

Chapter 7 Classical Fluids

Ye Liang

October 28, 2018

7.1

Since the partition function for N indistinguishable particles is

$$Q = \frac{1}{N!h^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)] \quad (1)$$

of which the $N!$ in the denominator comes because of the degeneracy of the states if the particles were treated as distinguishable. By analogy, the degeneracy of the states of three kinds of distinguishable particles should be $N_A!N_B!N_C!$. Therefore the partition function should be written as

$$Q = \frac{1}{N_A!N_B!N_C!h^{3(N_A+N_B+N_C)}} \int d\mathbf{r}^N \int d\mathbf{p}^N \exp[-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)]. \quad (2)$$

7.2

Since $\mathcal{H} = K(\mathbf{p}^N) + U(\mathbf{r}^N)$,

$$\begin{aligned} f(\mathbf{r}^N, \mathbf{p}^N) &= \frac{\exp[-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)]}{\int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)]} = \frac{\exp[-\beta K(\mathbf{p}^N)U(\mathbf{r}^N)]}{\int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)U(\mathbf{r}^N)]} \\ &= \frac{\exp[-\beta K(\mathbf{p}^N)]}{\int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)]} \frac{\exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \\ &= \Phi(\mathbf{p}^N)P(\mathbf{r}^N) \end{aligned} \quad (3)$$

where

$$\begin{aligned} \Phi(\mathbf{p}^N) &= \frac{\exp[-\beta K(\mathbf{p}^N)]}{\int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)]}, \\ P(\mathbf{r}^N) &= \frac{\exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]}. \end{aligned} \quad (4)$$

7.3

The canonical partition function is

$$Q = \frac{1}{N!h^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)] = \frac{1}{N!h^{3N}} \int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)] \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]. \quad (5)$$

The ideal gas partition function is

$$Q_{\text{ideal}} = \frac{1}{N!h^{3N}} \int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)] \int d\mathbf{r}^N = \frac{V^N}{N!h^{3N}} \int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)]. \quad (6)$$

Thus

$$Q = Q_{\text{ideal}} \frac{1}{V^N} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] = Q_{\text{ideal}} Q_{\text{con}} \quad (7)$$

where

$$Q_{\text{con}} = \frac{1}{V^N} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]. \quad (8)$$

7.4

(i)

$$\begin{aligned} \langle |\mathbf{p}| \rangle &= \frac{\int d\mathbf{p} |\mathbf{p}| \exp(-\beta p^2/2m)}{\int d\mathbf{p} \exp(-\beta p^2/2m)} = \frac{4\pi \int_0^\infty dp p \exp(-\beta p^2/2m)}{2^3 [\int_0^\infty dp \exp(-\beta p^2/2m)]^3} \\ &= \frac{8\pi m^2}{\beta^2} \frac{1}{8} \left(\sqrt{\frac{\pi m}{2\beta}} \right)^{-3} = \frac{m^{1/2}}{8^{-1/2} \pi^{1/2} \beta^{1/2}} = \sqrt{\frac{8k_B T m}{\pi}}. \end{aligned} \quad (9)$$

(ii)

$$\begin{aligned} \langle p_x^2 \rangle &= \frac{8 \int_0^\infty dp_x p_x^2 \exp(-\beta p_x^2/2m) \int_0^\infty dp_y \exp(-\beta p_y^2/2m) \int_0^\infty dp_z \exp(-\beta p_z^2/2m)}{8 [\int_0^\infty dp \exp(-\beta p^2/2m)]^3} \\ &= \frac{\int_0^\infty dp_x p_x^2 \exp(-\beta p_x^2/2m)}{\int_0^\infty dp \exp(-\beta p^2/2m)} = \frac{m}{\beta} = mk_B T. \end{aligned} \quad (10)$$

Thus

$$\langle p^2 \rangle = \langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle = 3mk_B T. \quad (11)$$

7.5

Because for a classical system,

$$\int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)] = \left\{ \int d\mathbf{p} \exp[-\beta K(\mathbf{p})] \right\}^N = \left\{ 4\pi \int_0^\infty dp p^2 \exp\left[-\beta \frac{p^2}{2m}\right] \right\}^N = \left(\sqrt{\frac{2^3 \pi^3 m^3}{\beta^3}} \right)^N \quad (12)$$

$$\begin{aligned} Q &= \frac{1}{N! h^{3N}} \int d\mathbf{p}^N \exp[-\beta K(\mathbf{p}^N)] \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \\ &= \frac{1}{N!} \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^3 \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \\ &= \frac{1}{N!} \lambda_T^{-3} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]. \end{aligned} \quad (13)$$

Here the thermal wavelength is

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (14)$$

7.6

Suppose the average speed of the particles is v , then the average relative speed is

$$u^2 = |\mathbf{v}_1 - \mathbf{v}_2|^2 = v_1^2 + v_2^2 - 2v_1 v_2 \cos(\theta_2 - \theta_1) = 2v^2 \quad (15)$$

Thus $u = \sqrt{2}v$. According to the scattering theory, the frequency of collision is

$$\mu = \rho S u \quad (16)$$

where $S = \pi\sigma^2$ is the cross section of the particles and u is the relative speed. Then the mean free path is

$$\lambda = \frac{vt}{\mu t} = \frac{v}{\rho\pi\sigma^2\sqrt{2}v} = \frac{1}{\sqrt{2}\pi\rho\sigma^2}. \quad (17)$$

For the liquid that has $\rho\sigma^3 \approx 1$,

$$\mu \approx \frac{\sqrt{2}\pi v}{\sigma}, \quad \lambda \approx \frac{\sigma}{\sqrt{2}\pi}. \quad (18)$$

For the ideal gas, $\rho = \frac{p}{k_B T}$,

$$\mu = \frac{\sqrt{2}\pi p \sigma^2 v}{k_B T}, \quad \lambda = \frac{k_B T}{\sqrt{2}\pi p \sigma^2}. \quad (19)$$

Around $T = 273$ K, $p = 1$ bar, assume $\sigma \sim 10^{-10}$ m, then $\mu_l \approx 10^{10}v$, $\mu_g \approx 10^6v$, and the average speed v is at the same magnitude. Thus $\lambda_l/\lambda_g \approx 10^{-4}$.

7.7

The triple point of nitrogen is $T = 63.1526$ K, $p = 12.53$ kPa. $m = M/N_A = 4.652 \times 10^{-26}$ kg.

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = 4.151 \times 10^{-11} \text{ m} = 0.4151 \text{ \AA} < \sigma \approx 4 \text{ \AA}. \quad (20)$$

7.8

$$n(r) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^r r'^2 \cos\theta g(r') dr' = 4\pi \int_0^r r'^2 g(r') dr'. \quad (21)$$

7.9

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] = 4\varepsilon(a^2 - a) = 4\varepsilon \left[\left(a - \frac{1}{2}\right)^2 - \frac{1}{4} \right] \quad (22)$$

where

$$a = \left(\frac{\sigma}{r}\right)^6. \quad (23)$$

Since u is a quadratic function of a , the minimum is located at $a = \frac{1}{2}$. Thus $r_0 = 2^{1/6}\sigma$ and $u(r_0) = -\varepsilon$.

7.10

$$\langle E \rangle = N \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \sum_{i>j=1}^N u(r_{ij}) \right\rangle + \left\langle \sum_{i>j>l=1}^N u^{(3)}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_j - \mathbf{r}_l) \right\rangle \quad (24)$$

$$\left\langle \sum_{i>j=1}^N u(r_{ij}) \right\rangle = \frac{1}{2} N \int d\mathbf{r} \rho g(r) u(r) \quad (25)$$

$$\left\langle \sum_{i>j>l=1}^N u^{(3)}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_j - \mathbf{r}_l) \right\rangle = \frac{N(N-1)(N-2)}{6} \langle u^{(3)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_2 - \mathbf{r}_3) \rangle \quad (26)$$

$$\langle u^{(3)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_2 - \mathbf{r}_3) \rangle = \frac{1}{N(N-1)(N-2)} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 u^{(3)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_2 - \mathbf{r}_3) \rho^{(3/N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad (27)$$

Thus

$$\left\langle \sum_{i>j>l=1}^N u^{(3)}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_j - \mathbf{r}_l) \right\rangle = \frac{1}{6} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 u^{(3)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_2 - \mathbf{r}_3) \rho^{(3/N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad (28)$$

Similar to the definition of $g(r_{ij})$, we can define

$$g^{(3)}(r_{ij}, r_{jl}) = \rho^{(3/N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) / \rho^3 \quad (29)$$

Then

$$\begin{aligned} \left\langle \sum_{i>j>l=1}^N u^{(3)}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_j - \mathbf{r}_l) \right\rangle &= \frac{1}{6} V \iint d\mathbf{r}_{12} d\mathbf{r}_{23} u^{(3)}(r_{12}, r_{23}) g^{(3)}(r_{12}, r_{23}) \rho^3 \\ &= \frac{1}{6} N \rho^2 \iint d\mathbf{r}_{12} d\mathbf{r}_{23} u^{(3)}(r_{12}, r_{23}) g^{(3)}(r_{12}, r_{23}). \end{aligned} \quad (30)$$

Thus

$$\langle E \rangle / N = \frac{3}{2} k_B T + \frac{1}{2} \rho \int d\mathbf{r} g(r) u(r) + \frac{1}{6} \rho^2 \iint d\mathbf{r}_{12} d\mathbf{r}_{23} u^{(3)}(r_{12}, r_{23}) g^{(3)}(r_{12}, r_{23}). \quad (31)$$

7.11

When $U(\mathbf{r}^N)$ is pair decomposable,

$$U(\mathbf{r}^N) = \sum_{i>j=1}^N u(r_{ij}), \quad (32)$$

$$\begin{aligned} \beta p &= \frac{\partial}{\partial V} \ln \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] = \frac{\partial}{\partial V} \ln \int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \\ &= \frac{\partial}{\partial V} \ln \left\{ V^N \int d\mathbf{x}^N \prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \right\} \\ &= \frac{N}{V} + \frac{\partial}{\partial V} \ln \int d\mathbf{x}^N \prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \end{aligned} \quad (33)$$

$$\begin{aligned}
& \frac{\partial}{\partial V} \ln \int d\mathbf{x}^N \left(\prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \right) \\
&= \frac{\int d\mathbf{r}^N \left(\prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \right) \left(\sum_{i>j=1}^N -\beta u'(r_{ij}) \frac{r_{ij}}{3V} \right)}{\int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u(r_{ij})]} \\
&= \frac{1}{2} N(N-1) \frac{\int d\mathbf{r}^N \left(\prod_{i>j=1}^N \exp[-\beta u(r_{ij})] \right) \left(-\beta u'(r_{12}) \frac{r_{12}}{3V} \right)}{\int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u(r_{ij})]} \\
&= \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \left(-\beta u'(r_{12}) \frac{r_{12}}{3V} \right) \\
&= -\frac{1}{6} \rho^2 \beta \int d\mathbf{r} g(r) u'(r) r. \tag{34}
\end{aligned}$$

Thus

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int d\mathbf{r} g(r) u'(r) r. \tag{35}$$

7.12

Insert $g(r) \approx \exp[-\beta u(r)]$ into equation (35),

$$\begin{aligned}
\beta p &= \rho - \frac{\beta \rho^2}{6} \int d\mathbf{r} e^{-\beta u(r)} u'(r) r \\
&= \rho - \frac{\beta \rho^2}{6} \int \left(-\frac{1}{\beta} \right) \mathbf{r} \cdot \nabla \left(e^{-\beta u(r)} \right) d\mathbf{r} \\
&= \rho + \frac{\rho^2}{6} \int \mathbf{r} \cdot \nabla \left(e^{-\beta u(r)} - 1 \right) d\mathbf{r} \\
&= \rho + \frac{\rho^2}{6} \left[r f(r) \Big|_{\infty} - \int d\mathbf{r} f(r) \nabla \mathbf{r} \right] \\
&= \rho + \frac{\rho^2}{6} \left[-3 \int d\mathbf{r} f(r) \right] \\
&= \rho - \frac{\rho^2}{2} \int d\mathbf{r} f(r). \tag{36}
\end{aligned}$$

7.13

$$B_2(T) = -\frac{1}{2} \int d\mathbf{r} f(r) = -2\pi \int_0^{\infty} r^2 \left(e^{-\beta u(r)} - 1 \right) dr \tag{37}$$

(i) For a hard sphere system,

$$B_2(T) = -2\pi \int_0^{\sigma} r^2 (-1) dr = \frac{2\pi}{3} \sigma^3. \tag{38}$$

(ii) For a square well system,

$$B_2(T) = -2\pi \left[\int_0^\sigma r^2(-1)dr + \int_\sigma^{\sigma'} r^2(e^{\beta\varepsilon} - 1) dr \right] = \frac{2\pi}{3}\sigma^3 - \frac{2\pi}{3}(e^{\beta\varepsilon} - 1)(\sigma'^3 - \sigma^3). \quad (39)$$

The Boyle temperature is decided by $B_2(T_B) = 0$. $\beta_B = 1/k_B T_B$. Then

$$\frac{2\pi}{3}\sigma^3 - \frac{2\pi}{3}(e^{\beta_B\varepsilon} - 1)(\sigma'^3 - \sigma^3) = 0 \quad (40)$$

$$e^{\beta_B\varepsilon} = \frac{\sigma'^3}{\sigma'^3 - \sigma^3} \quad (41)$$

$$\beta_B = \frac{1}{\varepsilon} \ln \frac{\sigma'^3}{\sigma'^3 - \sigma^3}. \quad (42)$$

7.14

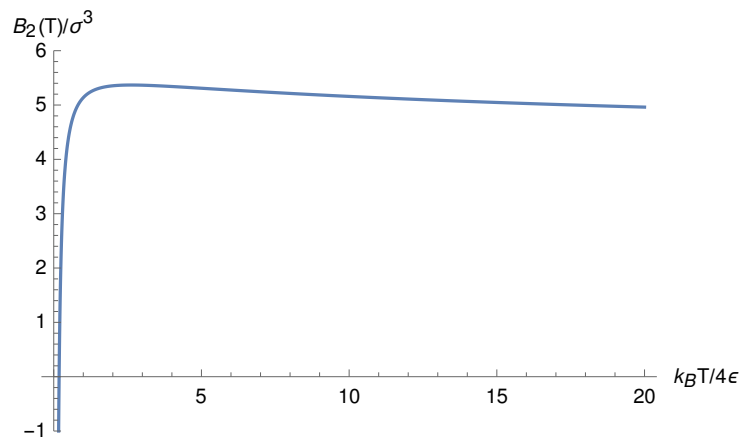


Figure 1: $B_2(T)$ for a Lennard-Jones fluid.

7.15

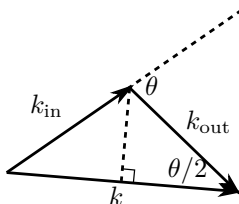


Figure 2: Wave vector addition.

Since $|\mathbf{k}_{\text{in}}| = |\mathbf{k}_{\text{out}}| = \frac{2\pi}{\lambda_{\text{in}}}$, according to figure 2,

$$k = 2 \frac{2\pi}{\lambda_{\text{in}}} \sin \frac{\theta}{2} = \frac{4\pi}{\lambda_{\text{in}}} \sin \frac{\theta}{2}. \quad (43)$$

7.16

$$S(k) = 1 + \rho \int d\mathbf{r} g(r) e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + 2\pi\rho \int_0^\pi d\theta \int_0^\infty r^2 \sin\theta g(r) e^{ikr \cos\theta} dr = 1 + 2\pi\rho \int_0^\infty \frac{2 \sin(kr)}{kr} r^2 g(r) dr \quad (44)$$

$$\therefore S(k) = 1 + \frac{4\pi\rho}{k} \int_0^\infty \sin(kr) r g(r) dr. \quad (45)$$

7.17

We start from

$$\frac{d \ln Q_\lambda}{d\lambda} = \frac{\int d\mathbf{r}^{N_A} \int d\mathbf{r}^{N_S} (-\beta U_{AS}) \exp(-\beta U_S - \beta \lambda U_{AS})}{\int d\mathbf{r}^{N_A} \int d\mathbf{r}^{N_S} \exp(-\beta U_S - \beta \lambda U_{AS})} \quad (46)$$

Because

$$U_{AS}(\mathbf{r}^{N_S}, \mathbf{r}^{N_A}) = \sum_{i=1}^{N_A} \sum_{j=1}^{N_S} u_{AS}(|\mathbf{r}_{iA} - \mathbf{r}_{jS}|), \quad (47)$$

$$\begin{aligned} \frac{d \ln Q_\lambda}{d\lambda} &= \frac{\sum_{i=1}^{N_A} \sum_{j=1}^{N_S} \int d\mathbf{r}^{N_A} d\mathbf{r}^{N_S} (-\beta u_{AS}(|\mathbf{r}_{iA} - \mathbf{r}_{jS}|)) \exp(-\beta U_S - \beta \lambda U_{AS})}{\int d\mathbf{r}^{N_A} d\mathbf{r}^{N_S} \exp(-\beta U_S - \beta \lambda U_{AS})} \\ &= -\beta \sum_{i=1}^{N_A} \sum_{j=1}^{N_S} \frac{\int d\mathbf{r}_{iA} \int d\mathbf{r}_{jS} u_{AS}(|\mathbf{r}_{iA} - \mathbf{r}_{jS}|) \int d\mathbf{r}^{N_A-1} \int d\mathbf{r}^{N_S-1} \exp(-\beta U_S - \beta \lambda U_{AS})}{\int d\mathbf{r}^{N_A} \int d\mathbf{r}^{N_S} \exp(-\beta U_S - \beta \lambda U_{AS})} \\ &= -\beta \sum_{i=1}^{N_A} \sum_{j=1}^{N_S} \int d\mathbf{r}_{iA} \int d\mathbf{r}_{jS} u_{AS}(|\mathbf{r}_{iA} - \mathbf{r}_{jS}|) N_A^{-1} \rho_A N_S^{-1} \rho_S g_{AS}(\mathbf{r}_{iA}, \mathbf{r}_{jS}; \lambda) \\ &= -\beta \int d\mathbf{r}_{iA} \int d\mathbf{r}_{jS} \rho_A \rho_S u_{AS}(|\mathbf{r}_{iA} - \mathbf{r}_{jS}|) g_{AS}(\mathbf{r}_{iA} - \mathbf{r}_{jS}; \lambda) \\ &= -\beta V \int d\mathbf{r} \rho_A \rho_S u_{AS}(r) g_{AS}(r; \lambda) \\ &= -\beta N_A \int d\mathbf{r} \rho_S u_{AS}(r) g_{AS}(r; \lambda). \end{aligned} \quad (48)$$

7.18

$$s_{AB}(r) = \frac{H_{AB}(r) \exp[-\beta u_{AB}(r) - \beta \Delta w_{AB}(r)]}{\int d\mathbf{r} H_{AB}(r) \exp[-\beta u_{AB}(r) - \beta \Delta w_{AB}(r)]}, \quad (49)$$

$$\int d\mathbf{r} s_{AB}^{(\text{id})}(r) y_{AB}(r) = \frac{\int d\mathbf{r} H_{AB}(r) \exp[-\beta u_{AB}(r) - \beta \Delta w_{AB}(r)]}{\int d\mathbf{r} H_{AB}(r) \exp[-\beta u_{AB}(r)]}, \quad (50)$$

$$s_{AB}^{(\text{id})}(r) = \frac{H_{AB}(r) \exp[-\beta u_{AB}(r)]}{\int d\mathbf{r} H_{AB}(r) \exp[-\beta u_{AB}(r)]}, \quad y_{AB}(r) = \exp[-\beta \Delta w_{AB}(r)]. \quad (51)$$

$$\begin{aligned} \therefore s_{AB}(r) &= \frac{H_{AB}(r) \exp[-\beta u_{AB}(r) - \beta \Delta w_{AB}(r)] \int d\mathbf{r} H_{AB}(r) \exp[-\beta u_{AB}(r)]}{\int d\mathbf{r} s_{AB}^{(\text{id})}(r) y_{AB}(r)} \\ &= \frac{s_{AB}^{(\text{id})}(r) y_{AB}(r)}{\int d\mathbf{r} s_{AB}^{(\text{id})}(r) y_{AB}(r)}. \end{aligned} \quad (52)$$

7.19

The van 't Hoff equation is

$$\Delta\mu = -k_B T \ln K. \quad (53)$$

Thus

$$\Delta\mu_{AB} = -k_B T \ln K = -k_B T \left[\ln K^{(\text{id})} + \ln \int d\mathbf{r} s_{AB}^{(\text{id})}(r) y_{AB}(r) \right]. \quad (54)$$

Because for ideal gas,

$$\Delta\mu^{(\text{id})} = \Delta\mu_A + \Delta\mu_B = -k_B T \ln K^{(\text{id})} \quad (55)$$

$$\therefore \Delta\mu_{AB} = \Delta\mu_A + \Delta\mu_B - k_B T \ln \int d\mathbf{r} s_{AB}^{(\text{id})}(r) y_{AB}(r). \quad (56)$$

7.20

The change of the chemical potential can be written as

$$\Delta\mu_n = n\Delta\mu_C - (n-1)k_B T \ln \int d\mathbf{r} s_{CC}^{(\text{id})}(r) y_{CC}(r). \quad (57)$$

The subscript C denotes a CH_2 piece. Thus it is approximately depends linearly upon n . For large n , the interaction between the sections of the alkane chains will become complicated, more than having linear CH_2 - CH_2 interactions. Therefore the linear dependence on n will not persist.

7.21

The figure 7.11 in the text is problematic. Here we refer to the figure given by [1], shown in figure 3. (i) The peak at $r = 1.5 \text{ \AA}$ is the C-C single bound length L .

(ii) The peak at $r = 2.5 \text{ \AA}$ is mainly for the C1-C3 distance R .

(iii) The peak at $r = 3.1 \text{ \AA}$ indicates the C1-C4 distance R' in a gauche conformation.

(iv) The peak at $r = 4.0 \text{ \AA}$ indicates the C1-C4 distance R'' in a trans conformation. It is also likely to indicate the van der Waals diameter of a methyl group σ .

(v) The peak at $r = 4.0 \sim 6.0 \text{ \AA}$ indicates the intermolecular contact with distance $\sigma + L = 5.5 \text{ \AA}$.

(vi) The broad peak at $r = 9 \text{ \AA}$ is the location of the second coordination shell $2(\sigma + L/2) = 9.5 \text{ \AA}$.

7.22

Since

$$\langle E \rangle / N = \frac{3}{2} k_B T + \frac{1}{2} \rho \int d\mathbf{r} g(r) u(r) \quad (58)$$

Because in water the pair correlation function $g(r)$ heavily depends upon temperature, the heat capacity, which is the derivative of the internal energy over temperature, is much larger in water than those in other simple liquids.

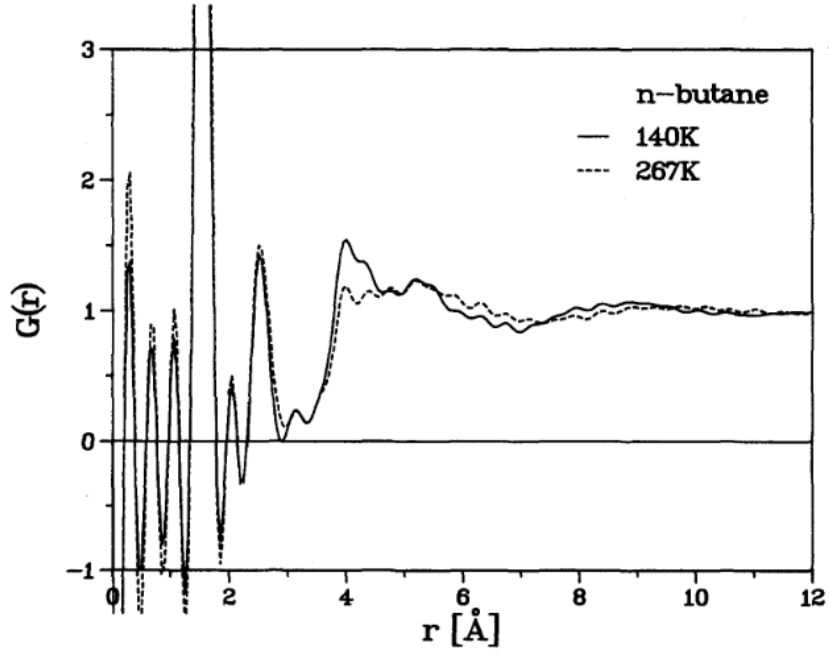


Figure 3: Experimental radial distribution function of n-butane.

7.23

Because

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T}\right)_p, \quad (59)$$

When temperature is much higher than the freezing point, naturally $\left(\frac{\partial s}{\partial p}\right)_T > 0$. When the temperature approaches the freezing point, for water $\left(\frac{\partial s}{\partial p}\right)_T < 0$. Because of the continuity, there is a point T_0 where $\left(\frac{\partial s}{\partial p}\right)_T = 0$. At this point the density ρ achieves its maximum.

7.24

For two-dimensional hard disks, when the disks are closest packed, the unit cell has a volume of $\frac{\sqrt{3}}{2}\sigma^2$. Therefore

$$\rho_{CP} = \frac{2}{\sqrt{3}}\sigma^{-2}. \quad (60)$$

The crystal structure could be square packing, whose packing density is $\sim 86\%$ of the closest (hexagonal) packing.

7.25

For one particle, the energy is

$$\varepsilon(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}' \rho(\mathbf{r}') u(|\mathbf{r} - \mathbf{r}'|) \quad (61)$$

Then

$$\langle \rho(\mathbf{r}) \rangle = c \exp \left[-\beta \phi(\mathbf{r}) - \beta \int d\mathbf{r}' \langle \rho(\mathbf{r}') \rangle u(|\mathbf{r} - \mathbf{r}'|) \right]. \quad (62)$$

To solve this equation, one of the numerical methods is the self-consistent field method: one gives an initial guess of $\langle \rho(\mathbf{r}) \rangle$ and generate new $\langle \rho(\mathbf{r}) \rangle$ iteratively until the density is converged. The analytical method can be a variational method based on the Gibbs-Bogoliubov-Feynman bound.

7.26

The choice of the shell width should be neither too large nor too small. If the shell width is too large, the resolution of the curve will be too low. While if the shell width is too small, the simulation may need more steps to achieve a smooth profile of $g(r)$.

7.27

If we fix the total number of Monte Carlo steps, we hope to have the largest acceptance rate as well as the lowest statistical error. Thus for a specific system, one should find a balance with these two factors when choosing the step size.

7.28

(i) The system is regarded as an ideal gas when it is dilute.

(a)

$$\begin{aligned} \langle v_x^2 \rangle &= \frac{\int d\mathbf{r} d\mathbf{p} v_x^2 \exp(-\beta p^2/2m)}{\int d\mathbf{r} d\mathbf{p} \exp(-\beta p^2/2m)} = \frac{\int d\mathbf{p} v_x^2 \exp(-\beta p^2/2m)}{\int d\mathbf{p} \exp(-\beta p^2/2m)} \\ &= \frac{\int_{-\infty}^{\infty} dp_x (p_x/m)^2 \exp(-\beta p_x^2/2m)}{\int_{-\infty}^{\infty} dp_x \exp(-\beta p_x^2/2m)} \\ &= \frac{1}{m\beta} = \frac{k_B T}{m}. \end{aligned} \quad (63)$$

(b) Because the velocity on x and y directions are independent for an ideal gas,

$$\langle v_x^2 v_y^2 \rangle = \langle v_x^2 \rangle \langle v_y^2 \rangle = \frac{1}{m^2 \beta^2} = \frac{k_B^2 T^2}{m^2}. \quad (64)$$

(c)

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{3}{m\beta} = \frac{3k_B T}{m}. \quad (65)$$

(d) Because of the symmetry, $\langle v_x \rangle = 0$.

$$\begin{aligned} \langle |v_x| \rangle &= \frac{\int d\mathbf{r}d\mathbf{p} |v_x| \exp(-\beta p^2/2m)}{\int d\mathbf{r}d\mathbf{p} \exp(-\beta p^2/2m)} = \frac{2 \int_0^\infty dp_x \frac{p_x}{m} \exp(-\beta p_x^2/2m)}{\int_{-\infty}^\infty dp_x \exp(-\beta p_x^2/2m)} \\ &= \sqrt{\frac{2}{\pi m \beta}} = \sqrt{\frac{2k_B T}{\pi m}}. \end{aligned} \quad (66)$$

(e)

$$\langle (v_x + bv_y)^2 \rangle = \langle v_x^2 \rangle + b \langle v_x \rangle \langle v_y \rangle + b^2 \langle v_y^2 \rangle = \frac{1 + b^2}{m^2 \beta^2}. \quad (67)$$

(ii) Once the system approaches the boiling point or the freezing point, it is no longer an ideal gas. But if the temperature is the same, the average velocity is the same.

7.29

(a)

$$\mathcal{H} = \sum_{i=1}^{3N} h_i, \quad h_i = \frac{p_i^2}{2m} + \frac{1}{2} k x_i^2. \quad (68)$$

h_i is the Hamiltonian of the one-dimensional harmonic oscillator. Then

$$Q = \prod_{i=1}^{3N} q_i, \quad q_i = \text{Tr}(e^{-\beta h_i}) = \sum_{n=0}^{\infty} \exp\left[-\beta \hbar \omega \left(n + \frac{1}{2}\right)\right] = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} = \frac{1}{2} \text{csch}\left(\frac{\beta \hbar \omega}{2}\right) \quad (69)$$

where

$$\omega = \sqrt{\frac{k}{m}}. \quad (70)$$

$$Q = \frac{1}{2^{3N}} \text{csch}^{3N}\left(\frac{\beta \hbar \omega}{2}\right) \quad (71)$$

(b)

$$q_i = \frac{1}{h} \int dx_i \int dp_i \exp(-\beta h_i) = \frac{1}{h} \int dx_i \exp\left(-\frac{\beta k x_i^2}{2}\right) \int dp_i \exp\left(-\frac{\beta p_i^2}{2m}\right) = \frac{2\pi}{h\beta\sqrt{\frac{k}{m}}} = \frac{1}{\beta \hbar \omega}. \quad (72)$$

$$Q = \frac{1}{(\beta \hbar \omega)^{3N}}. \quad (73)$$

(c) When $T \rightarrow \infty$, $\beta \rightarrow 0$. The quantities in (a) become

$$\text{csch}\left(\frac{\beta \hbar \omega}{2}\right) \rightarrow \frac{2}{\beta \hbar \omega}, \quad q_i \rightarrow \frac{1}{\beta \hbar \omega}, \quad Q \rightarrow \frac{1}{(\beta \hbar \omega)^{3N}}. \quad (74)$$

7.30

$$U(\mathbf{r}^N) = \sum_{i>j=1}^N u(r_{ij}) + \sum_{i>j>l=1}^N u^{(3)}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_j - \mathbf{r}_l) \quad (75)$$

$$\begin{aligned}
\beta p &= \frac{\partial}{\partial V} \ln \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \\
&= \rho + \sum_{i>j=1}^N \frac{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \left[-\beta u'(r_{ij}) \frac{r_{ij}}{3V} \right]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} + \sum_{i>j>l=1}^N \frac{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \left[-\beta(u_1^{(3)} r_{ij} + u_2^{(3)} r_{jl}) \frac{1}{3V} \right]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \\
&= \rho - \frac{\beta \rho^2}{6} \int d\mathbf{r} g(r) r u'(r) + \sum_{i>j>l=1}^N \frac{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \left[-\beta(u_1^{(3)} r_{ij} + u_2^{(3)} r_{jl}) \frac{1}{3V} \right]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \tag{76}
\end{aligned}$$

where

$$u_1^{(3)}(x, y) = \frac{\partial u^{(3)}(x, y)}{\partial x}, \quad u_2^{(3)}(x, y) = \frac{\partial u^{(3)}(x, y)}{\partial y}. \tag{77}$$

$$\begin{aligned}
&\sum_{i>j>l=1}^N \frac{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)] \left[-\beta(u_1^{(3)} r_{ij} + u_2^{(3)} r_{jl}) \frac{1}{3V} \right]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \\
&= \frac{1}{6} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \left[-\beta(u_1^{(3)} r_{12} + u_2^{(3)} r_{23}) \frac{1}{3V} \right] \rho^{(3/N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\
&= -\frac{\beta}{18V} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 (u_1^{(3)} r_{12} + u_2^{(3)} r_{23}) g^{(3)}(r_{12}, r_{23}) \rho^3 \\
&= -\frac{\beta \rho^3}{18} \iint d\mathbf{r}_{12} d\mathbf{r}_{23} g^{(3)}(r_{12}, r_{23}) (u_1^{(3)} r_{12} + u_2^{(3)} r_{23}). \tag{78}
\end{aligned}$$

Thus

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int d\mathbf{r} g(r) r u'(r) - \frac{\beta \rho^3}{18} \iint d\mathbf{r}_{12} d\mathbf{r}_{23} g^{(3)}(r_{12}, r_{23}) (u_1^{(3)} r_{12} + u_2^{(3)} r_{23}). \tag{79}$$

Therefore the second virial coefficient is explicitly independent of the three-body potential.

7.31

- (a) At high density, the sketch of the pair distribution function is shown in figure 4.
- (b) At extremely low density, the sketch of the pair distribution function is shown in figure 5.
- (c) For hard spheres, $g(r)$ is independent to T .
- (d) For $\rho \rightarrow \rho_{CP}$, the number of particles in the first coordination shell on one side should be 1. Thus

$$\begin{aligned}
\int_0^{(3/2)l} dx \rho_{CP} g(x) &= 1. \\
\int_0^{(3/2)l} dx g(x) &= 1/\rho_{CP} = l. \tag{80}
\end{aligned}$$

- (e) (i) $\langle \mathbf{v} \rangle = 0$. (ii) Because the momentums are uncorrelated and independent to the coordinates, this system has the same average speed as that of a one-dimensional ideal gas.

$$\langle v \rangle = \sqrt{\frac{2}{\pi m \beta}}. \tag{81}$$

- (iii)

$$\langle v^2 \rangle = \frac{1}{m \beta}. \tag{82}$$

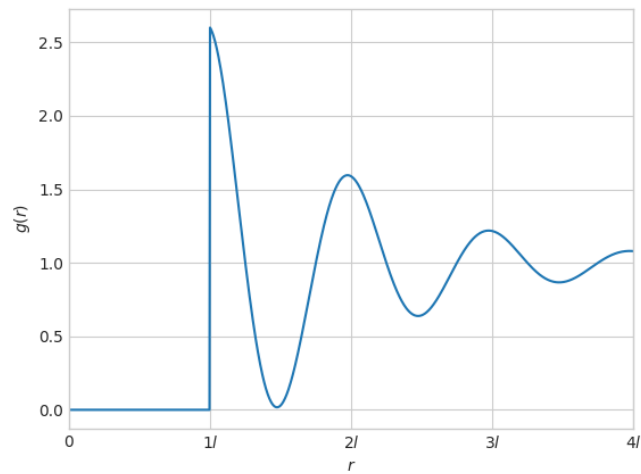


Figure 4: A sketch of the pair distribution function at high density.

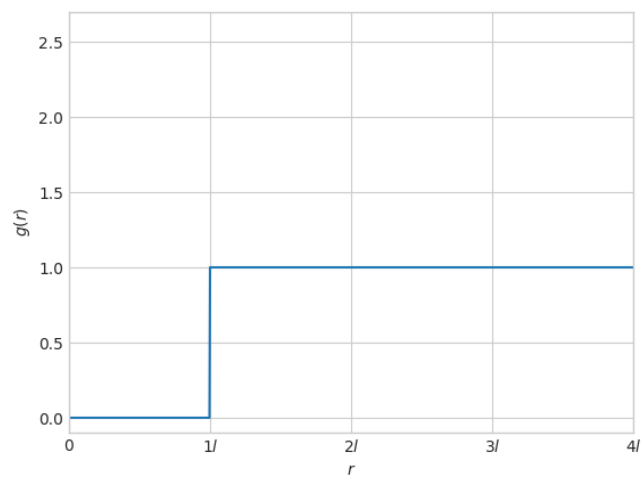


Figure 5: A sketch of the pair distribution function at low density.

$$\langle \varepsilon_k \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} k_B T. \quad (83)$$

(iv) Since $\langle U \rangle = 0$, $\langle K \rangle = N \langle \varepsilon_k \rangle$,

$$\langle E \rangle = \langle K \rangle + \langle U \rangle = \frac{1}{2} N k_B T. \quad (84)$$

(f) Since

$$\beta p / \rho = \frac{1}{1 - b\rho} = 1 + b\rho + \dots, \quad (85)$$

b is the second virial coefficient.

$$b = -\frac{1}{2} \int_{-\infty}^{\infty} dr \left(e^{-\beta u(r)} - 1 \right) = -\int_0^l (-1) dr = l. \quad (86)$$

Thus b is not a function of T .

(g)

$$-\beta A = \ln \left[\frac{1}{N! \lambda^N} \int_0^L dx_1 \int_0^L dx_2 \cdots \int_0^L dx_N e^{-\beta U} \right] \quad (87)$$

and

$$U = \begin{cases} 0, & r_{ij} \geq l \text{ for all } i, j = 1, 2, \dots, N \\ \infty, & r_{ij} < l \text{ if any } i, j = 1, 2, \dots, N. \end{cases} \quad (88)$$

Thus

$$-\beta A = \ln \left[\frac{1}{N! \lambda^N} (L - Nl)^N \right] = -\ln N! - N \ln \lambda + N \ln(L - Nl) \quad (89)$$

$$\beta p = \frac{\partial(-\beta A)}{\partial L} = \frac{N}{L - Nl} = \frac{\rho}{1 - \rho l} \quad (90)$$

Thus $b = l$.

7.32

(a)

$$-\beta A = \ln \frac{V^N}{N! \lambda^{3N}} = N \ln V - N \ln N + N - 3N \ln \lambda. \quad (91)$$

$$\beta \mu = \left(\frac{\partial(\beta A)}{\partial N} \right)_{V, \beta} = \ln N - \ln V - 3 \ln \lambda = -3 \ln \lambda + \ln \rho. \quad (92)$$

Thus

$$f(\beta) = -3 \ln \lambda. \quad (93)$$

λ is the thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (94)$$

(b) Using the coupling parameter method introduced in section 7.6 from the text,

$$\begin{aligned} Q_\lambda &= Q_W^{(\text{id})} Q_A^{(\text{id})} V^{-(N_A + N_W)} \int d\mathbf{r}^{N_A} \int d\mathbf{r}^{N_W} \exp[-\beta U_W(\mathbf{r}^{N_W}) - \beta \lambda U_{AW}(\mathbf{r}^{N_W}, \mathbf{r}^{N_A})] \\ &= Q_W^{(\text{id})} Q_A^{(\text{id})} Q_{AW}(\lambda) \end{aligned} \quad (95)$$

Notice

$$Q_{AW}(0) = Q_W^{(\text{ex})} \quad (96)$$

is the exceed partition function for water. Then

$$\ln Q_0 = \ln Q_W^{(\text{id})} + \ln Q_A^{(\text{id})} + \ln Q_W^{(\text{ex})} \quad (97)$$

By Newton-Leibniz formula,

$$\ln Q = \ln Q_1 = \ln Q_0 + \int_0^1 d\lambda \frac{\partial \ln Q_\lambda}{\partial \lambda} = \ln Q_0 + \int_0^1 d\lambda \frac{\partial \ln Q_{AW}(\lambda)}{\partial \lambda} \quad (98)$$

Then

$$A = A_A^{(\text{id})} + A_W^{(\text{id})} + A_W^{(\text{ex})} - \beta^{-1} \int_0^1 d\lambda \frac{\partial \ln Q_{AW}(\lambda)}{\partial \lambda} \quad (99)$$

$$\mu = \frac{\partial A}{\partial N_A} = \frac{\partial A_A^{(\text{id})}}{\partial N_A} - \beta^{-1} \frac{\partial}{\partial N_A} \int_0^1 d\lambda \frac{\partial \ln Q_{AW}(\lambda)}{\partial \lambda} = \mu^{(\text{id})} + \Delta\mu, \quad (100)$$

where

$$\Delta\mu = -\beta^{-1} \frac{\partial}{\partial N_A} \int_0^1 d\lambda \frac{\partial \ln Q_{AW}(\lambda)}{\partial \lambda}. \quad (101)$$

Therefore

$$\beta\mu = f(\beta) + \ln \rho + \beta\Delta\mu. \quad (102)$$

(c) In equilibrium $\mu_g = \mu_l$.

$$\ln \rho_g = \ln \rho_l + \beta\Delta\mu \quad (103)$$

$$\rho_g = \beta p \quad (104)$$

$$\rho_l = x\rho_W \quad (105)$$

Therefore

$$p = x\beta^{-1}\rho_W e^{\beta\Delta\mu} \quad (106)$$

Thus in Henry's law $p = xk_H$,

$$k_H = \beta^{-1}\rho_W e^{\beta\Delta\mu}. \quad (107)$$

(d) Taking the hint,

$$\begin{aligned} -\beta\Delta\mu &= \ln \frac{\int d\mathbf{r}^{N_W} d\mathbf{r}_A \exp[-\beta U_W(\mathbf{r}^{N_W})] \prod_{i=1}^{N_W} \exp[-\beta\lambda u_{AW}(|\mathbf{r}_A - \mathbf{r}_i|)]}{\int d\mathbf{r}^{N_W} \exp[-\beta U_W(\mathbf{r}^{N_W})]} \\ &= \ln \left\langle \int d\mathbf{r}_A \prod_{i=1}^{N_W} \exp[-\beta\lambda u_{AW}(|\mathbf{r}_A - \mathbf{r}_i|)] \right\rangle_W \end{aligned} \quad (108)$$

$$\begin{aligned} \frac{\partial(\beta\Delta\mu)}{\partial \lambda} &= \frac{\left\langle \int d\mathbf{r}_A [\sum_{i=1}^{N_W} \beta u_{AW}(|\mathbf{r}_A - \mathbf{r}_i|)] \prod_{i=1}^{N_W} \exp[-\beta\lambda u_{AW}(|\mathbf{r}_A - \mathbf{r}_i|)] \right\rangle_W}{\left\langle \int d\mathbf{r}_A \prod_{i=1}^{N_W} \exp[-\beta\lambda u_{AW}(|\mathbf{r}_A - \mathbf{r}_i|)] \right\rangle_W} \\ &= \beta \langle N_W u_{AW} \rangle \\ &= \beta \int d\mathbf{r} \rho_W g_{AW}(r; \lambda) u_{AW}(r) \end{aligned} \quad (109)$$

Thus, the excess chemical potential is

$$\Delta\mu = \int_0^1 d\lambda \int d\mathbf{r} \rho_W g_{AW}(r; \lambda) u_{AW}(r) \quad (110)$$

where in the subscript W stands for water and A for argon.

7.33

Similar to the three-dimensional system in Exercise 7.11,

$$\begin{aligned}\beta p/\rho &= 1 - \frac{\beta\rho}{4} \int d\mathbf{r} g(r) r u'(r) \\ &= 1 - \frac{\beta\rho\pi}{2} \int_0^\infty dr r^2 g(r) u'(r)\end{aligned}\quad (111)$$

Taking the hint,

$$-\beta g(r) u'(r) = y(r) \frac{d \exp[-\beta u(r)]}{dr} = y(r) \delta(r - \sigma) \quad (112)$$

$$\beta p/\rho = 1 + \frac{\pi\rho}{2} \int_0^\infty dr r^2 y(r) \delta(r - \sigma) = 1 + \frac{\pi\rho\sigma^2}{2} y(\sigma). \quad (113)$$

For $r > \sigma$, $g(r) = y(r)$, thus when $r \rightarrow \sigma^+$,

$$y(\sigma) = g(\sigma^+) \quad (114)$$

$$\beta p/\rho = 1 + \frac{\pi\rho\sigma^2}{2} g(\sigma^+). \quad (115)$$

7.34

Run the simulation code on computer.

7.35

(a) Define

$$Q_\lambda = \int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u_0(r_{ij})] \exp[-\beta \lambda u_1(r_{ij})] \quad (116)$$

$$Q_0 = \int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u_0(r_{ij})], \quad Q_1 = Q. \quad (117)$$

$$\begin{aligned}\frac{\partial \ln Q_\lambda}{\partial \lambda} &= \sum_{i'>j'=1}^N \frac{\int d\mathbf{r}^N [-\beta u_1(r_{i'j'})] \prod_{i>j=1}^N \exp[-\beta u_0(r_{ij})] \exp[-\beta \lambda u_1(r_{ij})]}{\int d\mathbf{r}^N \prod_{i>j=1}^N \exp[-\beta u_0(r_{ij})] \exp[-\beta \lambda u_1(r_{ij})]} \\ &= -\beta \frac{1}{2} \int d\mathbf{x}_i \int d\mathbf{x}_j u_1(r_{ij}) \rho^2 g_\lambda(r) \\ &= -\frac{1}{2} \beta \rho N \int d\mathbf{r}_{ij} u_1(r_{ij}) g_\lambda(r_{ij}).\end{aligned}\quad (118)$$

From Newton-Leibniz formula

$$\ln Q = \ln Q_0 + \int_0^1 d\lambda \int d\mathbf{r} \frac{\partial \ln Q_\lambda}{\partial \lambda} \quad (119)$$

$$A/N = A_0/N + \frac{1}{2} \rho \int d\mathbf{r} u_1(r) g_\lambda(r). \quad (120)$$

(b) From Gibbs-Bogoliubov-Feynman bound,

$$Q \geq Q_0 \exp(-\beta \langle U - U_0 \rangle_0) = Q_0 \prod_{j>i=1}^N \exp(-\beta \langle u_1 \rangle_0) \quad (121)$$

Considering $\langle u_1 \rangle_0 = \frac{1}{N(N-1)} \rho^2 V \int d\mathbf{r} g_0(r) u_1(r)$,

$$\ln Q \geq \ln Q_0 + \frac{N(N-1)}{2} (-\beta \langle u_1 \rangle_0) = \ln Q_0 - \frac{1}{2} \beta N \rho \int d\mathbf{r} u_1(r) g_0(r) \quad (122)$$

Therefore

$$A/N \leq A_0/N + \frac{1}{2} \rho \int d\mathbf{r} u_1(r) g_0(r). \quad (123)$$

References

- [1] A Habenschuss and AH Narten. X-ray diffraction study of liquid n-butane at 140 and 267 k. *The Journal of chemical physics*, 91(7):4299–4306, 1989.