# Problem Set 6: Solutions

1) For the diagrams see graphs in Fig.1. The expansion involves:

a) 12 diagrams like graph1 where

(a,b,c,d) = (1,2,3,4); (1,3,2,4); (1,3,4,2); (1,4,3,2); (2,4,1,3); (2,1,4,3); (3,1,2,4); (3,2,1,4); (1,2,4,3); (1,4,2,3); (2,1,3,4); (2,3,1,4)

b) 4 diagrams like graph2 where

(a,b,c,d) = (2,1,4,3); (3,2,1,4); (2,3,1,4); (3,4,2,1)

c) 12 diagrams like graph3 where

(a,b,c,d) = (1,2,3,4); (1,3,2,4); (1,4,3,2); (2,3,1,4); (2,4,1,2); (2,1,4,3); (3,1,2,4); (3,2,4,1); (3,4,1,2); (4,1,2,3); (4,2,3,1); (4,3,1,2)

d) 3 diagrams like graph4 where

(a,b,c,d) = (1,2,4,3); (1,3,2,4); (1,2,3,4)

e) 6 diagrams like graph5 where

(a,b,c,d) = (1,3,2,4); (1,2,3,4); (1,2,4,3); (2,4,3,1); (2,3,4,1); (3,2,4,1)

f) 1 diagram like graph6 where

(a,b,c,d) = (1,2,4,3)

The sum $S_4$ of the clusters is

$$S_4 = 12V\left(\int d^3x\ f(\vec{x})\right)^3 + 4V\left(\int d^3x\ f(\vec{x})\right)^3 + \tag{1}$$

$$+12V\int d\vec{x_1}\ f(\vec{x_1})\int d\vec{x_2}\ d\vec{x_3}\ f(\vec{x_2}-\vec{x_3})\ f(\vec{x_2})f(\vec{x_3}) + \tag{2}$$

$$+3V\int d\vec{x_1}\ d\vec{x_2}\ d\vec{x_3}\ f(\vec{x_2}-\vec{x_1})\ f(\vec{x_3}-\vec{x_2})\ f(\vec{x_1})f(\vec{x_3}) + \tag{3}$$

$$+6V\int d\vec{x_1}\ d\vec{x_2}\ d\vec{x_3}\ f(\vec{x_2}-\vec{x_3})\ f(\vec{x_1}-\vec{x_3})\ f(\vec{x_1})f(\vec{x_2})f(\vec{x_3}) + \tag{4}$$

$$+V\int d\vec{x_1}\ d\vec{x_2}\ d\vec{x_3}\ f(\vec{x_2}-\vec{x_3})\ f(\vec{x_1}-\vec{x_3})\ f(\vec{x_1}-\vec{x_2})f(\vec{x_1})f(\vec{x_2})f(\vec{x_3}) \tag{5}$$

and

$$b_4 = \frac{S_4}{V\lambda^{12}4!}$$

2)As shown in class,

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

where,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial(V,P)}{\partial(T,P)} = \frac{\partial(V,P)}{\partial(V,T)}\frac{\partial(V,T)}{\partial(T,P)} = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T}$$

Now, $P = nkT\left[1 - b_2\lambda^3 n\right]$ then

$$\left(\frac{\partial P}{\partial T}\right)_V = nk\left[1 - b_2\lambda^3 n - \frac{d(b_2\lambda^3)}{dT}Tn\right]$$

and

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nkT}{V} + \frac{2n^2 b_2 \lambda^3 kT}{V}$$

so,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nk\left[1 - b_2\lambda^3 n - \frac{d(b_2\lambda^3)}{dT}Tn\right]}{\frac{nkT}{V}[1 - 2nb_2\lambda^3]} = \frac{V}{T}\left[1 + b_2\lambda^3 n - \frac{d(b_2\lambda^3)}{dT}Tn\right]$$

Then,

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = V\left[b_2\lambda^3 n - \frac{d(b_2\lambda^3)}{dT}Tn\right]$$

and

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{n}{C_P}\left[b_2\lambda^3 - \frac{d(b_2\lambda^3)}{dT}T\right]$$

3) a) It is convenient to assume that particles feel the same potentials at walls, so that so particle can get closer to either wall than $r_0$ (this assumption does not matter at $L \to \infty$).

$$W_N = N! \int_{-L/2+r_0}^{L/2-Nr_0} dx_N \ldots \int_{x_4+r_0}^{L/2-3r_0} dx_3 \int_{x_3+r_0}^{L/2-2r_0} dx_2 \int_{x_2+r_0}^{L/2-r_0} dx_1$$

where we assume $x1 > x2 > \ldots > x_N$. The $N!$ factor takes care of all other orders. Then,

$$\int_{x_2+r_0}^{L/2-r_0} dx_1 = \frac{L}{2} - 2r_0 - x_2$$

$$\int_{x_3+r_0}^{L/2-2r_0} (\frac{L}{2} - 2r_0 - x_2)dx_2 = \frac{1}{2}\left(\frac{L}{2} - 2r_0 - x_3\right)^2$$

$$\int_{x_4+r_0}^{L/2-3r_0} \frac{1}{2}\left(\frac{L}{2} - 2r_0 - x_3\right)^2 dx_3 = \frac{1}{3!}\left(\frac{L}{2} - 4r_0 - x_4\right)^3$$

and so on. Finally we get,

$$W_N = (L - (N+1)r_0)^N \approx (L - Nr_0)^N$$

Therefore,

$$Z_N = \frac{(L - Nr_0)^N}{N!\lambda^N}$$

Then,

$$A = -kT\ln(Z_N) \approx -kTN\ln\left[\frac{e(L - Nr_0)}{N\lambda}\right]$$

where I used Stirling's formula.

$$P = -\left(\frac{\partial A}{\partial L}\right)_{N,T} = \frac{kTN}{L - Nr_0} = \frac{kTN}{L}\left[1 + \frac{N}{L}r_0 + \left(\frac{N}{L}r_0\right)^2 + \ldots\right]$$

b) $f(x) = e^{-\beta u(x)} - 1$, then $f(x) = -1$ for $|x| < r_0$ and $f(x) = 0$ for $|x| > r_0$.

$$b_2 = \frac{1}{2\lambda} \int_{-\infty}^{\infty} f(x)\ dx = -\frac{r_0}{\lambda}$$

$$b_3 - 2b_2^2 = \frac{1}{3!\lambda^2} \int f(x_1)\ f(x_2 - x_1)\ f(x_2)\ dx_1\ dx_2 = -\frac{1}{3!\lambda^2} \int_{-r_0}^{r_0} dx_1 \int_{-r_0}^{r_0} dx_2 \theta(r_0 - |x_1 - x_2|) = -\frac{1}{2} \left(\frac{r_0}{\lambda}\right)^2.$$

So,

$$\left[1 - b_2 n\lambda + (4b_2^2 - 2b_3) n^2 \lambda^2\right] = \left[1 + r_0 n + r_0^2 n^2\right]$$

4)

$$b_2 = \frac{4\pi}{2\lambda^3} \int r^2 \left[e^{-\beta u(r)} - 1\right]\ dr = \tag{6}$$

$$= \frac{2\pi}{\lambda^3} \left[ -\int_0^{r_0} r^2\ dr + \int_{r_0}^{r_1} r^2 \left[e^{\beta u_0} - 1\right]\ dr \right] = \tag{7}$$

$$= \frac{2\pi}{\lambda^3} \left[ -\frac{r_0^3}{3} + \left(e^{\beta u_0} - 1\right) \frac{1}{3}(r_1^3 - r_0^3) \right] = \tag{8}$$

$$= \frac{2\pi}{3\lambda^3} \left[ -r_0^3 e^{\beta u_0} + r_1^3 \left(e^{\beta u_0} - 1\right) \right] \tag{9}$$

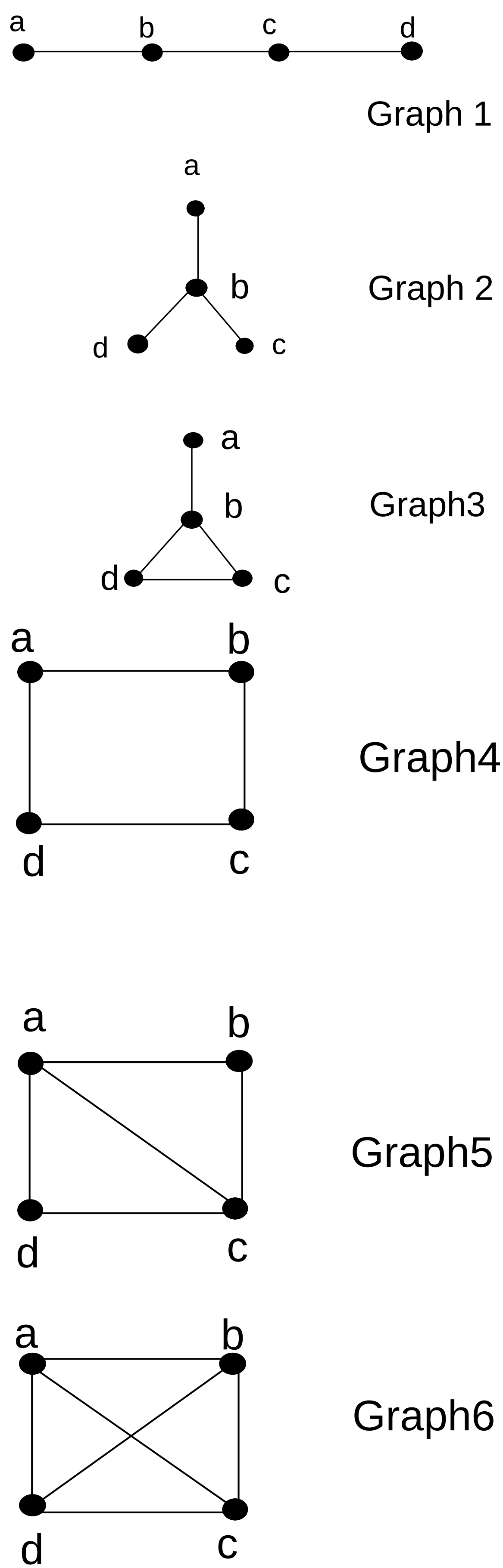


FIG. 1: (a) Graphs for expansion in Problem 1.