Application of Statistical Mechanics

Imperfect gases

Lecture 4: B_2 for imperfect gases

Recap of 3rd lecture

- 1st part of calculation of Second Virial Coefficient B_2

    - Pairwise additivity:

$$U_{tot} = \sum_{i>j} U(r_{ij})$$

    - Introduced Mayer f-function f:

$$e^{-\beta U(r_{ij})} \equiv 1 + f(r_{ij})$$

    - Configuration integral:

$$Z_N = V^N + N(N-1)V^{N-1}b + \ldots$$

$$b = 2\pi \int_0^\infty f(r)r^2 dr$$

Configuration integral

$$Z_N = V^N + N(N-1)V^{N-1}b + \ldots \qquad b = 2\pi \int_0^\infty f(r)r^2 dr$$

Assumption

Second term in expansion is small compared to first term

$$\frac{N^2 b}{V} \ll 1$$

Strategy to obtain B_2

$\checkmark$

$$Z_N = \int_V e^{-\beta U(x_1,\ldots,z_N)} dx_1 \cdots dz_N$$

today

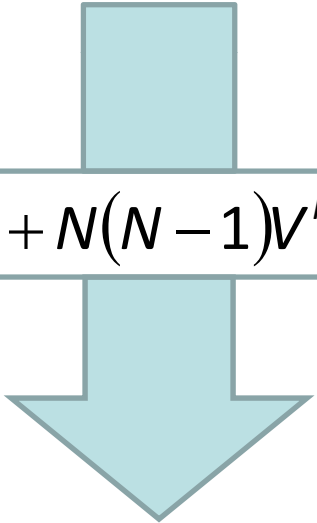$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$p = k_B T \left(\rho + B_2 \rho^2 + B_3 \rho^3 + \ldots \right)$$

Classical partition function Q

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

$$Z_N = V^N + N(N-1)V^{N-1}b + \ldots$$

$$Q_{class} = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \frac{V^N}{N!} \left[1 + \frac{N^2 b}{V} + \ldots \right] \qquad \left(\frac{N^2 b}{V} \ll 1 \right)$$

Strategy to obtain B$_2$

$$Z_N = \int_V e^{-\beta U(x_1,\ldots,z_N)} dx_1 \cdots dz_N$$

$$Q_{class} = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_N$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$p = k_B T\left(\rho + B_2 \rho^2 + B_3 \rho^3 + \ldots\right)$$

Calculation of the pressure

• pressure from the classical partition function

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$p = k_B T \left(\rho - b\rho^2 + \ldots \right)$$

Strategy to obtain B$_2$

✔ $$Z_N = \int_V e^{-\beta U(x_1,\ldots,z_N)} dx_1 \cdots dz_N$$

✔ $$Q_{class} = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_N$$

✔ $$p = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$p = k_B T\left(\rho + B_2\rho^2 + B_3\rho^3 + \ldots\right)$$

Compare to virial expansion

$$p = k_B T \left(\rho - b\rho^2 + \ldots \right)$$

$$p = k_B T \left(\rho + B_2 \rho^2 + B_3 \rho^3 + \ldots \right)$$

B$_2$: second virial coefficient

$$B_2 = -b = -2\pi \int_0^\infty f(r) r^2 dr$$

$$f(r) \equiv e^{-\beta U(r)} - 1$$

Second Virial Coefficient $B_2(T)$

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1\right) r^2 dr$$

(1st year states of matter)

Perfect gas limit: $U(r) = 0$

$$B_2(T) = -2\pi \int_0^\infty (1-1) r^2 dr = 0$$

(of course)
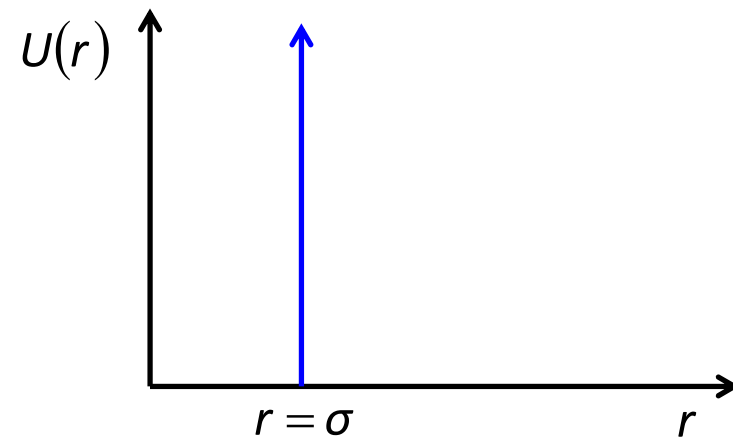
Content of the course

- Canonical Ensemble (recap)

- Classical Statistical Mechanics

- Second Virial Coefficient B_2

- *B_2 for imperfect gases*

    - *Hard spheres*

    - *Square well*

    - *Van der Waals*

B₂(T) for hard spheres

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1\right) r^2 dr$$

hard sphere potential:

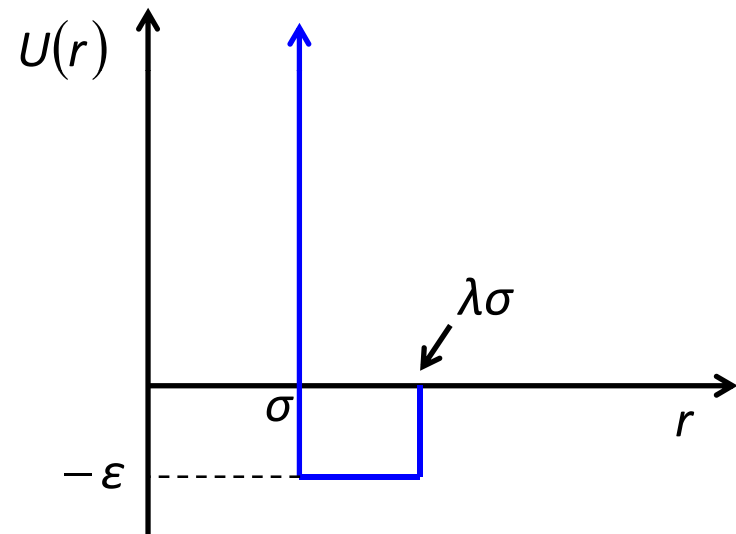$$U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

$U(r)$

$r = \sigma$ r

$$B_2 = \frac{2\pi\sigma^3}{3}$$

$B_2(T)$ for a square well potential

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1 \right) r^2 dr$$

square well potential:

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \le r \le \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

$$B_2 = \frac{2\pi\sigma^3}{3}\left\{ 1 - \left(\lambda^3 - 1\right)\left(e^{\beta\varepsilon} - 1\right) \right\}$$

(problem 4)

So …

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1 \right) r^2 dr$$
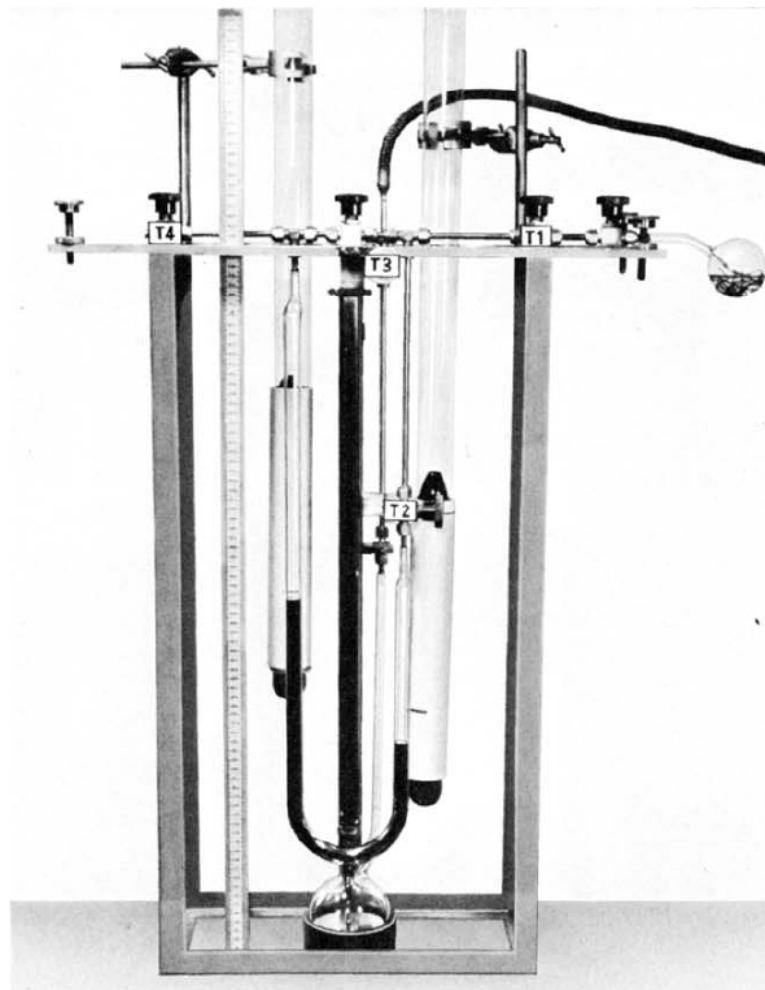
we can calculate B_2 for these models …

But we can also measure B_2 !

A Student Apparatus for Measuring the
Second Virial Coefficients of Vapors

Maurice L. Martin
and Peter J. Dunlop
University of Adelaide
Adelaide, South Australia

Journal of Chemical Education
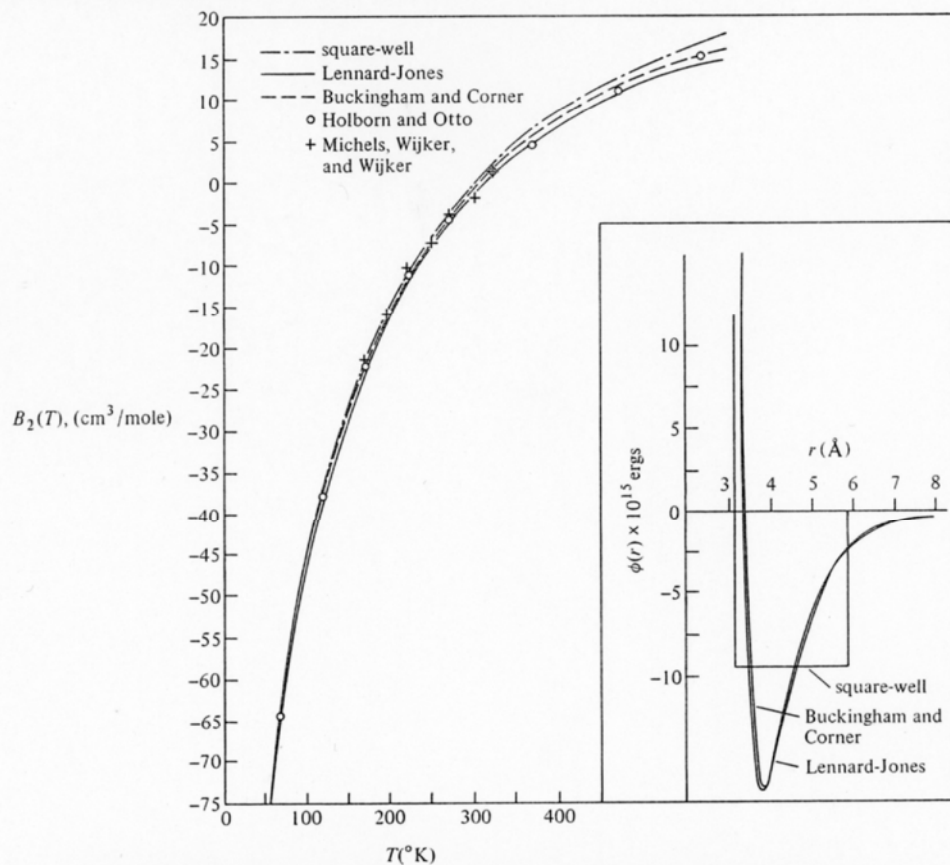
Measurements of B_2 ...

Figure 12–5. Second virial coefficients for argon calculated for several molecular models. The potential functions obtained from the experimental $B_2(T)$ data are also shown. (The experimental data are those of L. Holborn and J. Otto, *Z Physik*, **33**, 1, 1925, and A. Michels, Hub. Wijker, and Hk. Wijker, *Physica*, **15** 627, 1949, from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, New York: Wiley 1954.)

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1 \right) r^2 dr$$

square well potential:

$$U(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

Lennard-Jones potential:

$$U(r) = 4\varepsilon \left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right]$$

… lead to pair potential parameters

Table 12–3. Potential parameters determined from second virial coefficient data

substance	potential	λ	$\sigma(\text{Å})$	$\varepsilon/k(°\text{K})$
argon	SW	1.70	3.067	93.3
	LJ		3.504	117.7
krypton	SW	1.68	3.278	136.5
	LJ		3.827	164.0
methane	SW	1.60	3.355	142.5
	LJ		3.783	148.9
xenon	SW	1.64	3.593	198.5
	LJ		4.099	222.3
tetrafluoromethane	SW	1.48	4.103	191.1
	LJ		4.744	151.5
neopentane	SW	1.45	5.422	382.6
	LJ		7.445	232.5
nitrogen	SW	1.58	3.277	95.2
	LJ		3.745	95.2
carbon dioxide	SW	1.44	3.571	283.6
	LJ		4.328	198.2
n-pentane	SW	1.36	4.668	612.3
	LJ		8.497	219.5
benzene	SW	1.38	4.830	620.4
	LJ		8.569	242.7

Source: A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.*, **41**, p. 429, 1964.

description of gases beyond perfect gas behaviour

Content of the course

- Canonical Ensemble (recap)

- Classical Statistical Mechanics

- Second Virial Coefficient B_2

- B_2 for imperfect gases

  - *Hard spheres*

  - *Square well*

  - *Van der Waals*

Back to the Van der Waals
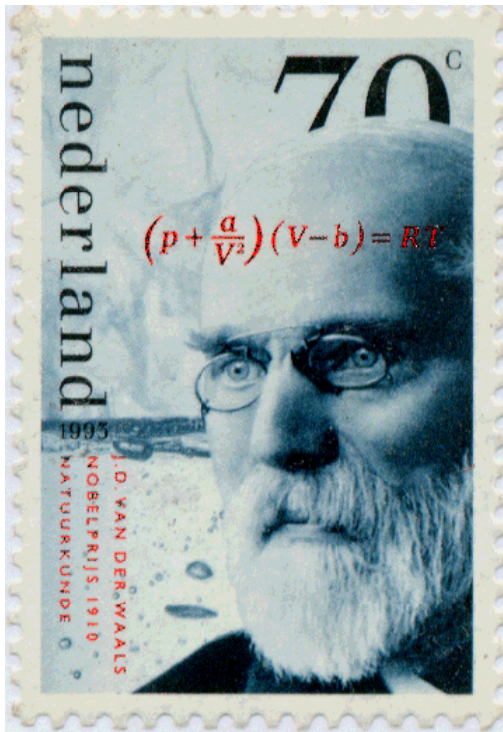

1st lecture

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp\left[\frac{aN^2}{Vk_B T} \right]$$
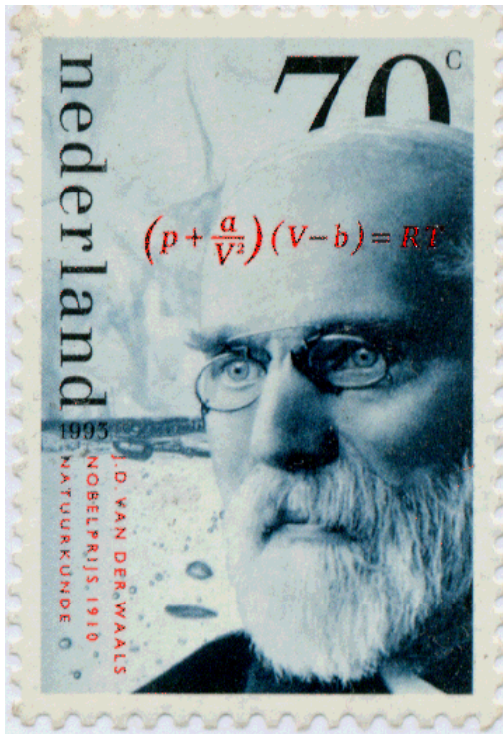
Van der Waals gas

$$P = \frac{Nk_B T}{V - Nb} - a\left(\frac{N}{V} \right)^2$$

Later on: expressions for *a* and *b* (see also problem set)
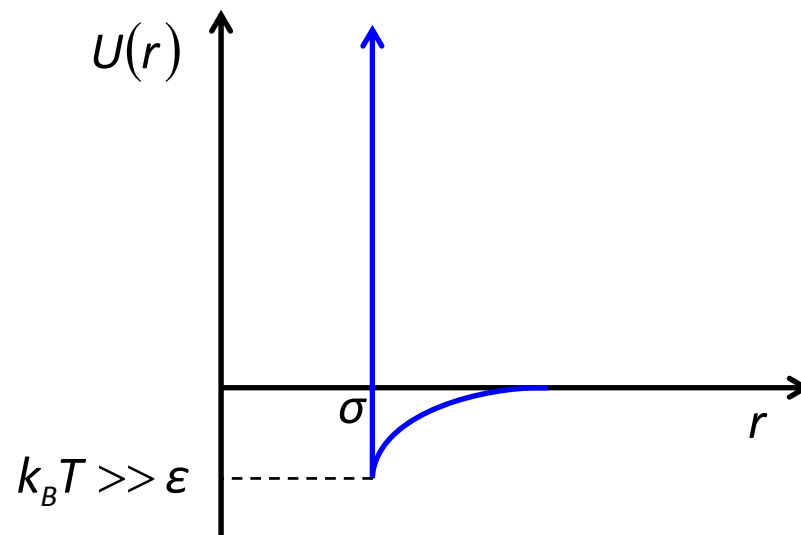
now

V/d Waals in terms of virial expansion

$$P = \frac{Nk_BT}{V - Nb} - a\left(\frac{N}{V}\right)^2$$

$$P = k_BT\left[\rho + \underbrace{\left(b - \frac{a}{k_BT}\right)}_{B_2}\rho^2 + \ldots\right]$$

Potential: hard core repulsion + weak attraction

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1 \right) r^2 dr$$

Potential of this form:

The Van der Waals parameters *a & b*

problem 5

$$a = -2\pi \int_{\sigma}^{\infty} U(r) r^2 \, dr$$ $\longrightarrow$ attractive interaction

$$b = 2\pi \int_{0}^{\sigma} r^2 \, dr = \frac{2\pi\sigma^3}{3}$$ $\longrightarrow$ excluded volume

Summary Imperfect Gases

- 6N-dimensional phase space

$$(p_x, p_y, p_z, x, y, z) = (p, \tau)$$

- Classical partition function

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

- Configuration integral

$$Z_N = \int_V e^{-\beta U(x_1, \ldots, z_N)} dx_1 \cdots dz_N$$

- Pairwise additivity

$$U_{tot} = \sum_{i>j} U(r_{ij})$$

- Mayer f-function

$$e^{-\beta U(r_{ij})} \equiv 1 + f(r_{ij})$$

- Second virial coefficient

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1 \right) r^2 dr$$

- $B_2(T)$ for imperfect gases (hard sphere, square well, Van der Waals)

Thanks and …

… that's all!