Problem Set 4 – Statistical Physics B

Problem 1: Reversible work theorem

Consider the radial distribution function $g(r)$ in a system with general potential energy $\Phi(\mathbf{r}^N)$. We define the function w as $g(r) = e^{-\beta w(r)}$. Prove that

$$-\frac{\partial}{\partial \mathbf{r}_1} w(\mathbf{r}_{12}) = \left\langle -\frac{\partial \Phi}{\partial \mathbf{r}_1} \right\rangle_{\mathbf{r}_1, \mathbf{r}_2 \text{ fixed}}.$$

Explain why $w(r)$ is sometimes called the potential of mean force.

Problem 2: Properties of bulk systems

We consider a bulk system for which the particles interact with each via pairwise-additive potentials, i.e. $\Phi(\mathbf{r}^N) = \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|)$.

(a) The classical density operator is given by $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$. Prove that in this case $\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$ equals a constant denoted by ρ_b. Derive an expression for ρ_b in the canonical ensemble and in the grand-canonical ensemble. Comment on how they differ.

(b) Consider the correlation function,

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle.$$

We define the radial distribution function as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho_\mathrm{b}^2 g(|\mathbf{r} - \mathbf{r}'|)$, which is valid for homogeneous and isotropic systems. Give two physical interpretations of $g(r)$. Motivate these interpretations sufficiently with mathematical equations.

(c) Sketch $g(r)$ for a typical gas, liquid, and solid and comment on the differences. Make sure to mark important features of $g(r)$ in your sketch.

(d) Consider a typical phase diagram of a one-component classical system. Can the liquid-solid melting transition line end in a critical point? Motivate your answer.

Problem 3: Virial route to thermodynamics

In the lectures we have derived the virial route to thermodynamics by using the virial theorem of classical mechanics. Here, we remind ourselves what are the contents of this theorem.

(a) Consider N particles with masses m_i, $i = 1, ..., N$. Define the scalar function $G(\mathbf{p}^N, \mathbf{r}^N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{p}_i$. Show that

$$\frac{dG}{dt} = 2T + \sum_{i=1}^{N} \mathbf{F}_i \cdot \mathbf{r}_i, \tag{1}$$

where $\mathbf{F}_i$ is the net force acting on particle i and T is the kinetic energy.

(b) We introduce the time average of a phase space function $A(\mathbf{p}^N(t), \mathbf{r}^N(t))$ as

$$\overline{A(\mathbf{p}^N(t), \mathbf{r}^N(t))} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt\, A(\mathbf{p}^N(t), \mathbf{r}^N(t)). \tag{2}$$

Argue that $\overline{G'(t)} = 0$ in the canonical ensemble. Using this property, derive the virial theorem $2\overline{T} = -\sum_{i=1}^{N} \overline{\mathbf{F}_i \cdot \mathbf{r}_i}$.

(c) We decompose the force in an internal and external part, $\mathbf{F}_i = \mathbf{F}_i^{\text{ext}} + \mathbf{F}_i^{\text{int}}$. The internal part arises because of interactions with other particles $\mathbf{F}_i = -\nabla_{\mathbf{r}_i}\Phi(\mathbf{r}^N)$, whereas the external part is due to the confining walls exerting forces on the particles to keep them within the volume V, because we are in the canonical ensemble. Often we do not write the wall contribution explicitly in the Hamiltonian. Argue that the force exerted by a surface element $d\mathbf{S}$ located at $\mathbf{r}$ is $-p\hat{\mathbf{n}}dS$, with $\hat{\mathbf{n}}$ an outward pointing unit normal. Show that for an ergodic system, we have

$$pV = Nk_{\mathrm{B}}T - \frac{1}{3}\sum_{i=1}^{N}\left\langle \mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}\Phi(\mathbf{r}^N)\right\rangle . \tag{3}$$

Specialise to a pair-wise additive interaction potential and derive the virial route to thermodynamics.

(d) Alternatively, the virial route can be derived from the partition function. Show first that $\beta p = (\partial \log Q/\partial V)_{N,T}$ and by going to scaled Cartesian coordinates $s_{i\alpha} = r_{i\alpha}/V^{1/3}$ that the virial route also follows.

Problem 4: Thermodynamics of hard sphere systems

Consider a three-dimensional hard-sphere system given by the pair potential

$$\phi(r) = \begin{cases} \infty, & (r < \sigma), \\ 0, & (r > \sigma). \end{cases}$$

Compute the internal energy E and the specific heat $C_V = (\partial E/\partial T)_{N,V}$ at constant volume. Do not use any approximations.