TSP-2022/23 — Thermal and Statistical Physics (Part II)

Problem sheet III: questions 1-9

1. **Virial coefficient and radial distribution function**
An inter-molecular potential takes the form

$$\begin{aligned} \phi(r) \;=\; & \infty \qquad r < a \\ & -\epsilon \qquad a < r < 2a \\ & 0 \qquad r > 2a. \end{aligned}$$

Within the virial expansion the radial distribution function is expanded in powers of the density.
(a) Sketch the form of the density-independent part of the radial distribution function versus r for $k_B T \gg \epsilon$ and $k_B T \ll \epsilon$.
(b) Evaluate the 2nd virial coefficient, $B_2(T)$, and the Boyle temperature of the gas.
(c) Identify a set of reduced units, v_0^* and T^*, for which $B_2(T^*)/v_0^*$ is independent of a and ϵ. Sketch $B_2(T^*)/v_0^*$ versus T^*.

2. **Liquid crystal**
The order parameter for a fluid of rod shaped molecules is their degree of alignment, Q, with $Q = 0$ corresponding to a disordered fluid, and $Q \neq 0$ corresponding to a nematic liquid crystal. The free energy can be written as

$$F(Q,T) \;=\; a(T - T_c)Q^2 - bQ^3 + cQ^4,$$

where a, b, c and T_c are positive constants. This system shows a first order phase transition, at a temperature T^*, between two states with $Q = 0$ and $Q = Q^*$.
(a) Calculate Q^* and T^*, using the conditions that the free energies of the two states are equal at the transition and that the free energies are stationary in equilibrium.
(b) Calculate the latent heat of the transition.

3. **Coupled order parameters**
The free energy of a ferroelectric crystal can be written as

$$F \;=\; \alpha(T - T_c)P^2 + bP^4 + cP^6 + D\varepsilon P^2 + E\varepsilon^2,$$

where P is the polarisation of the crystal and ε is the elastic strain. The coupling εP^2 can be found in most materials (in contrast to the linear 'piezoelectric' coupling εP that requires polar symmetry breaking). Show that the crystal will undergo a first order phase transition when $D^2/4E > b$, in spite of the even-power expansion required to make the scalar energy out of the vector P. Find the temperature of this first order transition.

4. **Particle number fluctuations**
Show that the fluctuations in particle number, N, at constant temperature, T, and volume, V, are given by

$$\langle \Delta N^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}.$$

5. **Energy fluctuations**
For a system of N free electrons the statistical weight, $\Omega(E)$, is proportional to $\exp[(NE/\epsilon_0)^{1/2}]$, where ϵ_0 is about 10^{-19} J. Calculate the heat capacity, C, of the system at room temperature. Show that the probability distribution of the energy of the system is approximately Gaussian and find the root mean square fractional energy fluctuation, $\sqrt{\langle \Delta E^2 \rangle / \langle E \rangle^2}$, for a system with $N = 10^{23}$ at room temperature.
[Answer: $C = 2.8 \times 10^{-25}$ J K^{-1} per electron; $\sqrt{\langle \Delta E^2 \rangle / \langle E \rangle^2} = 4.5 \times 10^{-11}$.]

6. **Critical fluctuations**
Find the mean square fluctuation of magnetisation, $\langle \Delta M^2 \rangle$, as a function of temperature on both sides of the critical point T_c of the ferromagnetic phase transition, which can be described by the Landau free energy expansion

$$F = a(T - T_c)M^2 + bM^4 \ .$$

7. **Anharmonic oscillator**
A system is governed by the anharmonic Hamiltonian $H(x) = ax^2 + bx^4$. This is evaluated by considering a harmonic Hamiltonian $H_\alpha = \alpha x^2$ with adjustable α, which generates a probability distribution $\rho_\alpha(x) = Z_\alpha^{-1} \exp(-\alpha x^2 \beta)$. The auxiliary Hamiltonian $\tilde{H} = H_\alpha + \langle H - H_\alpha \rangle_\alpha$, where the average $\langle ... \rangle_\alpha$ is evaluated with respect to the probability distribution $\rho_\alpha(x)$, has the same average as H itself: $\langle H \rangle_\alpha = \langle \tilde{H} \rangle_\alpha$

Explain why $\tilde{F}$ is an upper bound for F

$$F \leq \langle H \rangle_\alpha - TS_\alpha = F_\alpha + \langle H - H_\alpha \rangle_\alpha = \tilde{F}$$

and use this to show that $\tilde{F}$ most closely approximates F for $\alpha = a + 6b\langle x^2 \rangle_\alpha$. Calculate and sketch the temperature dependence of α and $\langle x^2 \rangle_\alpha$ for $a > 0$.

8. **Brownian motion**
Derive the Stokes-Einstein relationship for the diffusion constant of particles of radius R in a fluid of viscosity η

$$D = \frac{k_B T}{6\pi\eta R} \ .$$

In 1928 Pospisil observed the Brownian motion of soot particles of radius 0.4×10^{-7} m immersed in a water-glycerine solution of viscosity 2.78×10^{-3} kg m^{-1} s^{-1}, at a temperature of 292 K. The observed value of $\langle x^2 \rangle$ was 3.3×10^{-12} m^2 in a 10-second interval. Use these data to determine an estimate for k_B and compare it with the modern value.

9. **Diffusion**
Consider free Brownian particles diffusing along the axis $x \geq 0$, so that there is a reflecting wall at $x = 0$. Also there is a "sink" at $x = L$ where the particles can escape from the system, so that the probability at that point is $P(L, t) = 0$ at any time.

If the diffusion constant is D, estimate how long on average it would take for all the particles to escape from the system.