

Fundamentals of Condensed Matter (lecture 3)



Summary lecture 2

- Recap statistical mechanics

- Boltzmann distribution
- Canonical partition function
- Link to thermodynamics

- Classical statistical mechanics

- 6N-dimensional phase space
- Classical canonical partition function
- Classical configuration integral

$$P_i = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} = \frac{e^{-\beta E_i}}{Q}$$

$$Q = \sum_i e^{-E_i/k_B T}$$

$$A = -k_B T \ln Q$$

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

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

$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$

Content of the Liquids part (lectures 1-6)

- Recap thermodynamics and phase diagrams
- Recap statistical mechanics and classical statistical mechanics
- **Second virial coefficient and model liquids** → Today, lecture (3)
- Structure of liquids and compressibility relation
- Ornstein-Zernike relation and link to (scattering) experiments
- Complex and biological fluids

Today's lecture (3)

- From configuration integral to second virial coefficient
 - Pairwise additivity
 - Mayer functions
 - Second virial coefficient B_2
- Second virial coefficient for model liquids
 - Hard spheres and square well potentials
 - Van der Waals equations of state
 - Law of corresponding states (again)

Imperfect gases: Virial expansion

$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$$

$$\rho = \frac{N}{V}$$

B_2 : second virial coefficient \rightarrow relates interaction to thermo

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

Today's lecture: derive this expression for B_2

Strategy to obtain B_2



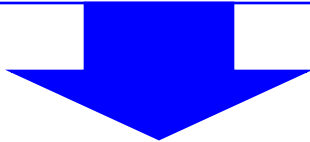
$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$



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



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



$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$$

Pairwise additivity

- Potential energy between **pair of particles** = **pair potential (or pair interaction) ϕ**
only depends on distance

$$U(r_{ij}) \equiv \phi(r_{ij}) = \phi_{ij}$$

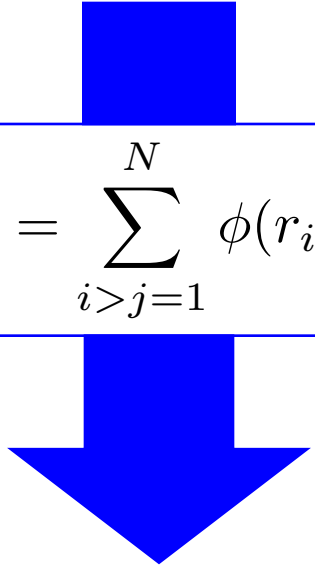
- Total potential energy = sum of potential energy contributions
between each pair of molecules (pair potential ϕ)

$$U_{tot} = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij})$$

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

Classical Configuration Integral Z_N

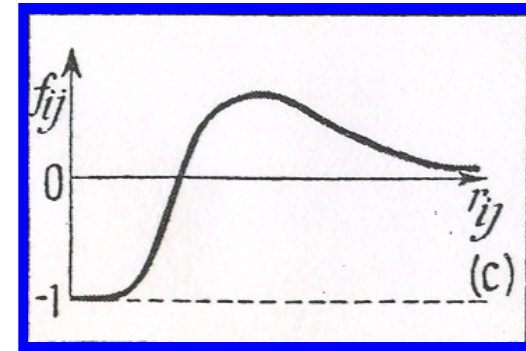
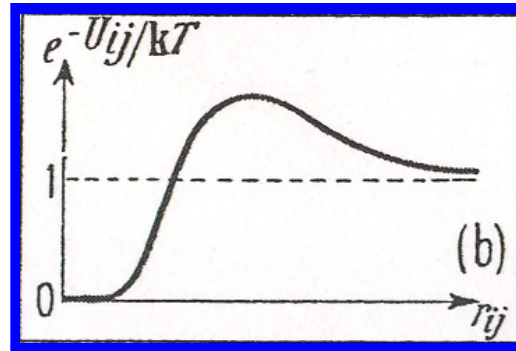
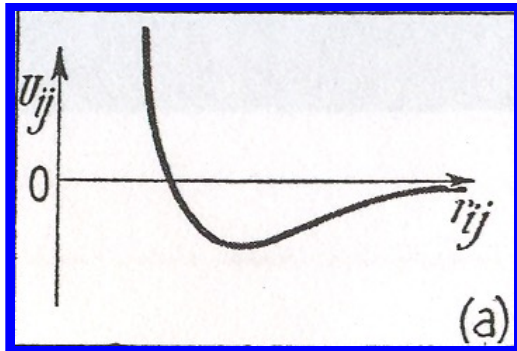
$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$


$$U = \sum_{i>j=1}^N \phi(r_{ij})$$

$$Z_N = \int \cdots \int e^{-\beta \sum_{i>j} \phi(r_{ij})} d\tau_1 \cdots d\tau_N$$

Cracking $Z_N \dots$: Mayer f -function $f(r_{ij})$

$$f(r_{ij}) = e^{-\beta\phi(r_{ij})} - 1$$



f_{ij} vanishes for large distances, i.e., when two particles are far apart

$$Z_N = \int \cdots \int \prod_{i>j} (1 + f_{ij}) d\tau_1 \cdots d\tau_N$$

Expanding the product ...

Only writing down terms that involve one or less Mayer function f_{ij}

Example: N=3

$N=3$

$$\prod_{i>j} (1 + f_{ij}) = (1 + f_{21}) (1 + f_{31}) (1 + f_{32})$$

$$= (1 + f_{21} + f_{31} + f_{21}f_{31}) (1 + f_{32})$$

$$= 1 + f_{21} + f_{31} + f_{32} + f_{21}f_{31} + f_{21}f_{32} + f_{31}f_{32} + f_{21}f_{31}f_{32}$$

pair-terms

higher order terms

General:

$$\prod_{i>j}^N (1 + f_{ij}) = 1 + \sum_{i>j} f_{ij} + \dots$$

Z_N in terms of Mayer f -functions

$$Z_N = \underbrace{\int \cdots \int d\tau_1 \cdots d\tau_N}_{\text{perfect gas}} + \underbrace{\int \cdots \int \sum_{i>j} f_{ij} d\tau_1 \cdots d\tau_N}_{\text{corrections to perfect gas}} + \cdots$$

perfect gas



V^N

corrections to perfect gas



continue ...

Z_N continued ...

$$Z_N = V^N + \underbrace{\int \cdots \int \sum_{i>j} f_{ij} d\tau_1 \cdots d\tau_N}_{\text{... each pair gives the same contribution ...}} + \dots$$

... each pair gives the same contribution ...


... $N(N-1)/2$ pairs ...

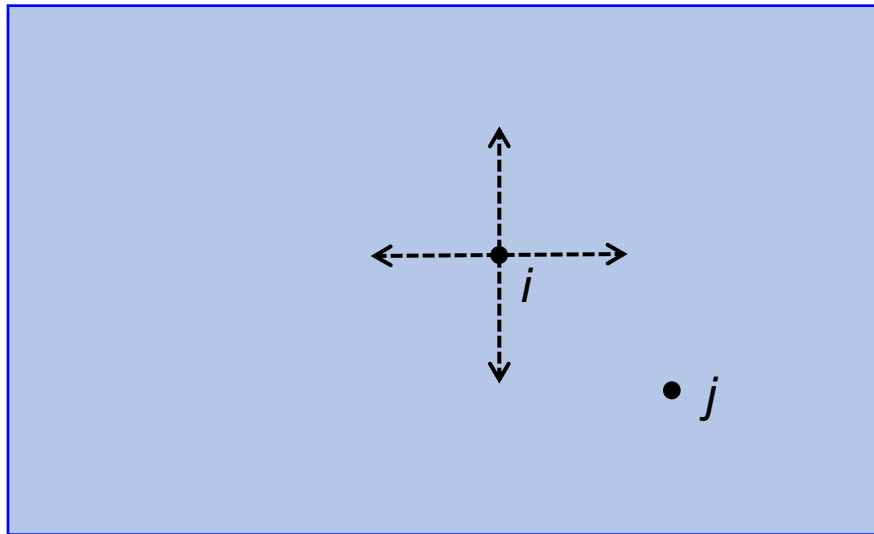


$$Z_N = V^N + \frac{N(N-1)}{2} \underbrace{\int \cdots \int f_{ij} d\tau_1 \cdots d\tau_N}_{\text{crack this (1)}} + \dots$$

Intermezzo: crack (1)

$$\int \cdots \int f_{ij} d\tau_1 \cdots d\tau_N =$$



crack (1) cont'd

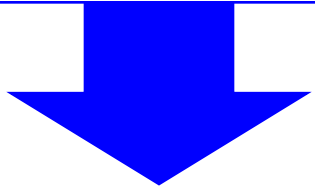


- choose position of particle j
- integrate over all positions of i
- integral same for all positions of j
- integral independent of position of j

Back to Z_N and short-hand notation for integral

$$Z_N = V^N + \frac{N(N-1)}{2} V^{N-1} \int_0^\infty 4\pi f(r) r^2 dr + \dots$$


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


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

Strategy to obtain B_2

✓

$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$

→

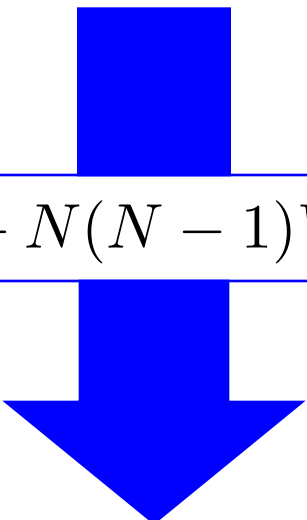
$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N$$

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

$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$$

Classical partition function Q

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


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

Assumption

Second term in expansion is small compared to first term

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

Strategy to obtain B_2

✓

$$Z_N = \int \cdots \int e^{-\beta U(x_1, \dots, z_N)} d\tau_1 \cdots d\tau_N$$

✓

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

→

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

$$p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$$

Calculate the pressure to obtain B_2

pressure in terms of the classical canonical partition function

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



Compare to virial expansion

$$\left\{ \begin{array}{l} p = k_B T (\rho - b\rho^2 + \dots) \\ p = k_B T (\rho + B_2\rho^2 + B_3\rho^3 + \dots) \end{array} \right.$$

Second virial coefficient B_2 :

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

$$\left[f(r) = e^{-\beta\phi(r)} - 1 \right]$$

Second Virial Coefficient $B_2(T)$

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

Perfect gas limit: $\phi(r) = 0$

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

(of course)

Today's lecture (3)

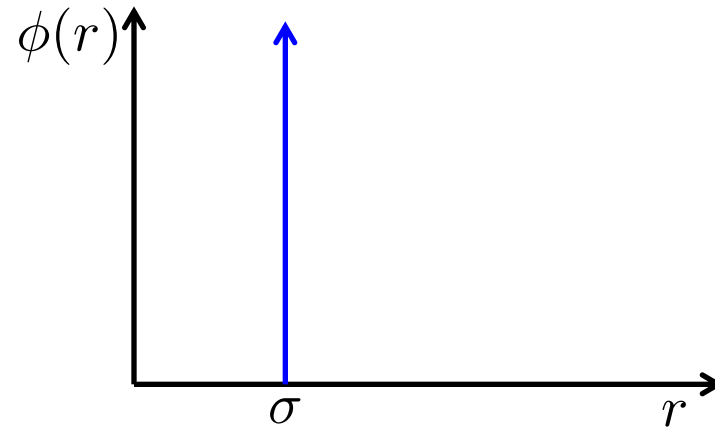
- From configuration integral to second virial coefficient
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- Second virial coefficient for model liquids
 - Hard sphere and square well potentials
 - Van der Waals equation of state
 - Law of corresponding states (again)

$B_2(T)$ for hard spheres

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

hard sphere potential:

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



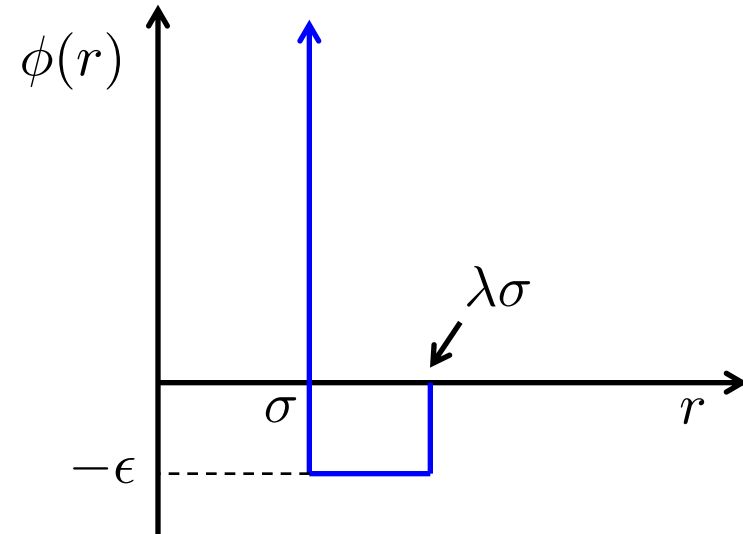
$$B_2 = \frac{2\pi\sigma^3}{3}$$

$B_2(T)$ for a square well potential

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

square well potential:

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



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

(problem set)

So ...

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

we can calculate B_2 for these model potentials ...

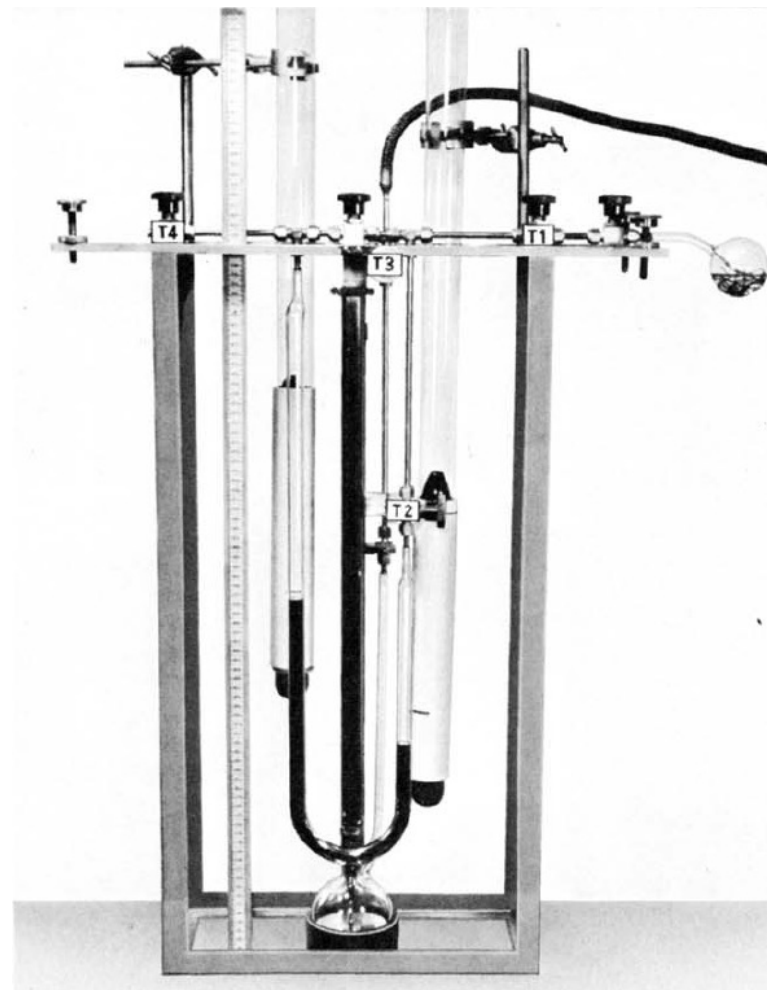
But we can also measure B_2 !

**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

Volume 46, Number 9, September 1969 / 615



Measurements of B_2 ...

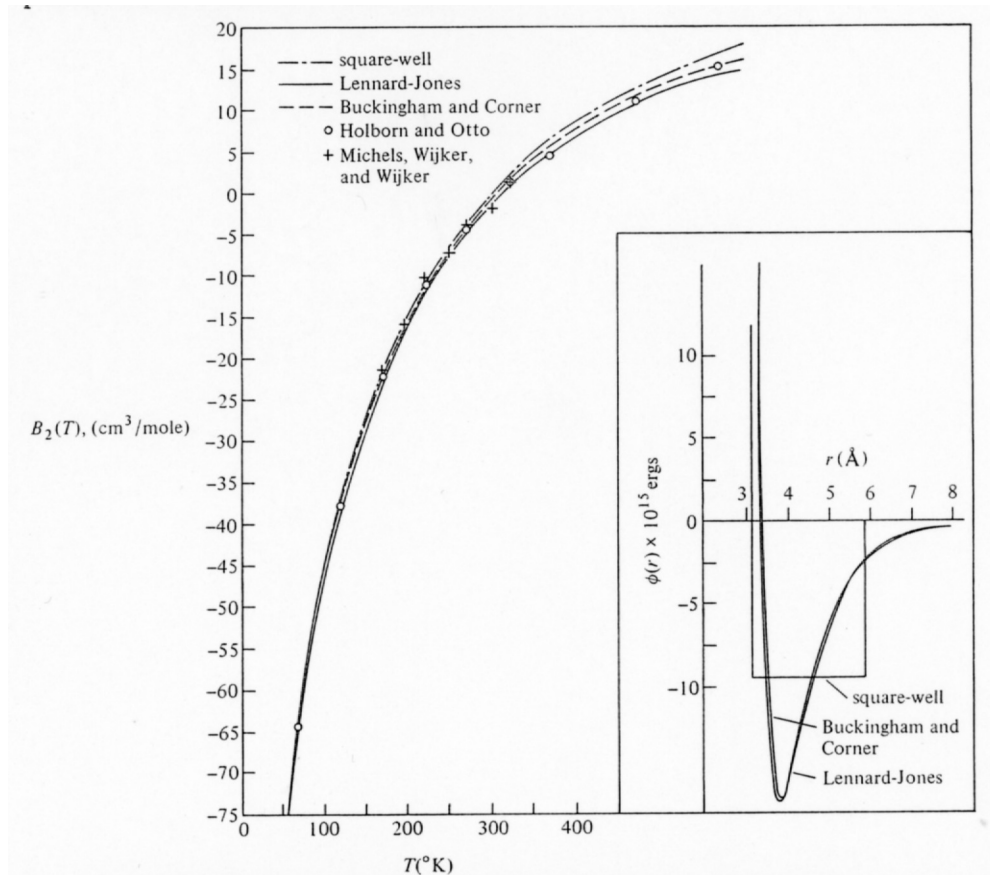


Figure 12-5. Second virial coefficients for argon calculated for several molecular models. The potential functions obtained from the experimental $B_2(T)$ data are also shown. (The experimental data are those of L. Holborn and J. Otto, *Z Physik*, 33, 1, 1925, and A. Michels, Hb. Wijker, and Hk. Wijker, *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.)

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

square well potential:

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

Lennard-Jones potential:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

... lead to pair potential parameters

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

substance	potential	λ	$\sigma(\text{\AA})$	$\epsilon/k(^{\circ}\text{K})$
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
<i>n</i> -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

Back to the Van der Waals

from 2nd lecture:

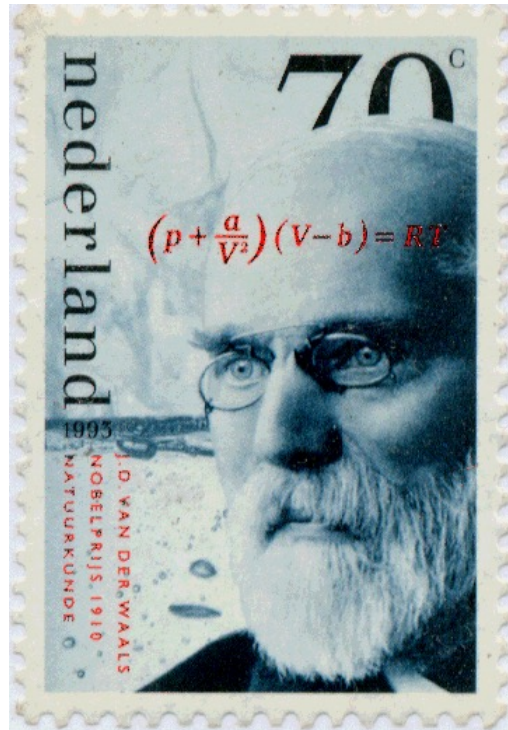
$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp \left[\frac{aN^2}{Vk_B T} \right]$$

Van der Waals equations of state:

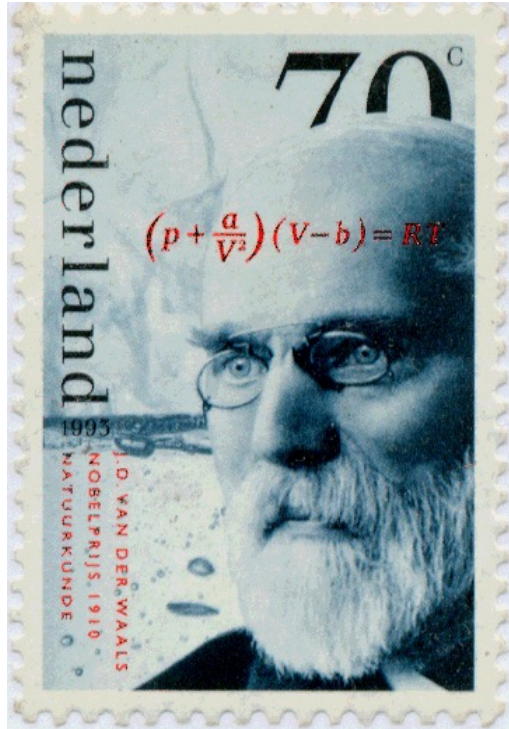
$$p = \frac{Nk_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2$$

expressions for a and b (see also problem set)

now



Van der Waals in terms of virial expansion



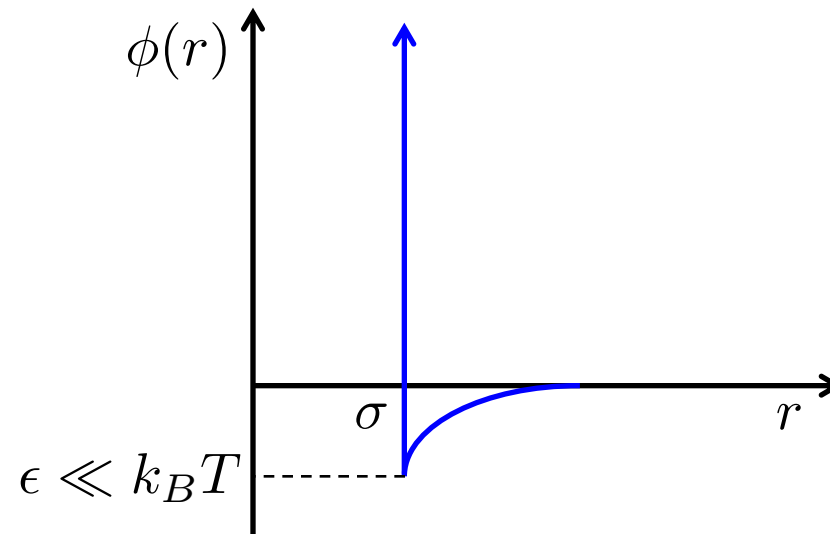
$$p = \frac{Nk_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2$$

$$p = k_B T \left[\rho + \underbrace{\left(b - \frac{a}{k_B T} \right)}_{B_2} \rho^2 + \dots \right]$$

Potential: hard core repulsion + weak attraction

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

Potential of this form:



From B_2 to the van der Waals parameters a & b

see problem set

$$a = -2\pi \int_{\sigma}^{\infty} \phi(r) r^2 dr \quad \longrightarrow \quad \text{attractive interactions}$$

$$b = 2\pi \int_0^{\sigma} r^2 dr = \frac{2\pi\sigma^3}{3} \quad \longrightarrow \quad \text{excluded volume}$$

Law of Corresponding States: Lennard-Jones potential

see problem set (extra)

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Reduced quantities:

$$y = \frac{r}{\sigma} \quad p^* = \frac{p\sigma^3}{\epsilon} \quad \rho^* = \rho\sigma^3 \quad T^* = \frac{k_B T}{\epsilon}$$

a)
$$B_2^*(T^*) = B_2(T)/\sigma^3$$

b)
$$\frac{p^*}{\rho^* T^*} = 1 + B_2^* \rho^* + B_3^* \rho^{*2} + \dots$$

All systems described by Lennard-Jones potential have the same equation of state expressed in reduced quantities

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- Recap thermodynamics and phase diagrams
- Recap statistical mechanics and classical statistical mechanics
- Second virial coefficient and model liquids
- **Structure of liquids and compressibility relation**
- Ornstein-Zernike relation and link to (scattering) experiments
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Next lecture (4)