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Problems in Advanced Statistical Physics

Problem 13: Virial expansion

The first virial coefficient B_2 is defined by the expansion

$$PV = k_{\mathrm{B}}TN[1 + B_2\rho + \mathcal{O}(\rho^2)] \tag{1}$$

of the equation of state in terms of the particle number density $\rho = N/V$. Equation (1) is based on the expansion of the grand canonical partition function in the fugacity $z = e^{\beta\mu}$:

$$Y(T, V, z) = \sum_{N=0}^{\infty} Z(N)z^N \tag{2}$$

where $Z(N) \equiv Z(T, V, N)$ is the canonical partition function for a system of N particles.

a.) Convert the expansion (2) into the form (1) by using the fact that $PV = k_{\mathrm{B}}T \ln Y$ and (to leading order) $z = \rho\lambda_{\mathrm{th}}^3$, where λ_{th} is the thermal de Broglie wavelength. Then B_2 can be expressed in terms of $Z(1)$ and $Z(2)$. Compute $Z(2)$ for a gas of particles interacting through a central pair potential $w(r)$, thus deriving the formula

$$B_2 = -2\pi \int_0^{\infty} dr\, r^2(e^{-\beta w(r)} - 1)$$

quoted in the lectures. In the evaluation of $Z(2)$ you may assume that the system size is large compared to the interaction range of the potential.

b.) Evaluate B_2 for a piecewise constant potential $w(r)$, which is infinite for $0 < r < R_1$, equal to $\bar{w} < 0$ for $R_1 < r < R_2$ and vanishes for $r > R_2$. Compare the resulting equation of state to the low density expansion of the van der Waals equation. Show that the two expressions match if one takes $\bar{w} \to 0$ and $R_2 \to \infty$ in an appropriate combination, and use this to write the van der Waals coefficients a and b in terms of the parameters of the potential. Is the leading order expansion sufficient to generate a phase transition?

Problem 14: Hard rods in one dimension [1]

Consider N classical particles with coordinates $0 < x_1 < ... < x_N < L$ on the interval $[0, L]$ which interact according to the hard rod potential, $w(x - x') = 0$ for $|x - x'| \geq a$ and $w(x - x') = \infty$ for $|x - x'| < a$. The canonical partition function is given by

$$Z(L, T, N) = \lambda_{\mathrm{th}}^{-N} Q(L, N), \tag{3}$$

where $Q(L, N)$ is the N-dimensional volume of the available configuration space. Compute $Q(L, N)$ and determine the equation of state for the gas. Compare the result to the van der Waals equation and to the leading order virial expansion.

Problem 15: One-dimensional lattice gas with extended particles

It is instructive to rederive the results of Problem 15 in a discrete setting. To this end we subdivide the interval $[0, L]$ into M boxes of length a_0. Each of the N particles occupies exactly $n = a/a_0$ boxes, where n is an integer.

a.) Compute the number $\Omega(M, N, n)$ of possible microstates and derive an expression for the (microcanonical) entropy $S = k_{\mathrm{B}} \ln \Omega$ in the limit $N, M \gg 1$.

Hint: Ω is equal to the number of ways in which the $M - Nn$ empty boxes can be distributed among the gaps between neighboring particles and between particles 1 and N and the boundaries of the system.

b.) Now take the continuum limit $a_0 \to 0$, $M, n \to \infty$ at fixed $a = a_0 n$, $L = a_0 M$ in the expression for the entropy, and derive the equation of state from $P = T\partial S/\partial L$. Compare to the result of Problem 14.

[1] L. Tonks, Phys. Rev. **50**, 955 (1936)