9.C.2. The Second Virial Coefficient

(9.46) & (9.39) give

$$B_2(T) = -\lim_{V\to\infty} \frac{1}{2V} \int d1 \int d2\, f_{12}$$
$$= -\lim_{V\to\infty} \frac{1}{2V} \int d\mathbf{Q} \int d\mathbf{q}_{12}\, J f_{12}$$

where

$$\mathbf{Q} = \frac{1}{2}(\mathbf{q}_1 + \mathbf{q}_2) \qquad \mathbf{q}_{12} = \mathbf{q}_2 - \mathbf{q}_1$$

$\rightarrow$ $$\mathbf{q}_1 = \mathbf{Q} - \frac{1}{2}\mathbf{q}_{12} \qquad \mathbf{q}_2 = \mathbf{Q} + \frac{1}{2}\mathbf{q}_{12}$$

$$J = \begin{vmatrix} \frac{\partial \mathbf{q}_1}{\partial \mathbf{Q}} & \frac{\partial \mathbf{q}_1}{\partial \mathbf{q}_{12}} \\ \frac{\partial \mathbf{q}_2}{\partial \mathbf{Q}} & \frac{\partial \mathbf{q}_2}{\partial \mathbf{q}_{12}} \end{vmatrix} = \begin{vmatrix} \mathbf{I} & -\frac{1}{2}\mathbf{I} \\ \mathbf{I} & \frac{1}{2}\mathbf{I} \end{vmatrix} = \begin{vmatrix} \mathbf{I} & -\frac{1}{2}\mathbf{I} \\ \mathbf{0} & \mathbf{I} \end{vmatrix} = 1$$

As $V \to \infty$, boundary effects, e.g., shape of volume, become negligible.

$\therefore$ $$B_2(T) = -\frac{1}{2} \int d\mathbf{q}_{12}\, f_{12}$$
$$= -\frac{1}{2} \int d1 \left(e^{-\beta \mathcal{V}(1)} - 1\right) \qquad (9.54)$$

We shall calculate $B_2(T)$ for the hard sphere, square-well, and Lennard-Jones potentials [see Fig.9.3a].

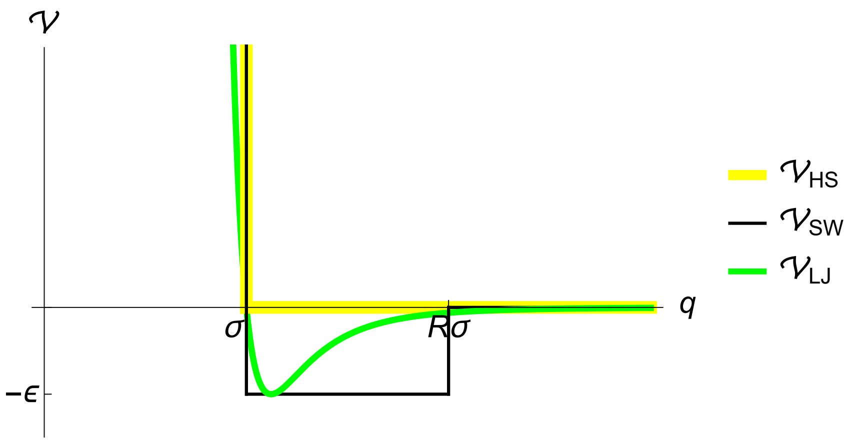


Fig.9.3a

Ex.9.2. Hard Sphere Gas

Compute $B_2(T)$ for a gas of N hard spheres of radius $\sigma/2$ confined in a volume V.
Write the equation of state as a virial expansion to 1st order in $\rho = N/V$.

Answer

The potential between a pair of hard spheres is [see Fig.9.3a]

$$\mathcal{V}_{HS}(q) = \begin{cases} \infty & q < \sigma \\ 0 & q \geq \sigma \end{cases}$$

$\rightarrow$ $$f_{12}(q)_{HS} = \begin{cases} -1 & q < \sigma \\ 0 & q \geq \sigma \end{cases}$$

Note:

Range of $\mathcal{V}_{HS}(q) =$ radius of the hard core σ

$= 2 \times$ (radius of hard sphere $\sigma/2$)

because the distance between the center of two hard spheres cannot be less then twice the radius.

(9.54) thus becomes

$$B_2(T)_{HS} = 2\pi \int_0^\sigma dq\, q^2 = \frac{2\pi}{3}\sigma^3 \equiv b_0 \qquad (2)$$

If we assume that the pair of particles occupy a volume of radius σ that no other particle can intrude, then b_0 is just the effective volume of each particle. Note that b_0 is half the hard core volume $\frac{4\pi}{3}\sigma^3$ and 4 times the particle size $\frac{4\pi}{3}\left(\frac{\sigma}{2}\right)^3$.

Introducing the dimensionless, reduced, 2nd virial coefficient as

$$B_2^*(T) = \frac{1}{b_0} B_2(T) \qquad (3)$$

we have

$$B_2^*(T)_{HS} = 1 \qquad (4)$$

The equation of state (9.43) becomes, to 1st order in N/V,

$$\frac{PV}{N k_B T} = 1 + b_0 \frac{N}{V}$$

$$\rightarrow \qquad P = \frac{N k_B T}{V\left(1 + b_0 \frac{N}{V}\right)^{-1}} \approx \frac{N k_B T}{V - N b_0}$$

Thus, the effect of $B_2(T)_{HS}$ is to reduce the volume of the gas by $N b_0$, the total effective volume of the particles. This seems reasonable since $V - N b_0$ is the volume in which the particles are free to move.

9.C.2.1. Square-Well Potential

In order to compare with the Lennard-Jones potential, we define the square-well potential as [see Fig.9.3a]

$$\mathcal{V}_{SW}(q) = \begin{cases} \infty & 0 \le q < \sigma \\ -\epsilon & \sigma \le q < R\sigma \\ 0 & R\sigma \le q \end{cases} \qquad (9.55)$$

where

$\epsilon =$ well depth (9.55a)

$\sigma =$ hard core radius

$R\sigma =$ interaction range

Hence,

$$f_{12}(q)_{SW} = \begin{cases} -1 & 0 \le q < \sigma \\ e^{\beta\epsilon} - 1 & \sigma \le q < R\sigma \\ 0 & R\sigma \le q \end{cases} \qquad (9.55b)$$

and

$$B_2(T)_{SW} = -2\pi \left[-\int_0^\sigma dq\, q^2 + \int_\sigma^{R\sigma} dq\, q^2 \left(e^{\beta\epsilon} - 1\right) \right]$$

$$= \frac{2}{3} \pi \sigma^3 \left[1 - \left(R^3 - 1\right)\left(e^{\beta \epsilon} - 1\right) \right] \qquad (9.56)$$

$$= b_0\, B_2^*(T)_{\text{SW}} \qquad (9.56a)$$

where

$$B_2^*(T)_{\text{SW}} = 1 - \left(R^3 - 1\right)\left(e^{\beta \epsilon} - 1\right)$$

$$= 1 - \left(R^3 - 1\right)\left(e^{1/T^*} - 1\right) \qquad (9.57)$$

and T^* is the dimensionless "temperature" defined by

$$T^* = \frac{1}{\beta \epsilon} = \frac{k_B T}{\epsilon} \qquad (9.57a)$$

Plot of $B_2^*(T)_{\text{SW}}$ is shown in Fig.9.4a below. Note that T^* is on log scale in order to conform with Reichl's Fig.9.4, which also shows experimental data on inert gases.

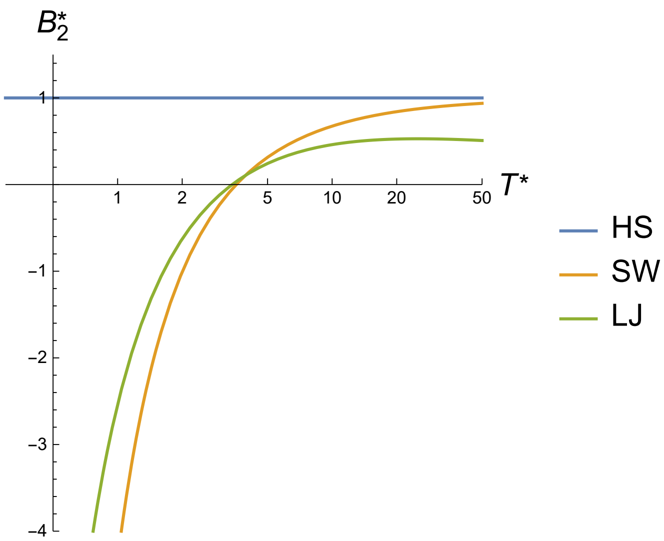


Fig.9.4a

Note that

$$\frac{\partial B_2^*(T)_{\text{SW}}}{\partial T^*} = -\frac{1}{T^{*2}} e^{1/T^*} - 1 = 0$$

has no real solutions. Therefore, $B_2^*(T)_{\text{SW}}$ increases indefinitely as T^* increases.

9.C.2.2. Lennard-Jones Potential

The Lennard-Jones 6-12 potential is given by [see Fig.9.3a]

$$\mathcal{V}_{\text{LJ}}(q) = 4 \epsilon \left[\left(\frac{\sigma}{q}\right)^{12} - \left(\frac{\sigma}{q}\right)^{6} \right] \qquad (9.58)$$

where the parameters have the same meanings described in (9.55a).

As can be easily checked either algebraically or graphically,

$$\mathcal{V}_{\text{LJ}}(\sigma) = 0 \quad \rightarrow \quad \sigma \approx \text{radius of potential core}$$

$$\frac{d\mathcal{V}_{\text{LJ}}}{dq} = 4 \epsilon \left[-\frac{12}{q}\left(\frac{\sigma}{q}\right)^{12} + \frac{6}{q}\left(\frac{\sigma}{q}\right)^{6} \right] \qquad (9.58a)$$

$\rightarrow$ min $\mathcal{V}_{\text{LJ}}$ is at $q_{\text{min}} = 2^{1/6} \sigma$

$$\mathcal{V}_{\text{LJ}}(q_{\text{min}}) = -\epsilon \quad \rightarrow \quad \epsilon = \text{depth of potential}$$

For central potentials, we can use

$$d\left[q^3 \left(e^{-\beta \mathcal{V}(q)} - 1 \right) \right] = -\beta q^3 \frac{d\mathcal{V}}{dq} e^{-\beta \mathcal{V}(q)}\, dq + 3 q^2 \left(e^{-\beta \mathcal{V}(q)} - 1 \right) dq$$

to write (9.54) as

$$B_2(T) = -\pi \int_0^\infty d\,q\,q^2\,\left(e^{-\beta \mathcal{V}(q)} - 1\right)$$
$$= -\frac{\pi}{3}\left[q^3\left(e^{-\beta \mathcal{V}(q)} - 1\right)_0^\infty + \beta \int_0^\infty d\,q\,q^3\,\frac{d\mathcal{V}}{d\,q}\,e^{-\beta \mathcal{V}(q)}\right]$$
$$= -\frac{\pi}{3}\,\beta \int_0^\infty d\,q\,q^3\,\frac{d\mathcal{V}}{d\,q}\,e^{-\beta \mathcal{V}(q)}$$

Using (9.58-a), we have,

$$B_2(T)_{\rm LJ} = \frac{4\,\pi}{3}\,\beta\,\epsilon \int_0^\infty d\,q\,q^2\,\left[12\left(\frac{\sigma}{q}\right)^{12} - 6\left(\frac{\sigma}{q}\right)^6\right]\exp\left\{-4\,\beta\,\epsilon\left[\left(\frac{\sigma}{q}\right)^{12} - \left(\frac{\sigma}{q}\right)^6\right]\right\}$$

Setting

$$x = \frac{q}{\sigma} \qquad\qquad B_2(T)_{\rm LJ} = b_0\,B_2^*(T)_{\rm LJ} \qquad\qquad (9.58b)$$

and using (9.57a), we have

$$B_2^*(T)_{\rm LJ} = \frac{4}{T^*}\int_0^\infty d\,x\,x^2\,\left[12\left(\frac{1}{x}\right)^{12} - 6\left(\frac{1}{x}\right)^6\right]\exp\left\{-\frac{4}{T^*}\left[\left(\frac{1}{x}\right)^{12} - \left(\frac{1}{x}\right)^6\right]\right\} \qquad (9.59)$$

Let

$$\xi^2 = \frac{4}{T^*}\left(\frac{1}{x}\right)^{12} \qquad \to \qquad \xi = \frac{2}{\sqrt{T^*}}\left(\frac{1}{x}\right)^6$$

then

$$x = \left(\frac{2}{\sqrt{T^*}\;\xi}\right)^{1/6}, \qquad x^2\,d\,x = -\frac{1}{6}\left(\frac{2}{\sqrt{T^*}}\right)^{1/2}\,\xi^{-3/2}\;d\,\xi$$

(9.59) becomes

$$B_2^*(T)_{\rm LJ} = \frac{2^{3/2}}{T^{*\,5/4}}\int_0^\infty d\,\xi\,\xi^{-1/2}\,\left(T^*\,\xi - \sqrt{T^*}\,\right)e^{-\xi^2}\,e^{2\,\xi/\sqrt{T^*}}$$
$$= \frac{2^{3/2}}{T^{*\,5/4}}\sum_{n=0}^\infty \frac{1}{n!}\left(\frac{2}{\sqrt{T^*}}\right)^n \int_0^\infty d\,\xi\,\xi^{n-1/2}\,\left(T^*\,\xi - \sqrt{T^*}\,\right)e^{-\xi^2}$$

In terms of the Gaussian integrals [see “9.C.2_Code.nb”]

$$G(m) = \int_0^\infty d\,\xi\,\xi^m\,e^{-\xi^2} \;= \frac{1}{2}\Gamma\left(\frac{m+1}{2}\right)$$

we have

$$B_2^*(T)_{\rm LJ} = \frac{2^{3/2}}{T^{*\,5/4}}\sum_{n=0}^\infty \frac{2^n}{n!}\left[T^{*\,1-n/2}\,G\left(n+\frac{1}{2}\right) - T^{*\,(1-n)/2}\,G\left(n-\frac{1}{2}\right)\right]$$
$$= \frac{2^{3/2}}{T^{*\,5/4}}\left[\sum_{n=0}^\infty \frac{2^n}{n!}\,T^{*\,1-n/2}\,G\left(n+\frac{1}{2}\right) - \sum_{n=1}^\infty \frac{2^{n-1}}{(n-1)!}\,T^{*\,1-n/2}\,G\left(n-\frac{3}{2}\right)\right]$$
$$= \frac{2^{3/2}}{T^{*\,5/4}}\left[T^*\,G\left(\frac{1}{2}\right) + \sum_{n=1}^\infty T^{*\,1-n/2}\;\frac{2^n}{n!}\left[G\left(n+\frac{1}{2}\right) - \frac{n}{2}\,G\left(n-\frac{3}{2}\right)\right]\right]$$
$$= 2^{3/2}\,T^{*-1/4}\,G\left(\frac{1}{2}\right) + \sum_{n=1}^\infty T^{*\,-(1+2\,n)/4}\;\frac{2^{n+3/2}}{n!}\left[G\left(n+\frac{1}{2}\right) - \frac{n}{2}\,G\left(n-\frac{3}{2}\right)\right]$$

$$= \sum_{n=0}^{\infty} T^{*\,-(1+2n)/4} \frac{2^{n+3/2}}{n!}\left[G\left(n+\frac{1}{2}\right)-\frac{n}{2}G\left(n-\frac{3}{2}\right)\right]$$

$$= \sum_{n=0}^{\infty} T^{*\,-(1+2n)/4}\,\alpha_n \qquad (9.60)$$

where

$$\alpha_n = \frac{2^{n+3/2}}{n!}\left[G\left(n+\frac{1}{2}\right)-\frac{n}{2}G\left(n-\frac{3}{2}\right)\right]$$

$$= \frac{2^{n+1/2}}{n!}\left[\Gamma\left(\frac{2n+3}{4}\right)-\frac{n}{2}\Gamma\left(\frac{2n-1}{4}\right)\right]$$

$$= \frac{2^{n+1/2}}{n!}\left(\frac{2n-1}{4}-\frac{n}{2}\right)\Gamma\left(\frac{2n-1}{4}\right) \qquad [\,n\,\Gamma(n)=\Gamma(n+1)\,]$$

$$= -\frac{2^{n+1/2}}{n!}\,\frac{1}{4}\,\Gamma\left(\frac{2n-1}{4}\right) \qquad (9.61)$$

The values of the first 7 values are [see “9.C.2_Code.nb” & Reichl’s Table 9.1]

n	0	1	2	3	4	5	6
α_n	1.733	-2.56369	-0.8665	-0.427282	-0.216625	-0.106821	-0.0505459

Some values for the reduced second virial coefficient as calculated using (9.60) are [see “9.C.2_Code.nb” & Reichl’s Table 9.2]

T^*	0.3	0.4	0.5	0.6	0.7
B_2^*	-27.8806	-13.7988	-8.72021	-6.19797	-4.71004

The convergence of the series is slow for small T^*, the results for summing only 5 terms are listed below

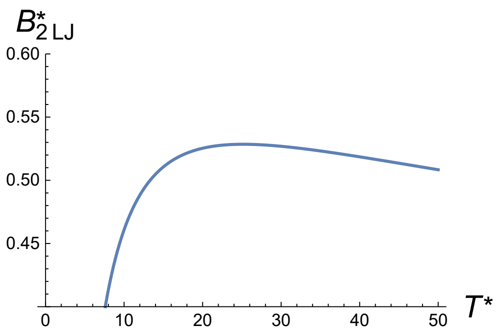
T^*	0.3	0.4	0.5	0.6	0.7
B_2^*	-17.5794	-10.7955	-7.49785	-5.59594	-4.37446

and those for summing 10 terms:

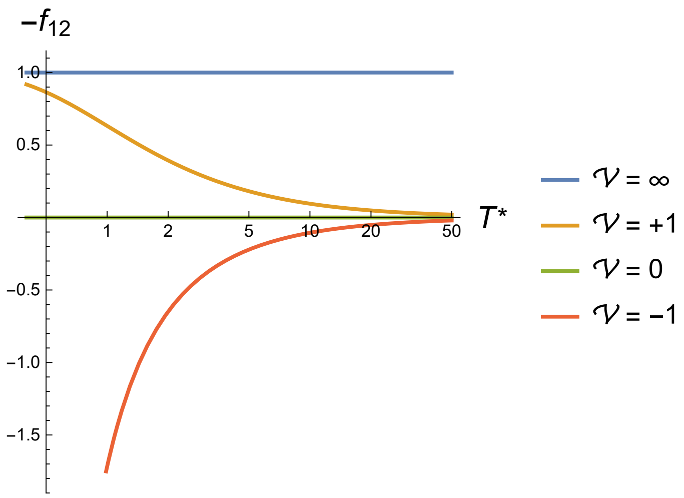
T^*	0.3	0.4	0.5	0.6	0.7
B_2^*	-26.0355	-13.5115	-8.6498	-6.17527	-4.70124

Plot of $B_2^*(T)_{\mathrm{LJ}}$ can be found in Fig.9.4a.

Note that $B_2^*(T)_{\mathrm{LJ}}$ has a maximum, as the following blow-up of the “knee” region clearly shows.



To explain this knee, which is absent in $B_2^*(T)_{\mathrm{SW}}$, we plot $-f_{12}$ vs T^* for 4 constant potentials.



As expected, both $\mathcal{V} = \infty$ and $\mathcal{V} = 0$ are T^* independent. Furthermore,

$$-f_{12} \begin{pmatrix} \text{decreases} \\ \text{increases} \end{pmatrix} \text{with increasing } T^* \text{ for} \begin{pmatrix} \mathcal{V} > 0 \\ \mathcal{V} < 0 \end{pmatrix}$$

Thus, the temperature dependence comes only from the attractive part of $\mathcal{V}_{SW}$. Therefore, $B_2^*(T)_{SW}$, as the integral of $-f_{12}/2\,V$, must be monotonically increasing with T^*.

In contrast, both repulsive & attractive parts of $\mathcal{V}_{LJ}$ contribute and we expect an extremum in $B_2^*(T)_{LJ}$. As a moderate modification of $B_2^*(T)_{SW}$, the extremum can only be a maximum, as observed.

As can be seen in Reich's Fig.9.4, excellent agreement was found between $B_2^*(T)_{LJ}$ and the measured data for all inert gases except He, for which quantum effects cannot be ignored.

Finally, we mention how to extract the values of ϵ & σ from experiments.

To begin, what is measured is $B_2(T)$ as a function of T. Next, $B_2^*(T^*)_{LJ}$ is a function of ϵ through $T^* = \dfrac{k_B T}{\epsilon}$, and is independent of σ [see (9.59)]. Since [see (9.58b)]

$$B_2^*(T^*)_{LJ} = \frac{1}{b_0} B_2(T)_{LJ}$$

we can replace $B_2(T)_{LJ}$ with the experimental data $B_2(T)_{exp}$ to get

$$\frac{B_2^*(T_1^*)_{LJ}}{B_2^*(T_2^*)_{LJ}} = \frac{B_2(T_1)_{exp}}{B_2(T_2)_{exp}} \qquad (9.62)$$

where T_1 and T_2 are two arbitrary temperatures. (9.62) can be solved for ϵ.

Once ϵ is known, we can get $\sigma = \left(\dfrac{3\,b_0}{2\,\pi}\right)^{1/3}$ from

$$b_0 = \frac{B_2(T_1)_{exp}}{B_2^*(T_1^*)_{LJ}} \qquad (9.63)$$

The 3 parameters R, σ & ϵ for $\mathcal{V}_{SW}$ can likewise be obtained from 3 data points.

Values of σ & ϵ thus obtained for a few gases are listed in Reichl's Table 9.3.