PHYSICS 210A : EQUILIBRIUM STATISTICAL PHYSICS
HW ASSIGNMENT #6 SOLUTIONS

(1) For the Mayer cluster expansion, write down all possible unlabeled connected subgraphs γ which contain four vertices. For your favorite of these animals, identify its symmetry factor s_γ, and write down the corresponding expression for the cluster integral b_γ. For example, for the $\square$ diagram with four vertices the symmetry factor is $s_\square = 8$ and the cluster integral is

$$\begin{aligned} b_\square &= \frac{1}{8V}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \!\int\! d^d\!r_4 \, f(r_{12})\, f(r_{23})\, f(r_{34})\, f(r_{14}) \\ &= \frac{1}{8}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_{12})\, f(r_{23})\, f(r_1)\, f(r_3) \quad . \end{aligned}$$

(You'll have to choose a favorite other than $\square$.) If you're really energetic, compute s_γ and b_γ for all of the animals with four vertices.

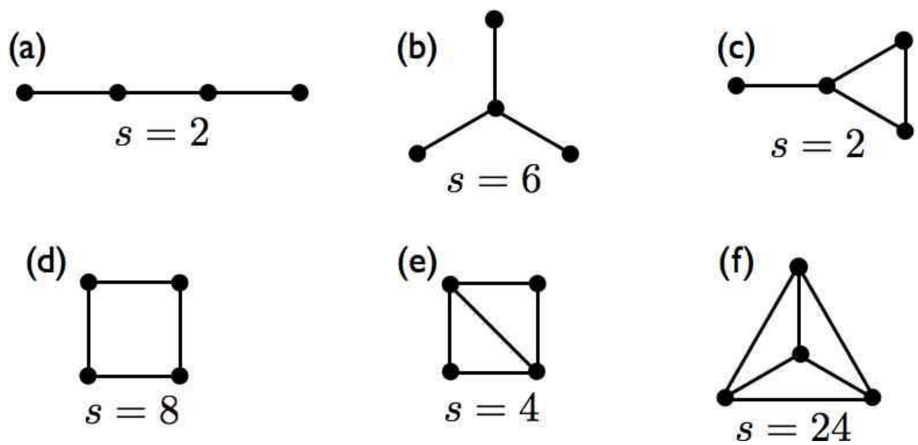

Figure 1: Connected clusters with $n_\gamma = 4$ sites.

Solution :

The animals and their symmetry factors are shown in fig. 1.

$$\begin{aligned} b_{\rm a} &= \frac{1}{2}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_{12})\, f(r_{23}) \\ b_{\rm b} &= \frac{1}{6}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_2)\, f(r_3) \\ b_{\rm c} &= \frac{1}{2}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_{12})\, f(r_{13})\, f(r_{23}) \\ b_{\rm d} &= \frac{1}{8}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_2)\, f(r_{13})\, f(r_{23}) \\ b_{\rm e} &= \frac{1}{4}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_2)\, f(r_{12})\, f(r_{13})\, f(r_{23}) \\ b_{\rm f} &= \frac{1}{24}\int\! d^d\!r_1 \!\int\! d^d\!r_2 \!\int\! d^d\!r_3 \, f(r_1)\, f(r_2)\, f(r_3)\, f(r_{12})\, f(r_{13})\, f(r_{23}) \quad . \end{aligned}$$

(2) Consider a three-dimensional gas of point particles interacting according to the potential

$$u(r) = \begin{cases} +\Delta_0 & \text{if } r \le a \\ -\Delta_1 & \text{if } a < r \le b \\ 0 & \text{if } b < r \quad , \end{cases}$$

where $\Delta_{0,1}$ are both positive. Compute the second virial coefficient $B_2(T)$ and find a relation which determines the inversion temperature in a throttling process.

Solution :

The Mayer function is

$$f(r) = \begin{cases} e^{-\Delta_0/k_B T} - 1 & \text{if } r \le 0 \\ e^{\Delta_1/k_B T} - 1 & \text{if } a < r \le b \\ 0 & \text{if } b < r \quad . \end{cases}$$

The second virial coefficient is

$$\begin{aligned} B_2(T) &= -\tfrac{1}{2} \int d^3\!r \, f(r) \\ &= \frac{2\pi a^3}{3} \cdot \Big[\big(1 - e^{-\Delta_0/k_B T}\big) + (s^3 - 1)\big(1 - e^{\Delta_1/k_B T}\big) \Big] \quad , \end{aligned}$$

where $s = b/a$. The inversion temperature is a solution of the equation $B_2(T) = T B_2'(T)$, which gives

$$\frac{k_B T + (\Delta_0 - k_B T)\, e^{-\Delta_0/k_B T}}{k_B T + (\Delta_1 + k_B T)\, e^{\Delta_1/k_B T}} = s^3 - 1 \quad .$$

(3) Consider a liquid where the interaction potential is $u(r) = \Delta_0\,(a/r)^k$, where Δ_0 and a are energy and length scales, respectively. Assume that the pair distribution function is given by $g(r) \approx e^{-u(r)/k_B T}$. Compute the equation of state. For what values of k do your expressions converge?

Solution:

According to the virial equation of state in eqn. 6.157 of the Lecture Notes,

$$p = n k_B T - \tfrac{2}{3}\pi n^2 \int_0^\infty dr \, r^3 \, g(r)\, u'(r) \, .$$

Substituting for $u(r)$ and $g(r)$ as in the statement of the problem, we change variables to

$$s \equiv \frac{u(r)}{k_B T} \quad \Rightarrow \quad ds = \frac{u'(r)}{k_B T}\, dr \, ,$$

so

$$r = a\left(\frac{\Delta_0}{k_B T}\right)^{1/k} s^{-1/k}$$

and

$$r^3\, g(r)\, u'(r)\, dr = k_B T\, a^3 \left(\frac{\Delta_0}{k_B T}\right)^{3/k} s^{-3/k}\, e^{-s}\, ds\ .$$

We then have

$$\begin{aligned} p &= nk_B T + \tfrac{2}{3}\pi n^3 a^3 k_B T \left(\frac{\Delta_0}{k_B T}\right)^{3/k} \int\limits_0^\infty ds\, s^{-3/k}\, e^{-s} \\ &= nk_B T \left\{ 1 + \tfrac{2}{3}\pi \Gamma\big(1 - \tfrac{3}{k}\big)\, na^3 \left(\frac{\Delta_0}{k_B T}\right)^{3/k} \right\} . \end{aligned}$$

Note that a minus sign appears because we must switch the upper and lower limits on the s integral. This expression converges provided $k < 0$ or $k > 3$.

(4) Consider the equation of state

$$p\sqrt{v^2 - b^2} = RT\, \exp\left(-\frac{a}{RTv^2}\right) .$$

(a) Find the critical point (v_c, T_c, p_c).

(b) Defining $\bar{p} = p/p_c$, $\bar{v} = v/v_c$, and $\bar{T} = T/T_c$, write the equation of state in dimensionless form $\bar{p} = \bar{p}(\bar{v}, \bar{T})$.

(c) Expanding $\bar{p} = 1 + \pi$, $\bar{v} = 1 + \epsilon$, and $\bar{T} = 1 + t$, find $\epsilon_{liq}(t)$ and $\epsilon_{gas}(t)$ for $-1 \ll t < 0$.

Solution :

(a) We write

$$p(T, v) = \frac{RT}{\sqrt{v^2 - b^2}}\, e^{-a/RTv^2} \qquad \Rightarrow \qquad \left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{2a}{RTv^3} - \frac{v}{v^2 - b^2}\right) p\ .$$

Thus, setting $\left(\frac{\partial p}{\partial v}\right)_T = 0$ yields the equation

$$\frac{2a}{b^2 RT} = \frac{u^4}{u^2 - 1} \equiv \varphi(u)\ ,$$

where $u \equiv v/b$. Differentiating $\varphi(u)$, we find it has a unique minimum at $u^* = \sqrt{2}$, where $\varphi(u^*) = 4$. Thus,

$$T_c = \frac{a}{2b^2 R} \quad , \quad v_c = \sqrt{2}\, b \quad , \quad p_c = \frac{a}{2eb^2}\ .$$

(b) In terms of $\bar{p}$, $\bar{v}$, and $\bar{T}$, we have the universal equation of state

$$\bar{p} = \frac{\bar{T}}{\sqrt{2\bar{v}^2 - 1}} \, \exp\!\left(1 - \frac{1}{\bar{T}\bar{v}^2}\right) .$$

(c) With $\bar{p} = 1 + \pi$, $\bar{v} = 1 + \epsilon$, and $\bar{T} = 1 + t$, we have from ch. 7 of the Lecture Notes,

$$\epsilon_{\mathsf{L,G}} = \mp\left(\frac{6\,\pi_{\epsilon t}}{\pi_{\epsilon\epsilon\epsilon}}\right)^{1/2} (-t)^{1/2} + \mathcal{O}(t) \ .$$

From `Mathematica` we find $\pi_{\epsilon t} = -2$ and $\pi_{\epsilon\epsilon\epsilon} = -16$, hence

$$\epsilon_{\mathsf{L,G}} = \mp\tfrac{\sqrt{3}}{2}\,(-t)^{1/2} + \mathcal{O}(t) \ .$$