta X_j \delta F_i \rangle = k \delta_{ij}$, where k is a constant, and hence $L_{ij} = L_{ji}$

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

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

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
$$Z(t) = \left(\frac{k_B T/m}{\alpha_- - \alpha_+}\right)\left[\alpha_+ \exp\left(-\alpha_-|t|\right) - \alpha_- \exp\left(-\alpha_+|t|\right)\right]$$
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 dampled 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 hyopthesis 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 a 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 thermdynamic 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 $t \to \infty$ 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 $\epsilon \to 0$ for $t \to \infty$. 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.

5 Spin glasses

5.1 Replica-symmetric solution of the Sherrington-Kirkpatrick model

[Sources: H. Nishimori "Statistical Physics of Spin Glasses and Information Processing: An Introduction"]

We consider the Sherrington-Kirkpatrick spin glass model in the absence of magnetic field

$$H = -\sum_{i=1}^{N}\sum_{j>i}^{N} J_{ij}\sigma_i\sigma_j$$

where $\sigma_i = \pm 1$ and J_{ij} are quenched random variables with Gaussian distribution an zero mean

$$p(J_{ij}) = \frac{1}{\sqrt{2\pi J^2/N}} \exp\left(-\frac{J_{ij}}{2J^2/N}\right)$$

Using the replica method, one obtains the free energy density

$$-\beta f = \lim_{N\to\infty}\lim_{n\to 0}\left\{\frac{\beta^2 J^2}{4} - \sum_{a=1}^{n}\sum_{b>a}^{n} q_{ab}^2 + \frac{1}{n}\log \mathrm{Tr}_{\sigma_a}\left[\exp L\right]\right\}$$

where

$$L = \beta^2 J^2 \sum_{a=1}^{n}\sum_{b>a}^{n} q_{ab}\sigma_a\sigma_b$$

and the extremum condition in the saddle point approximation yields the parameters q_{ab}

$$q_{ab} = \frac{\mathrm{Tr}_{\sigma_a}\left[\sigma_a\sigma_b \exp L\right]}{\mathrm{Tr}_{\sigma_a}\left[\exp L\right]}$$

1. Assuming a replica symmetric (RS) form for the parameters $q_{ab} = q$ show that

$$-\beta f = \frac{\beta^2 J^2}{4}(1-q)^2 + \int_{-\infty}^{\infty} dz \frac{\exp(-z^2/2)}{2\pi} \log\left[2\cosh\left(\beta J\sqrt{q}z\right)\right]$$

   with the extremum condition

$$\frac{\beta^2 J^2}{2}(q-1) + \int_{-\infty}^{\infty} dz \frac{\exp(-z^2/2)}{2\pi} \tanh\left(\beta J\sqrt{q}z\right)\frac{\beta J}{2\sqrt{q}}z = 0$$

2. By partial integration, show that

$$q = \int_{-\infty}^{\infty} dz \frac{\exp(-z^2/2)}{2\pi} \tanh^2\left(\beta J\sqrt{q}z\right)$$

3. We will assume that q acts as an order parameter for the spin glass transition. By a Taylor expansion to second order in q around $q = 0$, study the free energy density $f = f(q)$ in the proximity of the transition and determine the critical temperature T_c.
4. *Optional*: solve the RS equations numerically.