Hand-in sheet 5 – Statistical Physics B

- *Please hand in your solution before Wednesday 22 January 2025, 12:15.*
- *You can hand in your solutions in digital format as a pdf-file. Make sure to provide a file name which contains the hand-in number, your name, and your student number. You can send your solution to jeffrey.everts AT fuw.edu.pl. Also include your name and student number in the pdf file.*
- *In case of paper format, please do not forget to write your name and student number.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps.*
- *In total 100 points can be earned.*

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 $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{\text{b}}$, with ρ_{b} the bulk density and $\rho(\mathbf{r})$ the one-particle density of the inhomogeneous system.

(a) (*10 points*) 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) (*10 points*) 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

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

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 $t \to -\infty$ 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) (*10 points*) 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) (*10 points*) 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) (*10 points*) 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) (*10 points*) 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 particule 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) (*10 points*) 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) (*10 points*) 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) (*10 points*) 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) (*10 points*) 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.