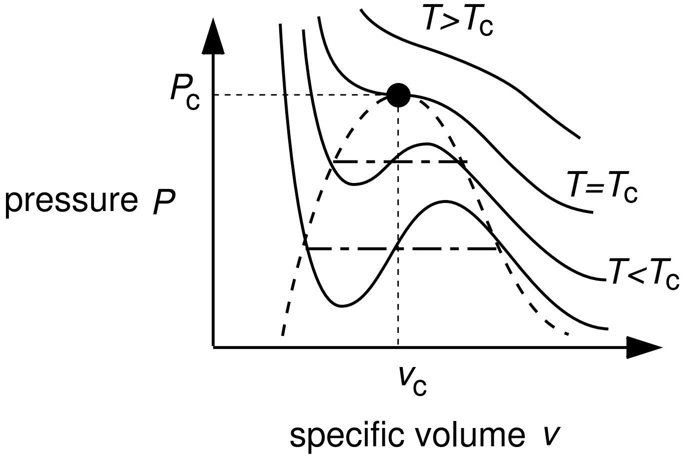
8.333: Statistical Mechanics I Problem Set # **9** Solutions Fall 2003

Phase Transitions

1. *Dieterici's equation:* The isotherms corresponding to Dieterici's equation of state,

$$P(v-b) = k_B T \exp\left(-\frac{a}{k_B T v}\right),$$

are sketched below in the plane of $(P, v = V/N)$.



(a) The critical point is the point of inflection, described by

$$\left.\frac{\partial P}{\partial v}\right|_{T_c,N} = 0, \qquad \text{and} \qquad \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c,N} = 0.$$

The first derivative of P is

$$\begin{aligned}\left.\frac{\partial P}{\partial v}\right|_{T_c,N} =& \frac{\partial}{\partial v}\left[\frac{k_B T}{v-b}\exp\left(-\frac{a}{k_B T v}\right)\right] = \frac{k_B T}{v-b}\exp\left(-\frac{a}{k_B T v}\right)\left(\frac{a}{k_B T v^2} - \frac{1}{v-b}\right) \\ =& P\left(\frac{a}{k_B T v^2} - \frac{1}{v-b}\right),\end{aligned}$$

while a second derivative gives

$$\begin{aligned}\left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c,N} &= \frac{\partial}{\partial v}\left[P\left(\frac{a}{k_B T v^2} - \frac{1}{v-b}\right)\right] \\ &= \frac{\partial P}{\partial v}\left(\frac{a}{k_B T v^2} - \frac{1}{v-b}\right) - P\left(\frac{2a}{k_B T v^3} - \frac{1}{(v-b)^2}\right).\end{aligned}$$

Therefore v_c and T_c are determined by

$$\frac{a}{k_B T_c v_c^2} - \frac{1}{v_c - b} = 0, \qquad \text{and} \qquad \frac{2a}{k_B T_c v_c^3} - \frac{1}{(v_c-b)^2} = 0,$$

with the solutions

$$v_c = 2b, \qquad \text{and} \qquad k_B T_c = \frac{a}{4b}.$$

The critical pressure is

$$P_c = \frac{k_B T_c}{v_c - b} \exp\left(-\frac{a}{k_B T_c v_c}\right) = \frac{a}{4b^2} e^{-2},$$

resulting in the ratio

$$\frac{P_c v_c}{k_B T_c} = 2e^{-2} \approx 0.27.$$

Note that for the van der Waals gas

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375,$$

while for some actual gases

$$\left(\frac{P_c v_c}{k_B T_c}\right)_{\text{water}} = 0.230, \qquad \text{and} \qquad \left(\frac{P_c v_c}{k_B T_c}\right)_{\text{Argon}} = 0.291.$$

(b) The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{v} \left.\frac{\partial v}{\partial P}\right|_{T,N},$$

and from part (a), given by

$$\left.\frac{\partial P}{\partial v}\right|_{T_c,N} = P\left(\frac{a}{k_B T v^2} - \frac{1}{v-b}\right).$$

Expanding this expression, at $v = v_c$, in terms of $t \equiv k_B T - k_B T_c$ (for $T > T_c$), yields

$$\left.\frac{\partial P}{\partial v}\right|_{T_c,N} \approx P_c\left(\frac{a}{(a/4b + t)\,4b^2} - \frac{1}{b}\right) \approx -\frac{P_c}{b}\frac{4bt}{a} = -\frac{2P_c}{v_c k_B T_c} t,$$

and thus

$$\kappa_T = \frac{k_B T_c}{2P_c}\frac{1}{t} = \frac{be^2}{2k_B(T - T_c)}.$$

Note that expanding any analytic equation of state will yield the same simple pole for the divergence of the compressibility.

(c) Perform a Taylor–series expansion along the critical isotherm $T = T_c$, as

$$P(v, T_c) = P_c + \left.\frac{\partial P}{\partial v}\right|_{T_c,v_c}(v - v_c) + \frac{1}{2!}\left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c,v_c}(v - v_c)^2 + \frac{1}{3!}\left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c}(v - v_c)^3 + \cdots.$$

The first two terms are zero at the critical point, and

$$\left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c} = -P_c\frac{\partial}{\partial v}\left(\frac{2a}{k_BT_cv^3} - \frac{1}{(v-b)^2}\right)$$

$$= -P_c\left(\frac{6a}{k_BT_cv_c^4} - \frac{2}{(v_c-b)^3}\right)$$

$$= -\frac{P_c}{2b^3}.$$

Substituting this into the Taylor expansion for $P(v,T_c)$, results in

$$P(v,T_c) = P_c\left(1 - \frac{(v-v_c)^3}{12b^3}\right),$$

which is equivalent to

$$\frac{P}{P_c} - 1 = \frac{2}{3}\left(\frac{v}{v_c} - 1\right)^3.$$

****

2. *2d Coulomb Gas:* The Hamiltonian for this system is

$$\mathcal{H} = \sum_{i=1}^{2N}\frac{p_i^2}{2m} - \sum_{i<j}^{2N} c_ic_j \ln|\vec{q}_i - \vec{q}_j|.$$

(a) There are N positively charged particles, and N negatively charged particles. Hence there are $N \cdot N = N^2$ pairs of opposite charges, and $n_{\text{attractive}} = N^2$. For like charges, we can choose pairs from the N particles of positive charge, or from the N particles with negative charges. Hence the number of pairs of like pairs is

$$n_{\text{repulsive}} = 2 \times \begin{pmatrix} N \\ 2 \end{pmatrix} = 2 \times \frac{N!}{2!(N-2)!} = N(N-1).$$

(b) The partition function is

$$Z(N,T,A) = \frac{1}{(N!)^2h^{4N}}\int\prod_{i=1}^{2N} d^2\vec{q}_i d^2\vec{p}_i \exp\left[-\beta\sum_{i=1}^{2N}\frac{p_i^2}{2m} + \beta\sum_{i<j}c_ic_j\ln|\vec{q}_i - \vec{q}_j|\right]$$

$$= \frac{1}{\lambda^{4N}(N!)^2}\int\prod_{i=1}^{2N} d^2\vec{q}_i \exp\left[\beta\ln|\vec{q}_i - \vec{q}_j|^{c_ic_j}\right],$$

where $\lambda = h/\sqrt{2\pi m k_B T}$. Further simplifying the expression for the partition function

$$Z(N,T,A) = \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} d^2\vec{q}_i \prod_{i<j}^{2N} |\vec{q}_i - \vec{q}_j|^{\beta c_i c_j},$$

where we have used the fact that $e^{\ln x} = x$.

(c) The only length scale appearing in the problem is set by the system size L. Rescaling the expression using $\vec{q}_i{}' = \vec{q}_i/L$, then yields

$$Z(N,T,A) = \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} \left(L^2 d^2\vec{q}_i{}'\right) \prod_{i<j}^{2N} L^{\beta c_i c_j} |\vec{q}_i{}' - \vec{q}_j{}'|^{\beta c_i c_j}.$$

Note that there are N^2 terms for which the interaction is attractive ($\beta c_i c_j = -\beta c_0^2$), and $N(N-1)$ terms for which the interaction is repulsive ($\beta c_i c_j = \beta c_0^2$). Thus

$$\begin{aligned} Z(N,T,A) &= L^{4N} \cdot L^{\beta c_0^2 N(N-1)} \cdot L^{-\beta c_0^2 N^2} \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} d^2\vec{q}_i{}' \prod_{i<j}^{2N} |\vec{q}_i{}' - \vec{q}_j{}'|^{\beta c_i c_j} \\ &= L^{4N - \beta N c_0^2} Z_0(N,T,A' = L'^2 = 1) \propto A^{2N - \beta c_0^2 N/2}, \end{aligned}$$

since $A = L^2$.

(d) The pressure is then calculated from

$$\begin{aligned} P &= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial A}\bigg|_{N,T} = k_B T \frac{\partial}{\partial A} \ln\left(A^{2N - \beta c_0^2 N/2} Z_0\right) \\ &= k_B T \left(2N - \beta c_0^2 N/2\right) \frac{\partial}{\partial A} \ln A = \frac{2N k_B T}{A} - \frac{N c_0^2}{2A}. \end{aligned}$$

At high temperatures,

$$P = \frac{2N k_B T}{A},$$

which is the ideal gas behavior for $2N$ particles. The pressure becomes negative at temperature below

$$T_c^0 = \frac{c_0^2}{4k_B},$$

which is unphysical, indicating the collapse of the particles due to their attractions.

(e) A complete collapse of the system (to a single point) can be avoided by adding a hard core repulsion which prevents any two particles from coming closer than a distance a. The partition function for two particles (i.e. $N = 1$) is now given by

$$Z(N=1,T,A) = \frac{1}{\lambda^4} \int d^2\vec{q}_1 d^2\vec{q}_2 \cdot |\vec{q}_1 - \vec{q}_2|^{-\beta c_0^2}.$$

To evaluate this integral, first change to center of mass and relative coordinates

$$\begin{cases} \vec{Q} =\frac{1}{2}(\vec{q}_1+\vec{q}_2), \\ \vec{q} =\vec{q}_1-\vec{q}_2. \end{cases}$$

Integrating over the center of mass gives

$$\begin{aligned} Z(N=1,T,A) &= \frac{A}{\lambda^4}\int d^2\vec{q}\; q^{-\beta c_0^2} \approx \frac{2\pi A}{\lambda^4}\int_a^L dq\cdot q^{1-\beta c_0^2} \\ &= \frac{2\pi A}{\lambda^4}\,\frac{q^{2-\beta c_0^2}}{2-\beta c_0^2}\bigg|_a^L = \frac{2\pi A}{\lambda^4}\,\frac{L^{2-\beta c_0^2}-a^{2-\beta c_0^2}}{2-\beta c_0^2}. \end{aligned}$$

If $2-\beta c_0^2<0$, as $L\to\infty$,

$$Z \approx \frac{2\pi A}{\lambda^4}\,\frac{a^{2-\beta c_0^2}}{2-\beta c_0^2},$$

is controlled by the short distance cutoff a; while if $2-\beta c_0^2>0$, the integral is controlled by the system size L, as assumed in part (c). Hence the critical temperature can be estimated by $\beta c_0^2=2$, giving

$$T_c = \frac{c_0^2}{2k_B},$$

which is larger than T_c^0 by a factor of 2. Thus the unphysical collapse at low temperatures is preempted at the higher temperature where the hard cores become important. The high temperature phase ($T>T_c$) is a dissociated plasma; while the low temperature phase is a gas of paired dipoles.

****

3. *One dimensional gas:*

(a) Each particle i interacts only with adjacent particles $i-1$ and $i+1$, as the hard cores from these nearest neighbors screen the interactions with any other particle. Thus we need only consider nearest neighbor interactions, and, included the kinetic energies, the Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i=2}^{N}\mathcal{V}(x_i-x_{i-1}), \qquad \text{for} \qquad 0\le x_1\le x_2\le\cdots x_N\le L.$$

(b) The partition function is

$$
\begin{aligned}
Z(T,N,L) &= \frac{1}{h^N}\int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1})\right] \\
&\quad \cdot \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \exp\left[-\beta \sum_{i=1} N \frac{p_i^2}{2m}\right] \\
&= \frac{1}{\lambda^N}\int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1})\right],
\end{aligned}
$$

where $\lambda = h/\sqrt{2\pi m k_B T}$. (Note that there is no $N!$ factor, as the ordering of the particles is specified.) Introducing a new set of variables

$$
\delta_1 = x_1, \quad \delta_2 = x_2 - x_1, \quad \cdots \quad \delta_n = x_N - x_{N-1},
$$

or equivalently

$$
x_1 = \delta_1, \quad x_2 = \delta_1 + \delta_2, \quad \cdots \quad x_N = \sum_{i=1}^N \delta_i,
$$

the integration becomes

$$
Z(T,N,L) = \frac{1}{\lambda^N}\int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \int_0^{L-(\delta_1+\delta_2)} d\delta_3 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N e^{-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)}.
$$

This integration can also be expressed as

$$
Z(T,N,L) = \frac{1}{\lambda^N}\left[\int d\delta_1 d\delta_2 \cdots d\delta_N\right]' \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)\right],
$$

with the constraint

$$
0 \le \sum_{i=1}^N \delta_i \le L.
$$

This constraint can be put into the equation explicitly with the use of the step function

$$
\Theta(x) = \begin{cases} 0 & \text{for} \quad x < 0 \\ 1 & \text{for} \quad x \ge 0 \end{cases},
$$

as

$$
Z(T,N,L) = \frac{1}{\lambda^N}\int_0^{\infty} d\delta_1 \int_0^{\infty} d\delta_2 \cdots \int_0^{\infty} d\delta_N \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)\right] \Theta\left(L - \sum_{i=1}^N \delta_i\right).
$$

(c) The Gibbs partition function is

$$\mathcal{Z}(T,N,P)=\int_0^\infty dL\exp(-\beta PL)Z(T,N,L).$$

The saddle point is obtained by extremizing the integrand with respect to L,

$$\frac{\partial}{\partial L}\exp(-\beta PL)Z(T,N,L)\bigg|_{T,N}=0,$$

which implies that

$$\beta P=\frac{\partial}{\partial L}\ln Z(T,N,L)\bigg|_{T,N},\qquad\Longrightarrow\qquad P=k_BT\,\frac{\partial\ln Z}{\partial L}\bigg|_{T,N}.$$

From thermodynamics, for a one–dimensional gas we have

$$dF=-SdT-PdL,\quad\Longrightarrow\quad P=-\frac{\partial F}{\partial L}\bigg|_{T,N}.$$

Further noting that

$$F=-k_BT\ln Z,$$

again results in

$$P_{\text{canonical}}=k_BT\,\frac{\partial\ln Z}{\partial L}\bigg|_{T,N}.$$

(d) The expression for the partition function given above is

$$Z(T,N,L)=\frac{1}{\lambda^N}\int_0^\infty d\delta_1\int_0^\infty d\delta_2\cdots\int_0^\infty d\delta_N\exp\left[-\beta\sum_{i=2}^N\mathcal{V}(\delta_i)\right]\Theta\left(L-\sum_{i=1}^N\delta_i\right).$$

The Laplace transform of this equation is

$$\begin{aligned}\mathcal{Z}(T,N,P)=\frac{1}{\lambda^N}&\int_0^\infty dL\exp(-\beta PL)\int_0^\infty d\delta_1\int_0^\infty d\delta_2\cdots\int_0^\infty d\delta_N\\&\cdot\exp\left[-\beta\sum_{i=2}^N\mathcal{V}(\delta_i)\right]\Theta\left(L-\sum_{i=1}^N\delta_i\right)\\=\frac{1}{\lambda^N\beta P}&\int_0^\infty d\delta_1\int_0^\infty d\delta_2\cdots\int_0^\infty d\delta_N\exp\left[-\beta\sum_{i=2}^N\mathcal{V}(\delta_i)\right]\exp\left[-\beta P\left(\sum_{i=1}^N\delta_1\right)\right]\\=&\frac{1}{\lambda^N(\beta P)^2}\int_0^\infty d\delta_2\cdots\int_0^\infty d\delta_N\exp\left\{-\sum_{i=2}^N\left[\beta\mathcal{V}(\delta_i)+\beta P\delta_i\right]\right\}.\end{aligned}$$

Since the integrals for different $\delta_i's$ are equivalent, we obtain

$$\mathcal{Z}(T,N,P)=\frac{1}{\lambda^N(\beta P)^2}\left\{\int_0^\infty d\delta\exp\left[-\beta\left(\mathcal{V}(\delta)+P\delta\right)\right]\right\}^{N-1}.$$

This expression can also be obtained directly, without use of the step function as follows.

$$\begin{aligned}\mathcal{Z}(T,N,P)=&\frac{1}{\lambda^N}\int_0^L d\delta_1\int_0^{L-\delta_1}d\delta_2\int_0^{L-(\delta_1+\delta_2)}d\delta_3\cdots\int_0^{L-\sum_{i=1}^N\delta_i}d\delta_N\\&\cdot\int_0^\infty dL\exp\left[-\beta PL-\beta\left(\sum_{i=2}^N\mathcal{V}(\delta)\right)\right]\\=&\frac{1}{\lambda^N}\int_0^L d\delta_1\int_0^{L-\delta_1}d\delta_2\cdots\int_0^{L-\sum_{i=1}^N\delta_i}d\delta_N\int_{-\sum_{i=1}^N\delta_i}^\infty d\left(L-\sum_{i=1}^N\delta_i\right)\\&\cdot\exp\left\{-\beta P\left[\sum_{i=1}^N\delta_i+\left(L-\sum_{i=1}^N\delta_i\right)\right]-\beta\left(\sum_{i=2}^N\mathcal{V}(\delta_i)\right)\right\}.\end{aligned}$$

Change variables to $\delta_{N+1}\equiv L-\sum_{i=1}^N\delta_i$, and note that each of the $\delta's$ indicates the distance between neighboring particles. The size of the gas L, has been extended to any value, hence each δ can be varied independently from 0 to ∞. Thus the Gibbs partition function is

$$\begin{aligned}\mathcal{Z}(T,N,P)=&\frac{1}{\lambda^N}\int_0^\infty d\delta_1\int_0^\infty d\delta_2\cdots\int_0^\infty d\delta_N\int_0^\infty d\delta_{N+1}\\&\cdot\exp\left[-\beta P\left(\sum_{i=1}^{N+1}\delta_i\right)-\beta\left(\sum_{i=2}^N\mathcal{V}(\delta_i)\right)\right]\\=&\frac{1}{\lambda^N}\left(\int_0^\infty d\delta\cdot\exp\left[-\beta\mathcal{V}(\delta)-\beta P\delta\right]\right)^{N-1}\int_0^\infty d\delta_1\exp(-\beta P\delta_1)\\&\cdot\int_0^\infty d\delta_{N+1}\exp(-\beta P\delta_{N+1})\\=&\frac{1}{\lambda^N(\beta P)^2}\left\{\int_0^\infty d\delta\exp\left[-\beta\left(\mathcal{V}(\delta)+P\delta\right)\right]\right\}^{N-1}.\end{aligned}$$

(e) The mean length is

$$\begin{aligned}L(T,N,P)&=-k_BT\,\frac{\partial}{\partial(\beta P)}\ln\mathcal{Z}(T,N,P)\Big|_{T,N}\\&=\frac{2}{\beta P}+(N-1)\frac{\int_0^\infty d\delta\cdot\delta\cdot\exp\left[-\beta\mathcal{V}(\delta)-\beta P\delta\right]}{\int_0^\infty d\delta\cdot\exp\left[-\beta\mathcal{V}(\delta)-\beta P\delta\right]},\end{aligned}$$

and the density n is given by

$$n = \frac{N}{L(T,N,P)} = N\left\{\frac{2k_BT}{P} + (N-1)\frac{\int_0^\infty d\delta \cdot \delta \cdot \exp\left[-\beta\left(\mathcal{V}(\delta) - P\delta\right)\right]}{\int_0^\infty d\delta \cdot \exp\left[-\beta\left(\mathcal{V}(\delta) - P\delta\right)\right]}\right\}^{-1}.$$

Note that for an ideal gas $\mathcal{V}_{\text{i.g.}}(\delta) = 0$, and

$$L_{\text{i.g.}}(T,N,P) = \frac{(N+1)k_BT}{P},$$

leading to

$$n(p)_{\text{i.g.}} = \frac{N}{N+1}\frac{P}{k_BT}.$$

(f) For a hard sphere gas

$$\delta_i \geq a, \qquad \text{for} \qquad i = 2, 3, \cdots, N,$$

the Gibbs partition function is

$$\begin{aligned}
\mathcal{Z}(T,N,P) &= \frac{1}{\lambda^N(\beta P)^2}\left[\int_a^\infty d\delta \exp\left(-\beta\mathcal{V}(\delta) - \beta P\delta\right)\right]^{N-1} \\
&= \frac{1}{\lambda^N(\beta P)^2}\left[\int_a^\infty d\delta \exp\left(-\beta P\delta\right)\right]^{N-1} \\
&= \frac{1}{\lambda^N}\left(\frac{1}{\beta P}\right)^{N+1}\exp\left(-\beta Pa\right)^{N-1}.
\end{aligned}$$

From the partition function, we can calculate the mean length

$$L = -k_BT\left.\frac{\partial \ln \mathcal{Z}}{\partial P}\right|_{T,N} = \frac{(N+1)k_BT}{P} + (N-1)a,$$

which after rearrangement yields

$$\beta P = \frac{(N+1)}{L-(N-1)a} = \frac{n+1/L}{1-(n-1/L)a} \approx (n+1/l)(1+(n-1/L)a + (n-1/L)^2a^2 + \cdots).$$

For $N \gg 1$, $n \gg 1/L$, and

$$\beta P \approx n(1 + na + n^2a^2 + \cdots) = n + an^2 + a^2n^3 + \cdots,$$

which gives the virial coefficients

$$B_\ell(T) = a^{\ell-1}.$$

The value of $B_3 = a^2$ agrees with the result obtained in PS# 8, problem 2, part (d). Also note that the exact 'excluded volume' is $(N-1)a$, as opposed to the estimate of $Na/2$ obtained in PS#6, problem 3.

****