Application of Statistical Mechanics

Imperfect gases

Lecture 2: Classical Statistical Mechanics

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

Recap of 1st lecture

- Need statistical approach to describe macroscopic systems of 10^{23} molecules
  - Molecular partition function q

- Interacting systems: Canonical Ensemble NVT
  - Canonical partition function Q
  - Connection to thermodynamics
  - EOS for perfect and v/d Waals gas from Q

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

Classical Statistical Mechanics

So far: classical stat mech = limiting case of QM

Example: partition function for a particle of mass m (lecture 1)

$$q = \sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right) \approx \int \exp\left(-\frac{\beta n^2 h^2}{8mL^2}\right) dn$$

High temperature limit:
energy levels close cf $k_B T$

Seek approach that uses classical mechanics throughout

Phase space

• Classical mechanical state is completely defined by specifying the positions (τ) and momenta (p) of all the particles simultaneously

• In 3D this means that 6 coordinates must be specified for each particle

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

• The 6N dimensional space spanned by the coordinates required for a system of N particles is called **phase space**

Classical molecular partition function

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

Quantum mechanical energy		Classical energy
ε_i	$\longrightarrow$	$H(p,\tau)$
Sum over quantum states i		Integral over classical states
$\sum_i$	$\longrightarrow$	$\int \cdots \int \ldots dp d\tau$

natural assumption

$$q_{class} \sim \int \cdots \int e^{-\beta H(p,\tau)} dp d\tau$$

q_{class} for monatomic perfect gas

$$H = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$q_{class} \sim \left(2\pi m k_B T\right)^{\frac{3}{2}} V$$

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

Where's Planck's constant?!?

factor $1/h^3$ missing

q_{class} for monatomic perfect gas

$$q = \sum_i e^{-\beta \varepsilon_i} \quad \rightarrow \quad q_{class} = \frac{1}{h^3} \int \cdots \int e^{-\beta H(p,\tau)} dp d\tau$$

<u>partition functions are dimensionless</u>

$$\left(2\pi m k_B T\right)^{\frac{3}{2}} V \quad \rightarrow \quad \left(\frac{kg \cdot m^2}{s}\right)^3$$

$$\text{h} = 6.626 \times 10^{-34} Js \quad \rightarrow \quad \frac{kg \cdot m^2}{s}$$

Classical canonical partition function for monatomic perfect gas

$$Q_{class} = \frac{q_{class}^N}{N!}$$

$$Q_{class} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p,\tau)} dp d\tau$$

$H_N(p,\tau)$: Hamiltonian of the *N*-body system

Q_{class} for interacting particles

<u>*Conjecture:*</u>

$$Q_{class} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p,\tau)} dp d\tau$$

$H_N(p,\tau)$: Classical N-body Hamiltonian for <u>***interacting***</u> particles

$H_N(p, \tau)$ for monatomic *interacting* gas

$$H_N(p,\tau) = \frac{1}{2m}\sum_{i=1}^{N}\left(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2\right) + U\left(x_1, y_1, z_1, \ldots, x_N, y_N, z_N\right)$$

Interactions!!

Classical Canonical partition function

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

Quantum mechanical energy E_i	$\longrightarrow$	Classical energy $H_N(p,\tau)$
Sum over quantum states i $\sum_i$	$\longrightarrow$	Integral over classical states $\int \cdots \int \ldots dp d\tau$

$$Q_{class} = \frac{1}{N! h^{3N}} \int \cdots \int e^{-\beta H_N(p,\tau)} dp d\tau$$

Integration out the momenta …

$$Q_{class} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H_N(p,\tau)} dp d\tau$$

$$H_N(p,\tau) = \frac{1}{2m} \sum_{i=1}^{N} \left(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2 \right) + U(\tau_1, \ldots, \tau_N)$$

$$Q_{class} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \int \cdots \int e^{-\beta U(x_1, \ldots, z_N)} dx_1 \cdots dz_N$$

Q_{class} for monatomic *interacting* gas

Interactions!!

$$Q_{class} = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \int \cdots \int e^{-\beta U(x_1,\ldots,z_N)} dx_1 \cdots dz_N$$

Classical Configuration Integral Z_N

- depends on relative distances between molecules
- in general, extremely difficult
- central equation in equilibrium stat mech research

Classical Configuration Integral Z_N

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

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

Fundamental equations in the study of monatomic, classical imperfect gases and liquids

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