

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