

Problem Set 13 – Statistical Physics B

Problem 1: Correlations in space and time and their connection with self-diffusion

Consider a Hamiltonian of the form

$$H = H_0 + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i),$$

where $V_{\text{ext}}(\mathbf{r})$ is an external potential and H_0 being a reference Hamiltonian of the bulk system. Consider $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_b$, with ρ_b the bulk density and $\rho(\mathbf{r})$ the one-particle density of the inhomogeneous system.

(a) Within linear response theory, we define the density response function $\chi(\mathbf{r}, \mathbf{r}')$ via the relation

$$\delta\rho(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') V_{\text{ext}}(\mathbf{r}').$$

Find an expression for $\chi(\mathbf{r}, \mathbf{r}')$ in terms of properties of the unperturbed system. Show explicitly that the linear response of the density to the external potential has a local and a non-local contribution. Connect your result to the fluctuation-dissipation theorem.

(b) Introduce the Fourier transform as $\delta\tilde{\rho}(\mathbf{k}) = \int d\mathbf{r} \delta\rho(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r})$. Prove that

$$\delta\tilde{\rho}(\mathbf{k}) = -\beta\rho_b S(\mathbf{k}) \tilde{V}_{\text{ext}}(\mathbf{k}),$$

with $S(k)$ the static structure factor.

Now we consider a non-equilibrium situation where we consider a dilute concentration of a solute in a solvent. Imagine that for $t \rightarrow -\infty$ we create an inhomogeneous density profile by turning on a suitable $V_{\text{ext}}(\mathbf{r})$. At $t = 0$ we turn off the external potential. The system will then relax from a given non-equilibrium initial state $\rho(\mathbf{r}, 0)$ to a new equilibrium state where the external potential is absent. We denote the non-equilibrium density by $\rho(\mathbf{r}, t)$, with $t \geq 0$.

(c) The density profile satisfies the so-called continuity equation

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t),$$

with \mathbf{j} the non-equilibrium average flux of solute particles. Derive this continuity equation.

(d) Give a microscopic expression for $\rho(\mathbf{r}, t)$ in terms of a non-equilibrium ensemble average. From it, derive a microscopic expression for $\mathbf{j}(\mathbf{r}, t)$ in terms of a non-equilibrium ensemble average and show that your expressions are consistent with the continuity equation.

For low concentrations of solute the flux satisfies Fick's law $\mathbf{j}(\mathbf{r}, t) = -D\nabla\rho(\mathbf{r}, t)$, with D the so-called self-diffusion coefficient. Our goal is to relate D to the microscopic dynamics of the system, for which we need to consider the behaviour of the correlation function $C(\mathbf{r}, t) = \langle \delta\rho(\mathbf{r}, t) \delta\rho(\mathbf{0}, 0) \rangle$.

(e) Prove that this correlation function satisfies the differential equation $\partial_t C(\mathbf{r}, t) = D\nabla^2 C(\mathbf{r}, t)$ by using the definition of the density response function in (a) generalised to the time-dependent case. How does your result relate to the Onsager regression hypothesis?

(f) Show that $\partial_t P(\mathbf{r}, t) = D\nabla^2 P(\mathbf{r}, t)$, where $P(\mathbf{r}, t)$ is the conditional probability that a solute particle is at position \mathbf{r} and time t given that the particle was in the origin for $t = 0$ (*Hint: relate $C(\mathbf{r}, t)$ to $P(\mathbf{r}, t)$ for dilute solute concentrations*). Does the diffusion equation for $P(\mathbf{r}, t)$ hold for all time and spatial variations?

(g) We define the mean-squared displacement of a tagged particle (here taken to be particle 1) as $\Delta R^2(t) = \langle |\mathbf{r}_1(t) - \mathbf{r}_1(0)|^2 \rangle$. Show that $\Delta R^2(t) = 6Dt$.

(h) Prove the so-called Green-Kubo relation

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle,$$

with $\mathbf{v}(t) = \dot{\mathbf{r}}_1(t)$.

(i) As a reasonable approximation, we take $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \approx \langle v^2 \rangle e^{-t/\tau}$. Use this approximation to compute $\Delta R^2(t)$ and sketch your result. Indicate in your plot that $\Delta R^2(t)$ changes from ballistic to diffusive behaviour after a time of the order of τ .

(j) In liquids we typically have that $D \sim 10^{-5} \text{ cm}^2/\text{s}$ at room temperature. Estimate the size of τ and comment on its value in terms of experimental accessibility.