Application of Statistical Mechanics

Imperfect gases

Lecture 3: Second Virial Coefficient

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

Recap of 2nd lecture

- Classical Statistical Mechanics
  - 6N-dimensional phase space

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

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

Recap of 2nd lecture

- Classical Statistical Mechanics
  - 6N-dimensional phase space
  - Classical molecular partition function

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

$$\downarrow$$

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

Classical energy $H(p,\tau)$

Recap of 2nd lecture

- Classical Statistical Mechanics
  - 6N-dimensional phase space
  - Classical molecular partition function
  - Classical canonical partition function

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

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

Recap of 2nd lecture

- Classical Statistical Mechanics
  - 6N-dimensional phase space
  - Classical molecular partition function
  - Classical canonical partition function
  - Configuration integral (including interactions!)

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

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

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

Content of the course

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

Imperfect gases: Virial expansion

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

B_2: second virial coefficient

(1st year states of matter)

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

Last two lectures: derive this expression for B_2

Strategy to obtain B_2

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

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

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

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

Pairwise additivity

- Potential energy between pair only depends on distance

$$U_{ij} = U(r_{ij})$$

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

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

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

Classical Configuration Integral Z_N

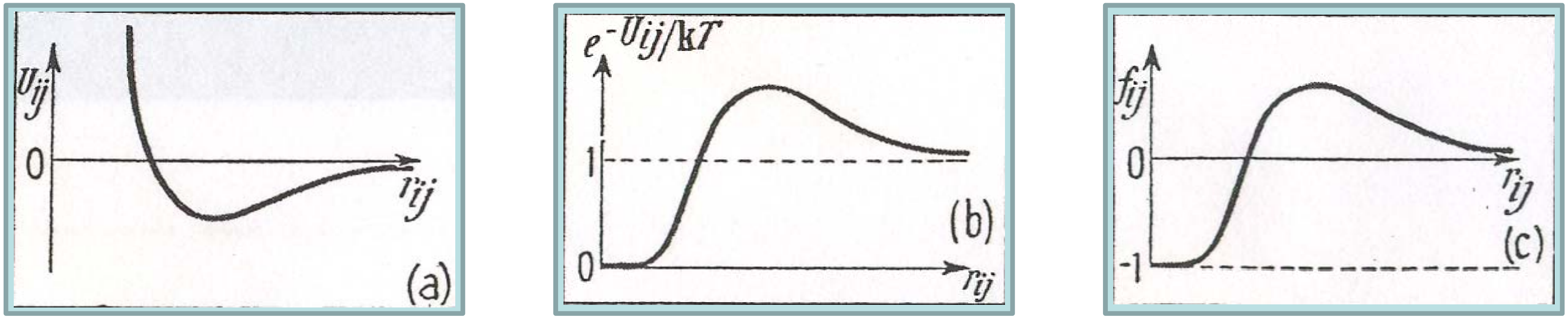
$$Z_N = \int_V e^{-\beta U(x_1,\ldots,z_N)} dx_1 \cdots dz_N$$

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

$$Z_N = \int_V e^{-\beta \sum_{i>j} U(r_{ij})} dx_1 \cdots dz_N$$

Cracking Z_N … : Mayer *f*-function $f(r_{ij})$

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



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

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

Expanding the product …

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

Example: N=3

$$\prod_{i>j}^{N=3}\left(1+f_{ij}\right)=\left(1+f_{21}\right)\left(1+f_{31}\right)\left(1+f_{32}\right)$$

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

$$=1+\underbrace{f_{21}+f_{31}+f_{32}}_{\text{pair-terms}}+\underbrace{f_{21}f_{31}+f_{21}f_{32}+f_{31}f_{32}+f_{21}f_{31}f_{32}}_{\text{higher order terms}}$$

General:

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

Z_N in terms of Mayer *f*-functions

$$Z_N = \int \cdots \int d\tau_1 \cdots d\tau_N + \int \cdots \int \sum_{i>j} f_{ij}\, d\tau_1 \cdots d\tau_N + \ldots$$

perfect gas → V^N

corrections to perfect gas → continue …

Z_N continued …

$$Z_N = V^N + \underbrace{\int \cdots \int \sum_{i>j} f_{ij}\, d\tau_1 \cdots d\tau_N}\ + \ldots$$

… each pair gives the same contribution …

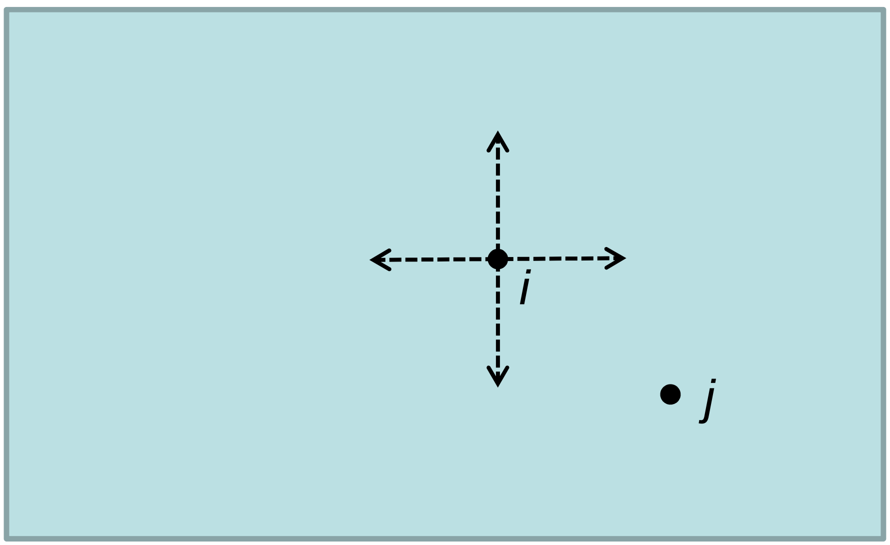
… *N(N-1)/2* pairs …

↓

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

Crack (1) continued …

$$\int \cdots \int f_{ij}\, d\tau_1 \cdots d\tau_N = V^{N-2} \underbrace{\int\int f_{ij}\, d\tau_i\, d\tau_j}_{\text{crack this (2)}}$$



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

So …

$$Z_N = V^N + \frac{N(N-1)}{2} \int \cdots \int f_{ij} \, d\tau_1 \cdots d\tau_N$$

$$V^{N-1} \int_{-\infty}^{\infty} 4\pi f(r) r^2 dr$$

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

Short-hand notation for integral

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

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

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

Strategy to obtain B_2

√

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

lecture 4

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

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