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Solutions in Advanced Statistical Physics

Solution 13: Virial expansion

a.)

$$\begin{aligned} \ln Y &= \ln(1 + Z(1)z + Z(2)z^2 + \ldots) \approx Z(1)z + \left(Z(2) - \frac{1}{2}Z(1)^2\right) z^2 \\ \Rightarrow PV &= k_B T Z(1) z \left(1 + \left(\frac{Z(2)}{Z(1)^2} - \frac{1}{2}\right) Z(1) z\right). \end{aligned} \tag{1}$$

From $N = z\frac{\partial}{\partial z}\ln Y$,

$$\begin{aligned} N &\approx Z(1)z\left(1 + 2\left(\frac{Z(2)}{Z(1)^2} - \frac{1}{2}\right) Z(1)z\right) \\ \Rightarrow Z(1)z &\approx N\left(1 - 2\left(\frac{Z(2)}{Z(1)^2} - \frac{1}{2}\right) N\right). \end{aligned} \tag{2}$$

Combining Eqs. (1) and (2), we get

$$PV \approx k_B T N \left(1 - \left(\frac{Z(2)}{Z(1)^2} - \frac{1}{2}\right) N\right) = k_B T N (1 + B_2 \rho),$$

with $B_2 = -\left(\frac{Z(2)}{Z(1)^2} - \frac{1}{2}\right) V$.

The system with central pair potential,

$$Z(2) = \frac{Z(1)^2}{2V^2}\int d^3x d^3y e^{-\beta w(|x-y|)} = \frac{Z(1)^2}{2V^2}\int d^3R \int d^3r e^{-\beta w(r)} = \frac{Z(1)^2}{2V}\int d^3 r e^{-\beta w(r)},$$

where $Z(1) = \frac{V}{\lambda_{\text{th}}^3}$, $R = (x+y)/2$, and $r = x - y$. $Z(1)z = \rho V = N$. Hence

$$B_2 = -\frac{1}{2}\int d^3 r \left(e^{-\beta w(r)} - 1\right) = -2\pi \int dr r^2 \left(e^{-\beta w(r)} - 1\right).$$

b.)

$$w(r) = \begin{cases} \infty & 0 < r < R_1 \\ \bar{w} & R_1 < r < R_2 \\ 0 & r > R_2 \end{cases} \Rightarrow \quad \begin{aligned} B_2 &= \frac{2\pi}{3}R_1^2 - \frac{2\pi}{3}(e^{-\beta\bar{w}} - 1)(R_2^2 - R_1^2) \\ &= \frac{2\pi}{3}e^{-\beta\bar{w}}R_1^2 - \frac{2\pi}{3}(e^{-\beta\bar{w}} - 1)R_2^2. \end{aligned}$$

Hence

$$P = k_B T\rho + k_B T\left(\frac{2\pi}{3}e^{-\beta\bar{w}}R_1^3 - \frac{2\pi}{3}(e^{-\beta\bar{w}}-1)R_2^3\right)\rho^2. \tag{3}$$

In the low density regime, van der Waals equation takes the form

$$P = \frac{k_B T N}{V - bN} - a\rho^2 \approx k_B T\rho + (bk_B T - a)\rho^2. \tag{4}$$

We cannot associate a and b in Eq. (4) with parameters in Eq. (3) in general. But if we take the limit $\bar{w} \to 0$ and $R_2 \to \infty$ with $\bar{w}R_2^3$ fixed, Eq. (3) becomes

$$P = k_B T\rho + k_B T\frac{2\pi}{3}R_1^3\rho^2 - \frac{2\pi}{3}|\bar{w}|R_2^3\rho^2,$$

which is now matched to Eq. (4) such that $b = \frac{2\pi}{3}R_1^3$ and $a = \frac{2\pi}{3}|\bar{w}|R_2^3$.

Now consider Eq. (4). The critical point will be determined by the condition $\frac{\partial P}{\partial \rho} = \frac{\partial^2 P}{\partial \rho^2} = 0$. One can easily see that the critical point does not exist from Eq. (4). So the leading order expansion is not enough to study the phase transition.

Solution 14: Hard rods in one dimension

The available volume is

$$\frac{a}{2} < x_1 < x_2 - a,\ \frac{3a}{2} < x_2 < x_3 - a\ \ldots, (2n-1)\frac{a}{2} < x_n < x_{n+1} - a, \ldots, (2N-1)\frac{a}{2} < x_N < L - \frac{a}{2}.$$

Hence

$$Q(L,N) = \int_{(2N-1)a/2}^{L-a/2} dx_N \int_{(2N-3)a/2}^{x_N - a} dx_{N-1} \cdots \int_{3a/2}^{x_3 - a} dx_2 \int_{a/2}^{x_2 - a} dx_1.$$

To calculate Q, let us introduce a sequence of integrals such that

$$q_n = \int_{(2n-1)a/2}^{x_{n+1}-a} dx_n q_{n-1}, \quad q_1 = \int_{a/2}^{x_2 - a} dx_1 = x_2 - \frac{3a}{2} \Rightarrow Q = \int_{(2N-1)a/2}^{L-a/2} dx_N q_{N-1}.$$

Now make an ansatz such that (after trying one or two more integrals, one can easily guess this pattern)

$$q_n = \frac{1}{n!}\left(x_{n+1} - \frac{(2n+1)a}{2}\right)^n.$$

Then

$$q_{n+1} = \frac{1}{n!}\int_{(2n+1)a/2}^{x_{n+2}-a} dx_n \left(x_{n+1} - \frac{(2n+1)a}{2}\right)^n = \frac{1}{(n+1)!}\left(x_{n+2} - \frac{(2n+3)a}{2}\right)^{n+1}.$$

Since the ansatz correctly reproduces q_1, by mathematical induction we can say that

$$q_{N-1} = \frac{1}{(N-1)!}\left(x_N - \frac{(2N-1)a}{2}\right)^{N-1}.$$

So,

$$Q(L, N) = \frac{1}{N!}(L - Na)^N$$

follows.

The equation of state is

$$P = k_B T \frac{\partial \ln Z}{\partial L} = \frac{k_B T N}{L - Na} \approx k_B T \rho (1 + a\rho), \tag{5}$$

which is exactly the same as the van der Waals equation without the long-range attraction. The first virial coefficient is

$$B_2 = -\frac{1}{2} \int dr (e^{-\beta w(r)} - 1) = \frac{1}{2} \int_{-a}^{a} dr = a,$$

which is exactly the leading correction in Eq. (5).

Solution 15: One-dimensional lattice gas with extended particles

a.) The number of microstates is (as hinted in the problem)

$$\Omega(M, N, n) = \binom{M - Nn + N}{N} = \frac{(M - Nn + N)!}{N!(M - Nn)!}.$$

Using Stirling's formula, we get

$$S = k_B \ln \Omega(M, N, n) = k_B (M - Nn) \ln \left(1 + \frac{N}{M - Nn}\right) + k_B N \ln \left(\frac{M - Nn + N}{N}\right).$$

b.)

$$S = k_B \frac{1}{a_0}(L - Na) \ln \left(1 + \frac{Na_0}{L - Na}\right) + k_B N \ln \left(\frac{L - Na + Na_0}{Na_0}\right)$$
$$\to k_B N + k_B N \ln(L - Na) - k_B N \ln(Na_0)$$

Hence

$$P = T \partial S / \partial L = \frac{k_B T N}{L - Na},$$

which is same as the result of the previous problem.