Lecture 11

20.02.2018

Configurational partition function, correlation functions and virial expansion

Module III:
Weakly-interacting particles and Van der Waals fluid

on. 20. feb.	Configurational partition function, correlation functions
fr. 22. feb.	Virial theorem, mean field theory
on. 27. feb.	Mean field, Phase transitions
fr. 1. mar.	Summary and questions

Classical gases and liquids

- Statistical mechanics of *weakly-interacting* classical *indistinguishable* particles
- Translational and rotational symmetric Hamiltonian H_N

$$H_N(p,q) = \sum_{j=1}^{3N} \frac{p_j^2}{2m} + U(q_1, q_2, \cdots q_{3N})$$

$$H_N = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m} + \frac{1}{2}\sum_{j\neq i} u(r_{ij})\,, \qquad r_{ij} = \left|\vec{r}_i - \vec{r}_j\right|, \qquad \vec{r} = (x, y, z), \qquad \vec{p} = (p_x, p_y, p_z)$$

- Homogeneous and isotropic matter: gases and liquids

Pair interaction potential $u(r)$

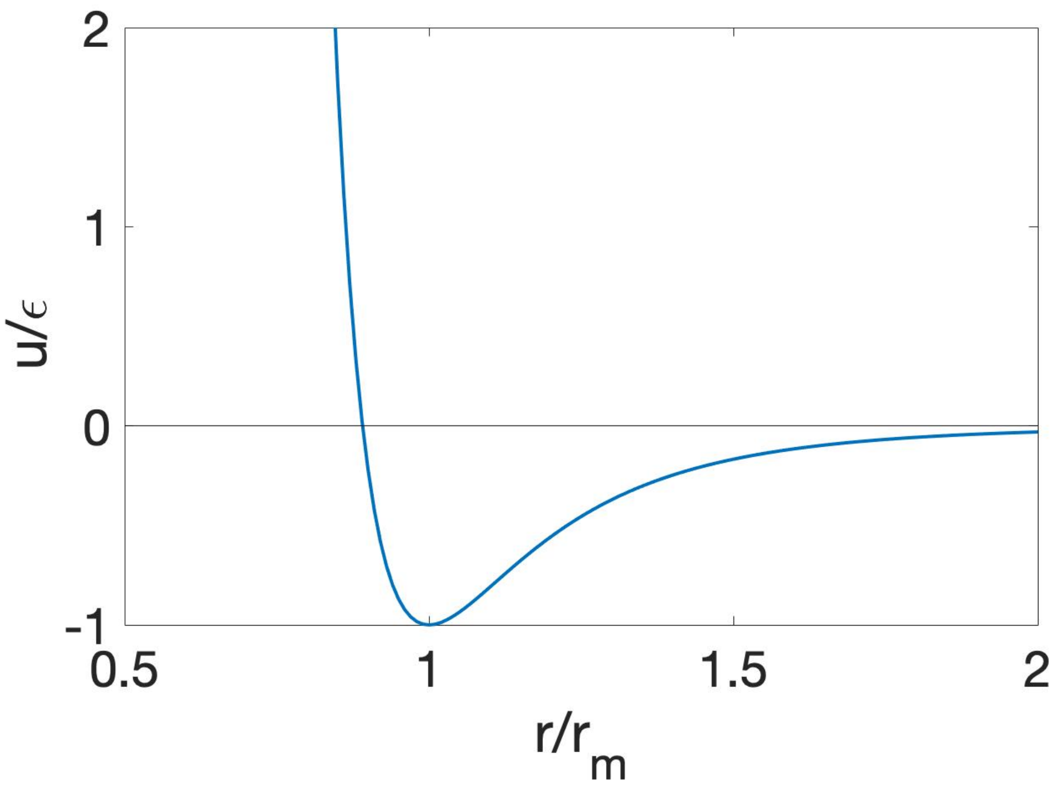
- $u(r)$ is typically repulsive on short distances and attractive on large distances

- Lenard Jones potential (1924)

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

$$u(r) = \epsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right]$$

- $r_m = 2^{1/6}\sigma$



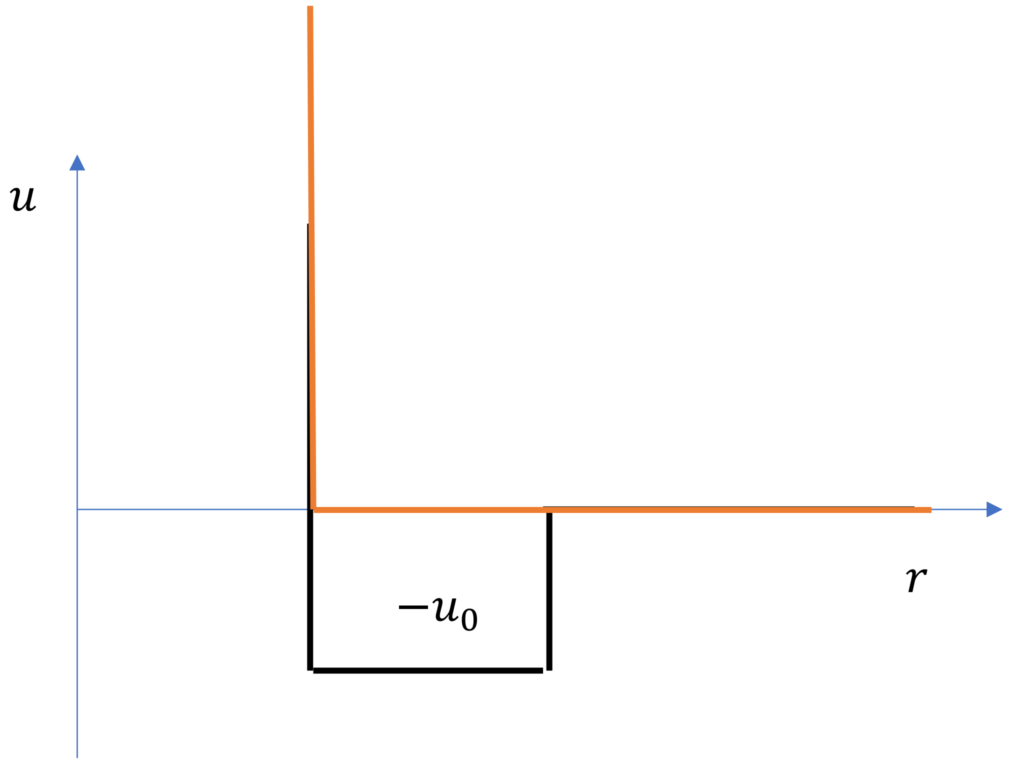
Pair interaction potential

- $u(r)$ is typically repulsive on short distances and attractive on large distances

- Hard-core potential

$$u(r) = \begin{cases} \infty, & r < d \\ 0, & r > d \end{cases}$$

$$u(r) = \begin{cases} \infty, & r < d \\ -u_0, & d < r < d_1 \\ 0, & r > d_1 \end{cases}$$



Configurational partition function

- $Z_N(T,N) = \frac{1}{N!}\int d\omega\; e^{-\beta H_N(p,q)}$

- $Z_N(T,N) = \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int d^{3N}q\; e^{-\beta U(q)}\int d^{3N}p e^{-\beta\sum_i \frac{p_i^2}{2m}}$

- $Z_N(T,N) = \frac{1}{N!}\frac{Q_N}{\Lambda^{3N}},\qquad \Lambda(\mathrm{T}) = \frac{h}{\sqrt{2\pi mkT}}$

- $Q_N = \int d^N\vec{r}\; e^{-\beta U(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)}$

configurational partition function: contains all the information about the particle spatial configurations

Configuration probability distribution

Probability for a microstate with a spatial configuration of particles at positions $\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N$

$$P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{Q_N} e^{-\beta U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}$$

For homogeneous and isotropic systems $P_N(\vec{r}, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{Q_N} \prod_{i<j} e^{-\beta u(r_{ij})}$

- PROBLEM!

  $P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$ is a multidimensional function, and generally difficult to compute

- SOLUTION:
  - We construct an hierarchie of reduced particle configurations (clusters expansion) in which we fix few particle positions and integrate out the remaining spatial coordinates

  - We contruct the first two terms in the cluster expansion: mean particle density and pair-correlation function
  - Thermodyamic properties, like *pressure, internal energy*, can be expressed in terms of these reduced probabilities

One-point cluster: Average density

Average number of particles per unit volume at given position in space is defined in terms of the probability that each particle can occupy that position

- $\langle n(\vec{r})\rangle = \left\langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\right\rangle$

- $\langle n(\vec{r})\rangle = \sum_{i=1}^{N} \int\, d\vec{r}_1 \cdots d\vec{r}_N \delta(\vec{r}-\vec{r}_i) P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$
  - identical terms in the sum

- $\langle n(\vec{r})\rangle = N\int d\vec{r}_1 \cdots d\vec{r}_N \delta(\vec{r}-\vec{r}_1) P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

$$\langle n(\vec{r})\rangle = N\int d\vec{r}_2 \cdots d\vec{r}_N P_N(\vec{r}, \vec{r}_2, \cdots, \vec{r}_N)$$

One-point cluster: Average density

$$\langle n(\vec{r})\rangle = N\int d\vec{r}_2 \cdots d\vec{r}_N P_N(\vec{r},\vec{r}_2,\cdots,\vec{r}_N)$$

For homogenerous and isotropic systems

$P_N(\vec{r},\vec{r}_2,\cdots,\vec{r}_N) = \frac{1}{Q_N}\prod_{i<j} e^{-\beta u(r_{ij})}$

depends only in the relative distance

- $\langle n(\vec{r})\rangle$ is independent of $\vec{r}$
- $\langle n(\vec{r})\rangle = \frac{N}{V} \equiv \rho$, uniform density

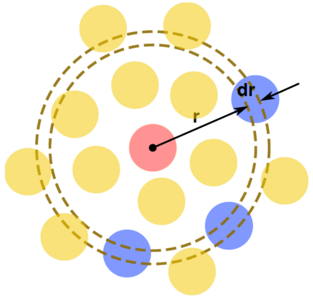
Particles have the equal probability to occupy any available position in space (no prefered spatial coordinates)

Two-point clusters: Pair-correlation function

Density of particles pairs that are separated by $\vec{r} - \vec{r}'$

- $\langle n(\vec{r}) n(\vec{r}') \rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_i)\, \delta\left(\vec{r}' - \vec{r}_j\right) \right\rangle \equiv G(\vec{r}, \vec{r}')$

$G(\vec{r}, \vec{r}')$ is related to the probability to find one particle (*any)* at position $\vec{r}$ and another particle (*any other*) at $\vec{r}$' simultaneously



Sampling over pair particles that are a fixed distance apart

- $G(\vec{r}, \vec{r}') = \sum_{i=1}^{N} \sum_{j=1}^{N} \int d\vec{r}_1 \cdots d\vec{r}_N\, \delta(\vec{r} - \vec{r}_i) \delta\left(\vec{r}' - \vec{r}_j\right) P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

$$G(\vec{r}, \vec{r}') = N(N-1) \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \cdots d\vec{r}_N\, \delta(\vec{r} - \vec{r}_1) \delta(\vec{r}' - \vec{r}_2) P_N(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

$$+\delta(\vec{r} - \vec{r}') \underbrace{N \int d\vec{r}_2 \cdots d\vec{r}_N P_N(\vec{r}, \vec{r}_2, \cdots, \vec{r}_N)}_{\rho}$$

Two-point clusters: Pair-correlation function

- Homogeneity

$$G(\vec{r},\vec{r}') = \rho^2 g(\vec{r}-\vec{r}') + \rho\delta(\vec{r}-\vec{r}'),$$

$$\rho^2 g(\vec{r}-\vec{r}') = N(N-1)\frac{1}{Q_N}\int d\vec{r}_3 \cdots d\vec{r}_N e^{-\beta U(\vec{r},\vec{r}',\cdots,\vec{r}_N)}$$

- Isotropy

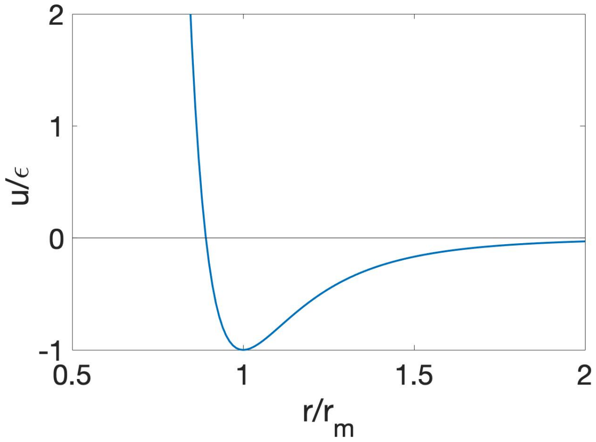
$$\rho^2 g(\vec{r}-\vec{r}') \equiv \rho^2 g(|\vec{r}-\vec{r}'|) = \rho^2 g(r)$$

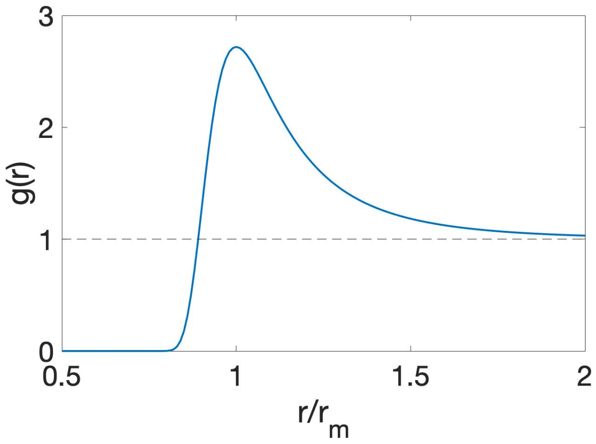
$$\rho^2 g(r) = N(N-1)e^{-\beta u(r)}\frac{1}{Q_N}\int d\vec{r}_3 \cdots d\vec{r}_N\, e^{-\frac{\beta}{2}\sum_{i\neq j\neq 1,2} u(r_{ij})}$$

$g(r)$ pair distribution function is the probability of finding two particles that are separated by a distance r.

$$g(r) \approx e^{-\beta u(r)} \approx \begin{cases} 0, & u(r)\to\infty, \quad r < r_m \\ 1, & u(r)\to 0, \quad r \gg r_m \end{cases}$$

$$r \gg r_m \to u(r) \approx 0 \to \rho^2 g(r) \approx \frac{N(N-1)}{V^2}$$



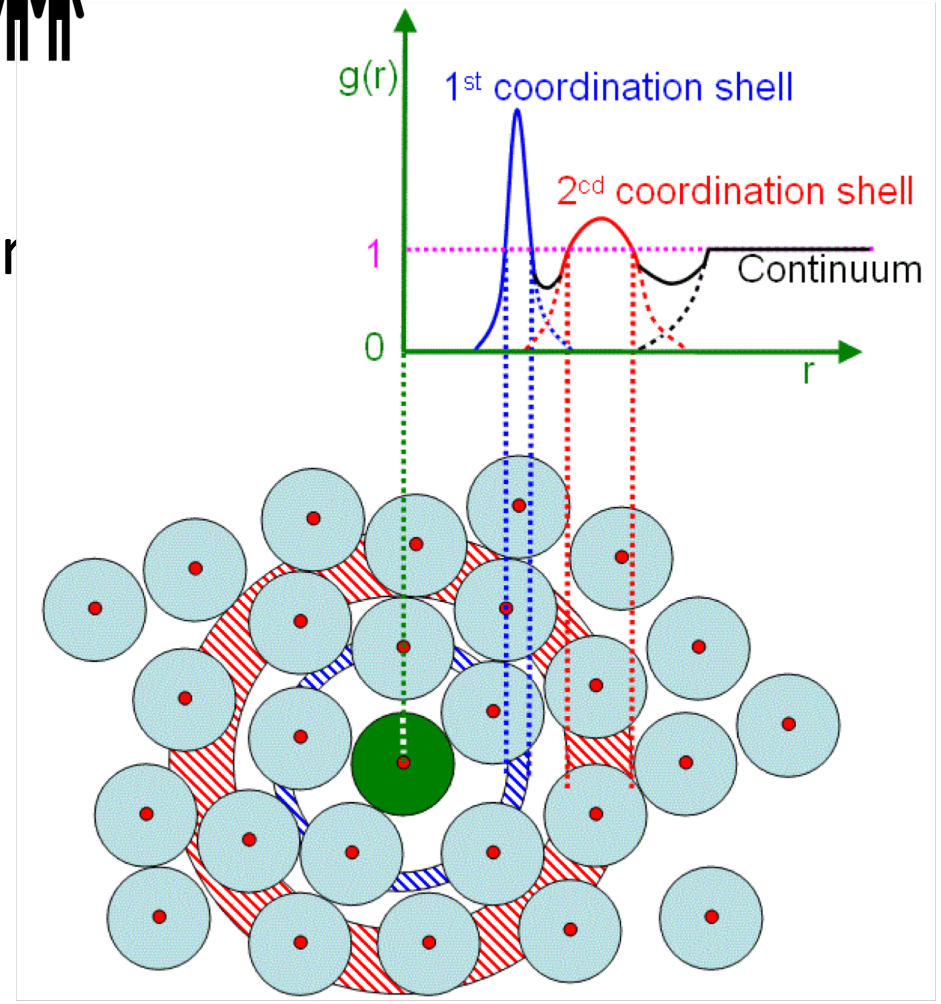


Pair Distribution Function $g(r)$ (PDF)

- PDF show oscillations due to nearest neighbor next nearest neighbor shells, etc.

- Oscillations damped out as r increases

- $g(r) \sim 1$ for large $r \gg r_m$

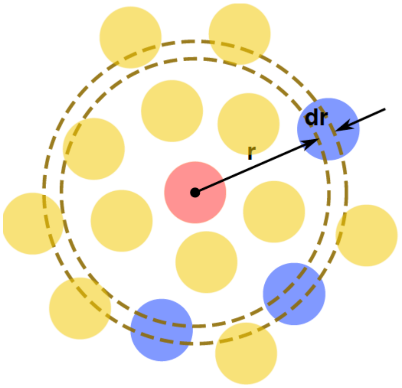


Two-point clusters: Pair-correlation function

- $\rho g(r)$ is the average density of particles at a distance r away from another particle at a given position (origin)

- $(3D)$ $\rho g(r)\ 4\pi r^2 dr$ is the average number of particles in a shell of thikness dr at a distance r away from origin
- Number of particles within a distance R from origin

$$n(R) = 4\pi\rho \int_0^R dr\, r^2 g(r)$$



- Ideal gas limit: $r \gg r_m \rightarrow n(R) \approx 4\pi\rho \frac{R^3}{3}$

Average potential energy

$$\langle U\rangle = \int d\vec{r}_1 \cdots d\vec{r}_N \, U(\vec{r}_1,\cdots,\vec{r}_N) P_N(\vec{r}_1,\cdots,\vec{r}_N)$$

$$\langle U\rangle = \frac{1}{2}\sum_{i\neq j}\int d\vec{r}_1 \cdots d\vec{r}_N \; u(r_{ij}) P_N(\vec{r}_1,\cdots,\vec{r}_N) = \frac{N(N-1)}{2}\langle u(r)\rangle$$

$$\langle U\rangle = \frac{N(N-1)}{2}\frac{1}{Q_N}\int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \, u(r_{12}) \, e^{-\beta U(\vec{r}_1,\cdots,\vec{r}_N)}$$

$$\langle U\rangle = \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \, u(r_{12}) \frac{N(N-1)}{Q_N}\int d\vec{r}_3 \cdots d\vec{r}_N e^{-\beta U(\vec{r}_1,\cdots,\vec{r}_N)}$$

$$\langle U\rangle = \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \, u(r_{12}) \, \rho^2 g(r_{12})$$

$$\langle U\rangle = 2\pi V\rho^2\int dr\, r^2 \; u(r)g(r) = 2\pi N\rho\int dr\, r^2 \; u(r)g(r)$$

Internal energy of an equilibrium macrostate

$$\langle E\rangle = \langle K\rangle + \langle U\rangle$$

$$\frac{\langle E\rangle}{N} = \frac{3}{2}kT + \ 2\pi\rho\int dr\, r^2\, u(r)g(r)$$

Low-density limit

$$\frac{\langle E\rangle}{N} = \frac{3}{2}kT + \frac{4\pi\rho}{2}\int dr\, r^2\, u(r)e^{-\beta u(r)}$$

$$\frac{\langle E\rangle}{N} = \frac{3}{2}kT - \frac{\rho}{2}\frac{\partial}{\partial\beta}Q_1, \qquad Q_1 = \int d\vec{r}\, e^{-\beta u(r)}$$

High temperature limit $e^{-\beta u(r)} \approx 1$

$$\frac{\langle E\rangle}{N} = \frac{3}{2}kT$$

Particle number fluctuations

$$\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \int d\vec{r}_1 d\vec{r}_2 [\langle n(\vec{r}_1) n(\vec{r}_2) \rangle - \langle n(\vec{r}_1) \rangle \langle n(\vec{r}_2) \rangle]$$

$$\langle \Delta N^2 \rangle = \int d\vec{r}_1 d\vec{r}_2 [\rho^2 g(r_{12}) + \rho \delta(r_{12}) - \rho^2]$$

Relative coordinates $\vec{r} = \vec{r}_1 - \vec{r}_2, \vec{r}' = (\vec{r}_1 + \vec{r}_2)/2$ and using isotropy $d\vec{r} \rightarrow 4\pi r^2 dr$

$$\int d\vec{r}_1 d\vec{r}_2 = \int d\vec{r}' \int d\vec{r} \rightarrow \langle \Delta N^2 \rangle = \rho \int d\vec{r}' \int d\vec{r}\, \delta(r) + \rho^2 \int d\vec{r}' \int d\vec{r} [g(r) - 1]$$

$$\langle \Delta N^2 \rangle = \langle N \rangle + \langle N \rangle \rho \int d\vec{r}\, [g(r) - 1]$$

$Low\ density\ limit\ g(r) \approx e^{-\beta u(r)}$

$$\langle \Delta N^2 \rangle = \langle N \rangle \left(1 - \rho \int d\vec{r} \left[1 - e^{-\beta u(r)}\right]\right)$$

$\langle \Delta N^2 \rangle \approx \langle N \rangle$ Poisson statistics

Interaction potential leads to «anomalous» statistics of number fluctuations