Application of Statistical Mechanics

Imperfect gases

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Recommended literature

- Introduction to Statistical Mechanics by G.S. Rushbrooke, Oxford University Press, (1964 or another edition)
- Introduction to Statistical Thermodynamics by T.L. Hill, Dover Publications, New York (1986)
- Statistical Mechanics by D.A. McQuarrie, University Science Books, Sausalito (2000)

Lecture slides: *http://dullens.chem.ox.ac.uk/main/teaching.html*

Imperfect gases?

- Low densities: all perfect gas

$$p = \rho k_B T \qquad \text{with } \rho = \frac{N}{V}$$

- Deviations at higher densities: Virial expansion

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

- Higher order terms: account for intermolecular interactions

Goal: develop statistical mechanics to derive expression for B_2 in terms of intermolecular potential

Content of the course

- Canonical Ensemble (recap)
- Classical Statistical Mechanics
- Second Virial Coefficient B_2
- B_2 for imperfect gases

Macroscopic properties of 10^{23} molecules?

Thermodynamics

• Description of macroscopic systems (10^{23} molecules) in equilibrium

• Variables like volume, pressure, temperature, ….

$$p = \rho k_B T$$

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

• No interpretation or explanation at the molecular level

Macroscopic properties of 10^{23} molecules?

<u>Quantum/Classical mechanics</u>

• Description on a microscopic, i.e. molecular, level

$$\hat{H}\psi_{\mathrm{i}} = \varepsilon_i \psi_{\mathrm{i}}$$

• How to calculate macroscopic properties from molecular properties?

each (pointlike) molecule is described by 3 position and 3 momentum coordinates: *6N* variables required … hmmm…

We have to use a statistical approach to tackle this

Statistical Mechanics:
independent systems

From 2nd year stat mech:

Boltzmann distribution

$$P_i = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

Molecular partition function

$$q = \sum_i e^{-\beta\varepsilon_i}$$

Partition function for a particle of mass *m* in 3D:

$$q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V$$

Statistical Mechanics:
independent systems

From 2nd year stat mech:

Example: average internal energy per particle

$$E = Nk_BT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$$

<u>Equipartition!</u>

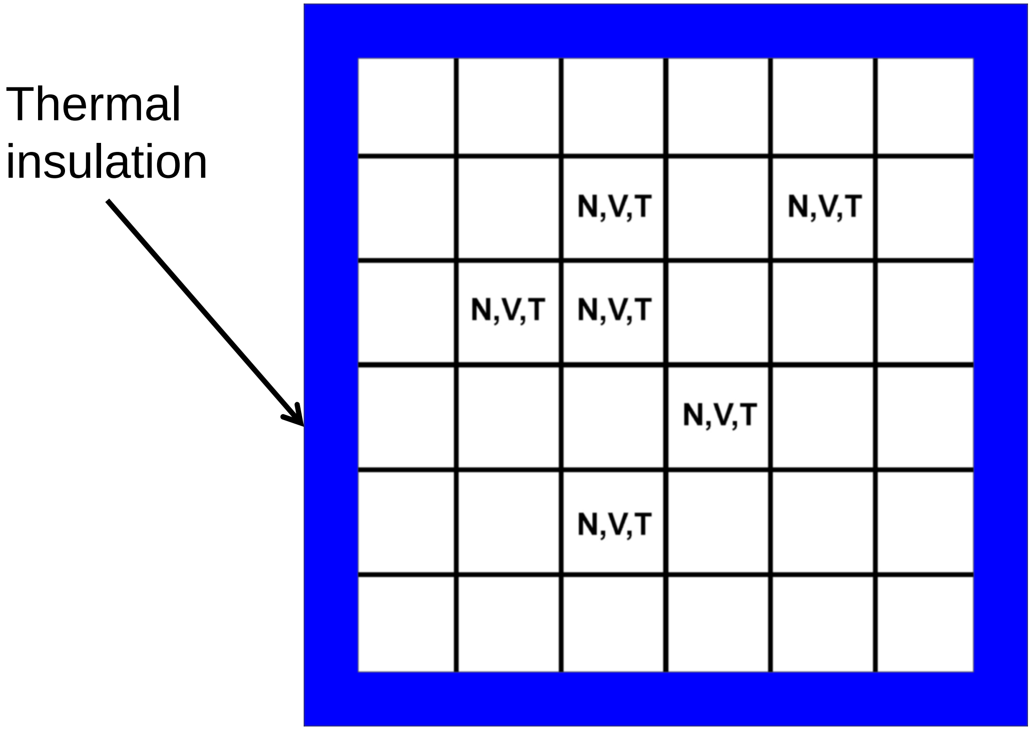
Statistical Mechanics:
interacting systems

<u>Canonical Ensemble</u>

Canonical Ensemble

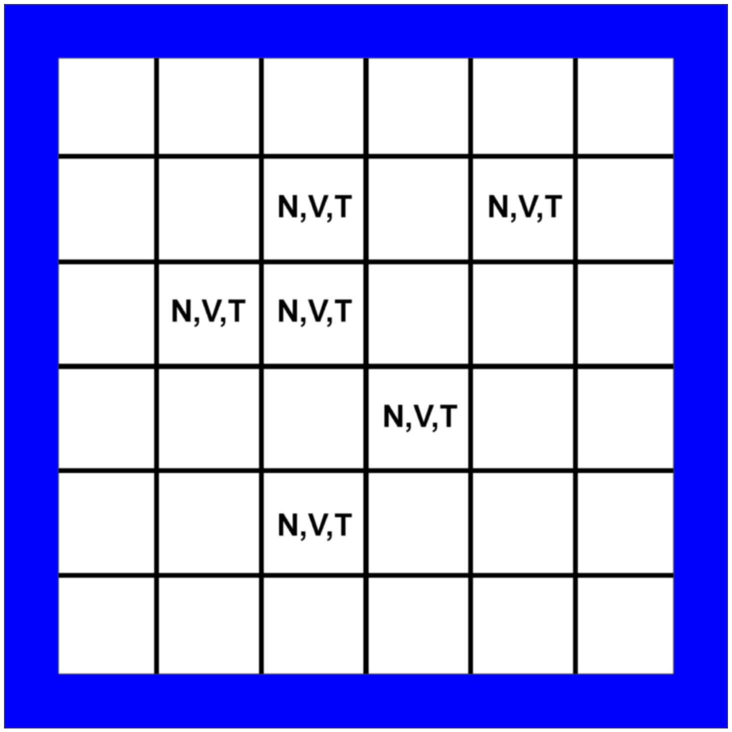
From 2nd year stat mech:

Collection of a vary large number of systems, each replicating at a thermodynamic level the closed isothermal system of interest i.e. each system in ensemble has same fixed N, V, T.



- Fixed total energy
- Fixed volume
- Fixed number of systems
- Assume: E_i's are known

Canonical Ensemble



Canonical distribution

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Canonical partition function

$$Q = \sum_i e^{-\beta E_i}$$

Q contains all thermodynamic information about system of (in general) interacting molecules

Connection to thermodynamics

From 2nd year stat mech:

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \qquad S = \frac{E}{T} + k_B \ln Q$$

Important for us: the equation of state (*p*) in terms of Q

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

Canonical Ensemble: perfect gas

$$q = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V$$

$$Q = \frac{q^N}{N!}$$

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

Equation of state (of course):

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

Canonical Ensemble: imperfect gas

$$Q = \frac{q^N}{N!}$$

X

<u>The trouble is finding the canonical partition function for interacting systems*</u>

* This is actually the point of this lecture course

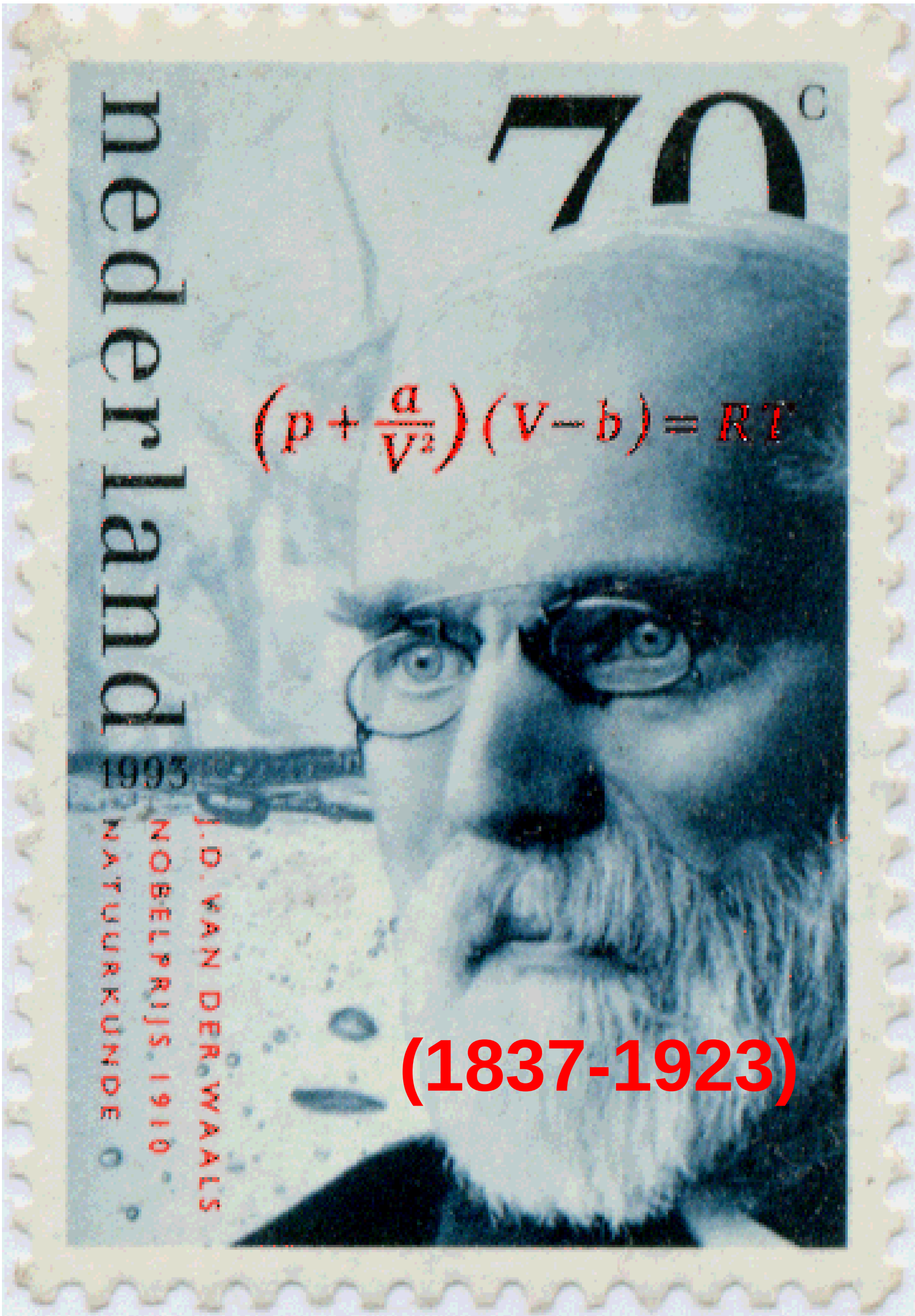
Example of canonical partition function for an imperfect gas

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

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)



Johannes Diderik Van der Waals

Over de continuiteit van den gas – en vloeistof toestand.

PhD-Thesis, Leiden, 1873
The Netherlands

Condensation requires *attraction* and *repulsion*

Content of the course

Statistical mechanics to derive expressions for the canonical partition function and B_2 in terms of intermolecular potential

- Canonical Ensemble (recap)
- Classical Statistical Mechanics
- Second Virial Coefficient B_2
- B_2 for imperfect gases