I. LIQUID MATTER: INTRODUCTION AND EXAMPLES

A remarkable observation (initiating thermodynamics and statistical mechanics): *macroscopic* amounts of chemically well defined substances (macroscopic: number of particles $N \sim N_A \approx 6 \cdot 10^{23}$ (Avogadro's number))

- can exists in several states with very different physical properties

- can be transformed between these states by changing ambient parameters (thermodynamic observables) like pressure and temperature

- may be classified as

  - hard or solid: long–range ordered arrangement of particles (atoms) $\rightarrow$ small perturbations: elastic response and return to original shape

  - fluid: further subdivided in

    * gas or vapor: almost no order and correlations between atoms $\rightarrow$ very volatile and of small density which constitutes a *small parameter* in which perturbation theory around an *ideal state* is possible

    * liquid: short–ranged order (of the order of atomic size) and of much higher density (no perturbation theory possible) $\rightarrow$ flows away upon perturbation and dissipates energy (viscous behavior)
      ! Correlations near critical points
      ! Correlations near interfaces or on substrates ($\rightarrow$ wetting)
      different types of "atoms" (molecules, polymers, amphiphiles, colloids, . . .) and mixtures $\rightarrow$ large variety of physical properties ("dirty" subject)

A. Fluid states in simple phase diagrams

We consider simple, pure substances (argon, methane, water ...):

Figure 1.1. Schematic phase diagrams of a simple one-component substance, in the temperature (T)–pressure (P), density (ρ)–T and ρ–P planes. The shaded areas in the middle and right panels indicate regions of two-phase coexistence. The bold line in the right panel is an isotherm while t and c show the locations of the triple and critical points.
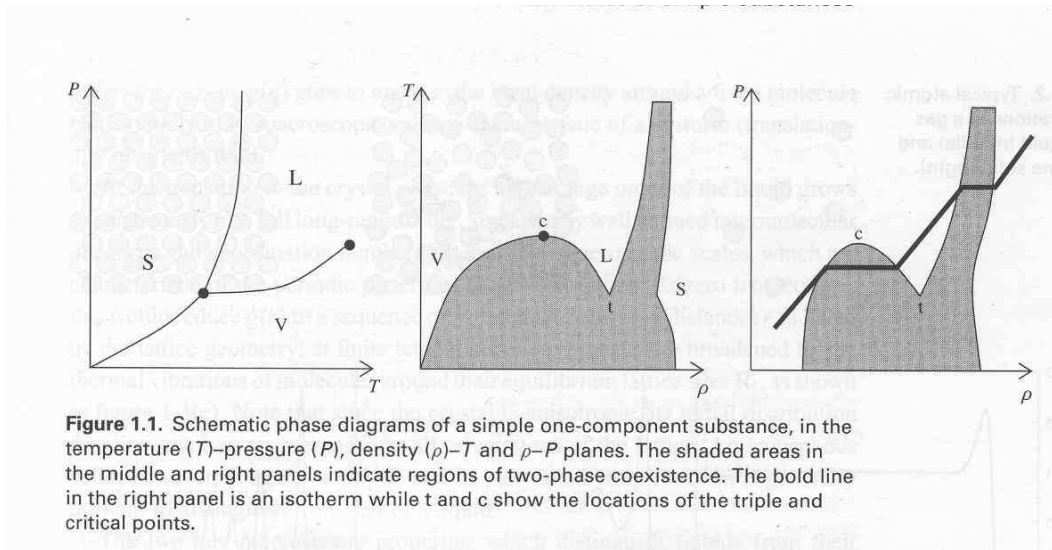
FIG. 1: Schematic phase diagram for a simple liquid. (taken from Barrat&Hansen)

- sufficiently high T and not too high p (both on the scale of standard atmospheric conditions): gas phase

    - molecules are far apart, only occasionally binary colllisions

    - static properties: ideal gas model (no interactions between molecules)

    - dynamic properties: Boltzmann kinetic equation

    - highly disordered → large entropy per molecule

    - full rotational and translational symmetry

- T ↓: vapor condenses into droplets (two–phase region of phase diagram) and droplets merge until all vapor is gone

    - greatly reduced entropy per molecule

2

– usually preserved rotational and translational symmetry

- T ↓: liquid freezes into solid

  – qualitative explanation: ordered arrangement maximizes entropy or available space for individual molecules

  – discrete reflection, rotational and translational symmetry (embodied in 230 space groups)

Typical pair distribution functions for gases, liquids and solids:

Pair distribution function $g(\mathbf{r})$: Probability to find a second molecule at position $\mathbf{r}$ if a first molecule (or test particle) is fixed at the origin. For gases/simple liquids – $g(\mathbf{r}) \equiv g(r)$, for solids $g(\mathbf{r})$ orientation dependent.
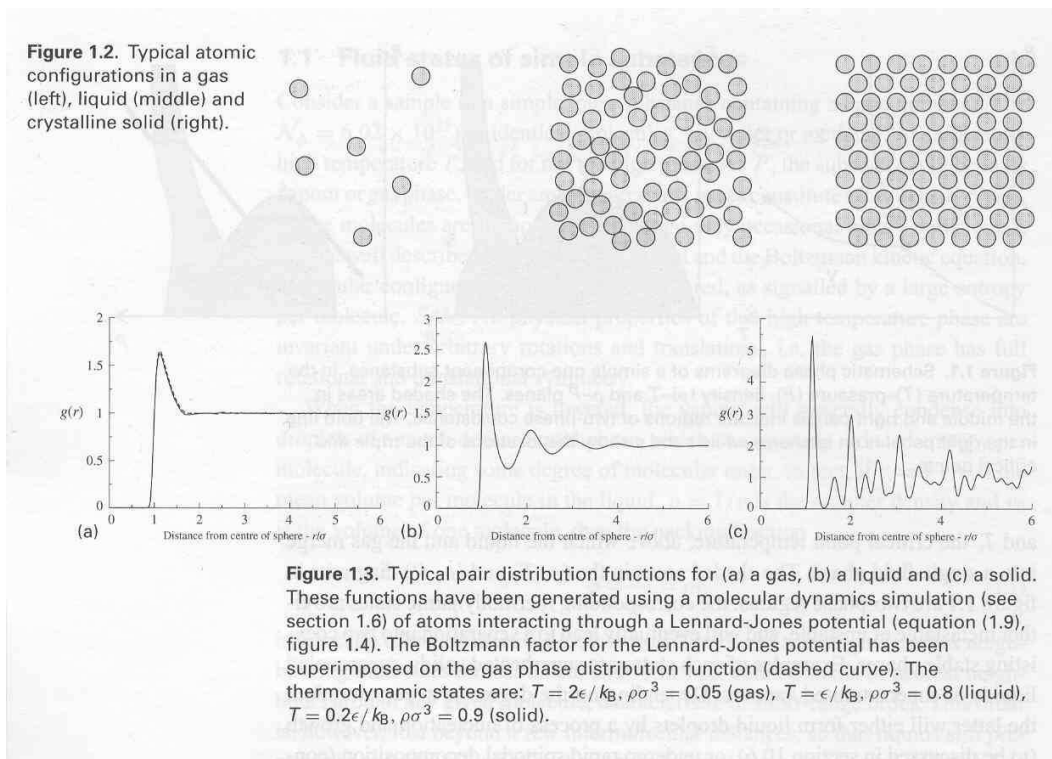

Figure 1.2. Typical atomic configurations in a gas (left), liquid (middle) and crystalline solid (right).

Figure 1.3. Typical pair distribution functions for (a) a gas, (b) a liquid and (c) a solid. These functions have been generated using a molecular dynamics simulation (see section 1.6) of atoms interacting through a Lennard-Jones potential (equation (1.9), figure 1.4). The Boltzmann factor for the Lennard-Jones potential has been superimposed on the gas phase distribution function (dashed curve). The thermodynamic states are: $T = 2\epsilon/k_B$, $\rho\sigma^3 = 0.05$ (gas), $T = \epsilon/k_B$, $\rho\sigma^3 = 0.8$ (liquid), $T = 0.2\epsilon/k_B$, $\rho\sigma^3 = 0.9$ (solid).

FIG. 2: Pair distribution functions for 2d gas, liquid and solid. (taken from Barrat&Hansen)

Metastable and instable states:

if cooling is done carefully and quickly (smooth containers, no dirt), the gas remains gaseous upon crossing the phase boundary (binodal) → supersaturated vapor

- condensation of droplets inhibited by energy barrier (competition of surface free energy and condensation free energy release)

- all dirt particles act as condensation nuclei

- upon crossing spinodal line: spinodal decomposition - (initially) exponentially fast transformation of gas into liquid, reason: tiny density fluctuations are not smoothed out but become amplified

Likewise supercooled/–heated liquid and superheated solids exist. Glasses may be considered supercooled liquids obtained by a very rapid temperature quench.

Special points:

- Critical point: end point of two–phase region, correlations become long–ranged (*critical opacity:* clear liquids become milky)

- Triple point: gas, liquid and solid phases may coexist

B. From simple to complex fluids

Simple liquids:

- ideally spherical molecules

- only two–body potentials between molecules

- the "fruit flies" of liquid state theory: hard spheres and Lennard–Jonesium

  Hard sphere fluids:

- $u_{\mathrm{HS}}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \qquad \rightarrow \qquad f(r) = \exp(-\beta u_{\mathrm{HS}}(r)) - 1 = \begin{cases} -1 & r < \sigma \\ 0 & r > \sigma \end{cases}$

  $\text{(Mayer } f\text{–bond)}$

- completely *athermal*; no internal energy $\rightarrow$ properties purely driven by entropy, i.e. free volume available to spheres

- theoretical phase diagram: only a liquid and a solid phase $\rightarrow$ intermolecular attractions are necessary for liquid–gas phase separation but not for freezing into a solid!

- experimental realizations: solid polymeric colloids (polystyrene – PS, poly–methylmethacrylate – PMMA) covered with hairy polymers
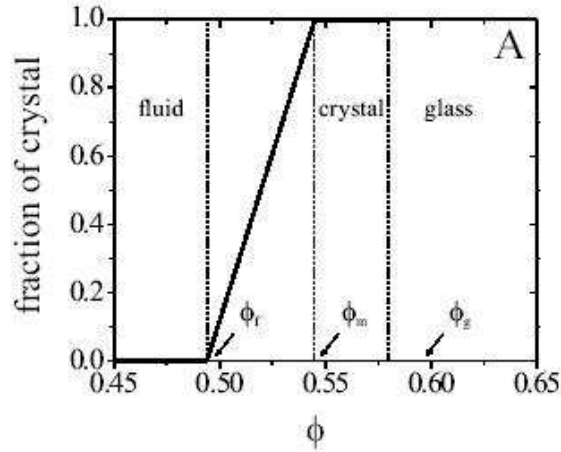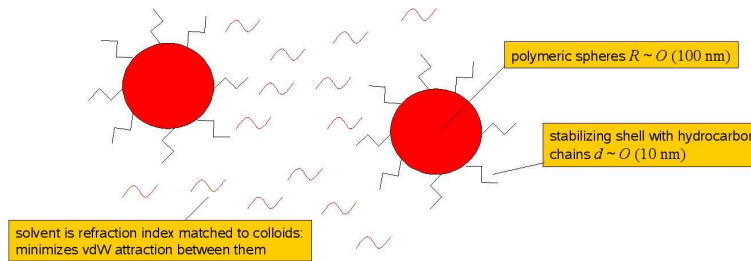
FIG. 3: HS phase diagram.

FIG. 4: HS realization.

Lennard–Jonesium:

- model interaction between electrically neutral, spherical atoms (purely two–body interaction)

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

  energy scale $\epsilon \sim k_{\mathrm{B}} T \approx 4 \cdot 10^{-21}$ J or 0.025 eV (coexistence region, room temperature)

  steeply rising repulsion for overlapping cores ($r < \sigma$), power–law chosen for pure convenience:

  exact form arises from interaction of atomic orbitals with energies

  ~ 10 eV $\gg k_B T$

  quantum–mechanical interaction between dipole fluctuations in each atom $\rightarrow$ universal power

  law for attractions (van–der–Waals attraction)

- phase diagram:

6

glassy phase: dynamical arrest in metastable minimum

homogeneous nucleation of fcc crystals

heterogeneous nucleation of fcc crystals
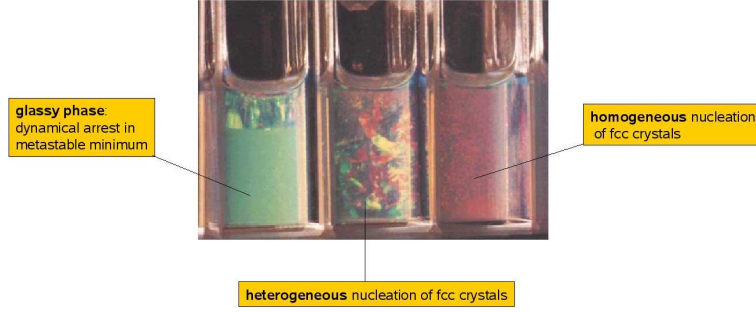
FIG. 5: Pusey's hard–colloid phases.
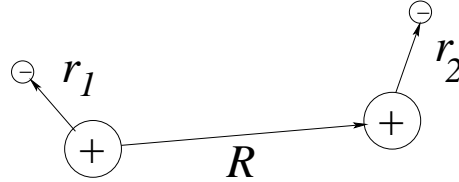
Excursion: Origin of the van–der Waals attraction

Consider two H–atoms at distance R with Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{1}$$

unperturbed Hamiltonian $(R \to \infty)$:

$$\hat{H}_0 = \hat{H}_1 + \hat{H}_2 \tag{2}$$

with eigenstates $|0n\rangle = |n_1\rangle|n_2\rangle$ corresponding to eigenenergies $E_{0n} = \epsilon_{n_1} + \epsilon_{n_2}$

$$\hat{V} = e^2 \left(\frac{1}{R} + \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} \right) \tag{3}$$

$$\approx -\frac{e^2}{R^3} \left[3(\mathbf{r}_1 \cdot \mathbf{e}_R)(\mathbf{r}_2 \cdot \mathbf{e}_R) - \mathbf{r}_1 \cdot \mathbf{r}_2 \right] + O(R^{-5}) \tag{4}$$

perturbation Hamiltonian: two interacting "fluctuating" dipoles $(e\mathbf{r}_1)$ and $(e\mathbf{r}_2)$

Perturbation theory to second order for non–degenerate states:

$$E_n = E_{0n} + \langle 0n|\hat{V}|0n\rangle + \sum_{j \neq n} \frac{\left| \langle 0n|\hat{V}|0j\rangle \right|^2}{E_{0n} - E_{0j}} + \dots \tag{5}$$

First order terms are zero since they contain only expectation values of the type,

$$\langle n_1|\hat{x}_{i,1}|n_1\rangle\langle n_2|\hat{x}_{i,2}|n_2\rangle = 0 \tag{6}$$

(ground state of hydrogen is of even parity!). Therefore:

$$E_n(R) = \epsilon_{n_1} + \epsilon_{n_2} - \frac{e^2}{a_0} \frac{A_n}{(R/a_0)^6} \tag{7}$$

where the Bohr radius a_0 (typical size of H atom) has been introduced to define the dimensionless amplitude

$$A_n = \frac{e^2}{a_0^5} \sum_{(j_1,j_2)\neq(n_1,n_2)} \frac{|\langle n_1|\langle n_2|(\hat{x}_1\hat{x}_2 + \hat{y}_1\hat{y}_2 - 2\hat{z}_1\hat{z}_2)|j_1\rangle|j_2\rangle|^2}{\epsilon_{j_1} + \epsilon_{j_2} - \epsilon_{n_1} - \epsilon_{n_2}} \tag{8}$$

Observations:

- if $|0n\rangle$ ground state, $A_n > 0$ and $E_n - E_{n0} < 0 \rightarrow$ van–der–Waals attraction

- three–body potential appears in third–order perturbation theory:

$$u^{3-\text{body}} \sim \frac{1}{R_{12}^3 \, R_{23}^3 \, R_{31}^3} \frac{\langle 0n|\hat{V}_{12}|0j\rangle\langle 0j|\hat{V}_{23}|0l\rangle\langle 0l|\hat{V}_{31}|0n\rangle}{(E_{0n} - E_{0j})(E_{0n} - E_{0l})} \tag{9}$$

if $|0n\rangle = |s_1\rangle|s_2\rangle|s_3\rangle$ is the s–wave ground state, leading contributions (smallest energy denominator) arise from $|0j\rangle = |p_1\rangle|p_2\rangle|s_3\rangle$ and $|0l\rangle = |p_1\rangle|s_2\rangle|p_3'\rangle \rightarrow$

$$u^{3-\text{body}} \sim \frac{1}{R_{12}^3 \, R_{23}^3 \, R_{31}^3}(1 + 3\cos\gamma_1 \cos\gamma_2 \cos\gamma_3) \tag{10}$$

Axilrod and Teller, J. Chem. Phys. **11**, *299 (1943)*
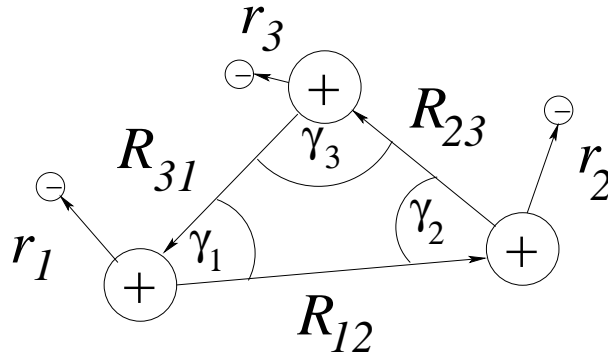
- relativistic effects: finite time photon exchange between atoms leads to retardation:

$E_n - E_{n0} \sim R^{-7}$

Anisotropic liquids:

1. Long–range anisotropy: multipole potentials

- electric dipole in weakly asymmetric atoms (NH_3, CO, …), magnetic dipoles in magnetically doped colloids or ferrofluids

$$u(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}) = \frac{A}{r^3} \left[(\mathbf{p}_1 \cdot \mathbf{e}_r)(\mathbf{p}_2 \cdot \mathbf{e}_r) - \mathbf{p}_1 \cdot \mathbf{p}_2 \right] \tag{11}$$

  tendency to form chains of aligned dipoles

2. Short–range anisotropy

2.1 H–bonds

- strongly polar molecules with H^+ groups (HF, H_2O, H_3N, …): size asymmetry between H^+ and Y^- (F^-, O^{2-}, N^{3-}, …) leads to strongly asymmetric electrostatic interactions between neighbouring molecules ($\rightarrow$ breakdown of dipole approximation)

- H_2O: tetrahedral network structure present (due to H–bonds) present in solid and liquid state $\rightarrow$ water anomalies

  - highest liquid density not at melting point

  - pressure $\uparrow$, viscosity $\downarrow$ (breaking of H–bonds)

Theoretical description: Details of intermolecular potential are important to capture the subtleties of water behaviour $\rightarrow$ molecular simulations

2.2 Nematic substances (liquid crystals)

- characteristics: hard-core repulsion between molecules is highly anisotropic

- phase transition possible between isotropic phase (random orientation of the molecules) and ordered phases (preferred orientation of molecules)
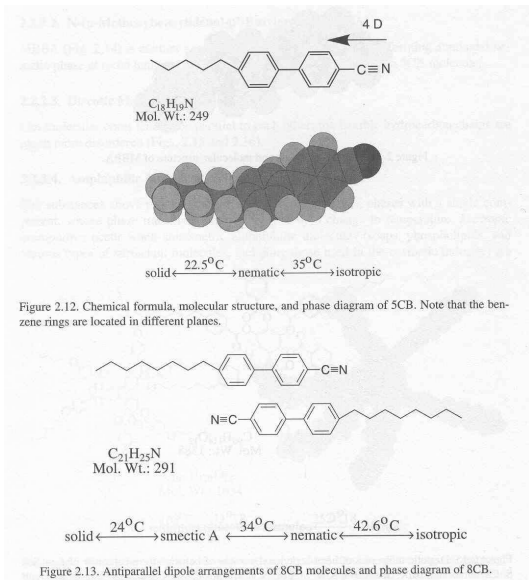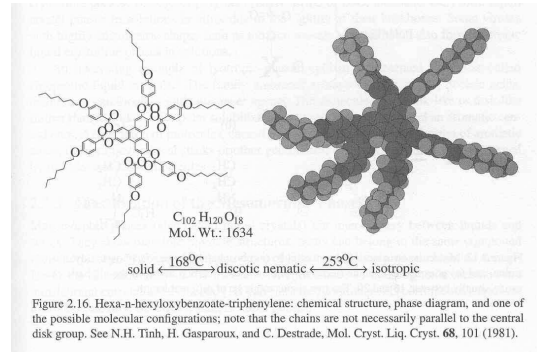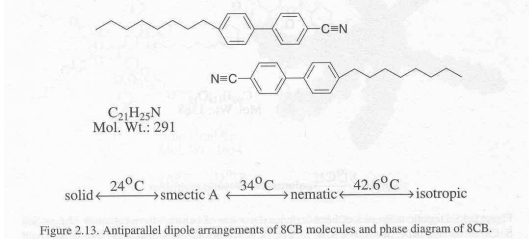
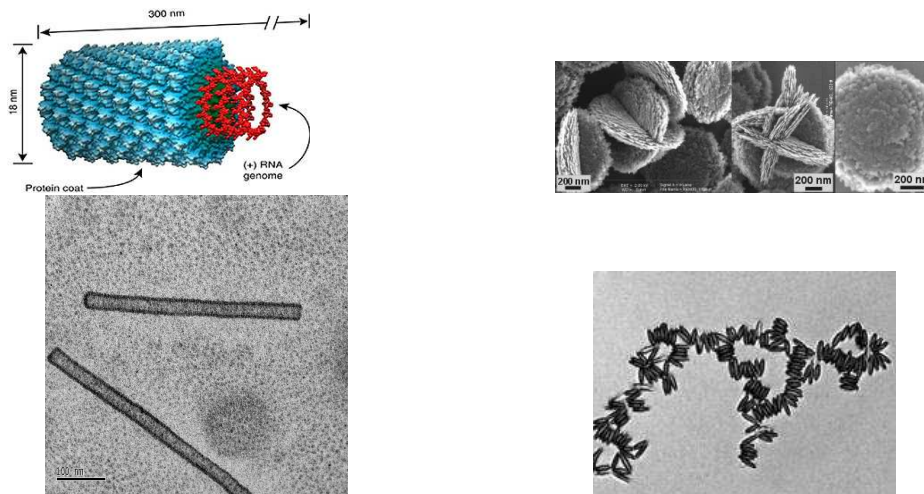FIG. 6: Nematic molecules. (taken from Kleman&Lavrentovich)

FIG. 7: Nematic colloids.

(upper left) schematic composition of a tobacco mosaic virus (TMV)

(lower left) electron micrograph of TMV's

(upper right) electron micrograph of Haematit plates

(lower right) optical micropgraph of polystyrene ellipsoids (axes $a \approx 6$ μm and $b \approx 1$ μm)

- molecular realizations: rod–like or disklike colloidal realizations: tobacco mosaic virus (rod–like), clay (disklike), stretched polymeric ellipsoids

- Ordered phases for rods:

10

1. *Nematic:* one preferred direction for rods (director)

2. *Smectic A:* breaking of translational symmetry in one direction $\rightarrow$ rods arranged in layers, orientation normal to layer

3. *Smectic C:* $\qquad \sim \qquad$, orientation inclined to layer normal

4. *Cholesteric:* director rotation along one axis

Figure 1.6. Typical configurations of the isotropic (upper left), nematic (upper right), smectic (lower right) and crystalline phases of a system of mesogenic molecules modelled as hard spherocylinders (i.e. cylinders capped by hemispheres of the same diameter). (Courtesy of P. Bolhuis.)
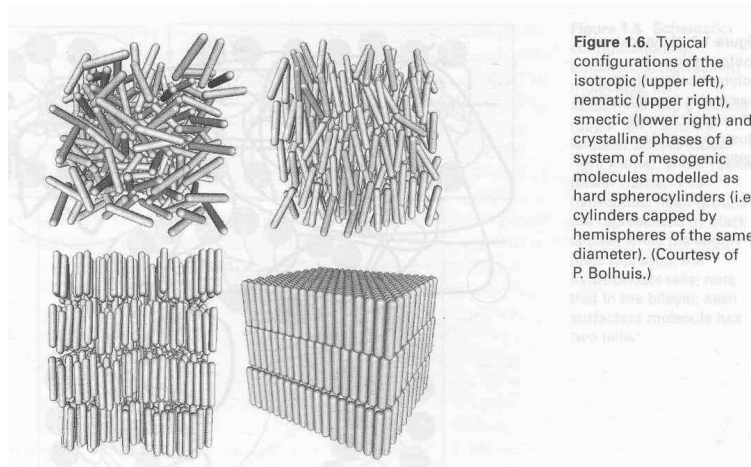
FIG. 8: Typical hard rod configurations seen in simulations. (taken from Barrat&Hansen)

Theoretical description: Most of the effects associated with the ordered phases are (at least semi-quantitatively) succesfully explained by coarse grained, local field theories.

- field theory: e.g., director orientation is treated as a continuous vector function on $\mathbb{R}^3$, $\mathbf{n} = \mathbf{n}(\mathbf{r})$ – a field

- local: free energy density at a point $\mathbf{r}$ depends only on $n_i(\mathbf{r})$ and $\partial_j n_i(\mathbf{r})$

- coarse–grained: characteristic length of noticeable changes in $\mathbf{n}$ is much larger than the size of molecules

Therefore, the appearance of ordered phases within the coarse–grained theories points to collective behavior of the molecules.

Mixtures

Many interesting effects appear when the size of the mixture components are grossly different.

1. Charged solutes in solvent with counterions:

most interesting systems for chemistry and biology

- solvent: usually water, counterions of molecular size (Na^+, K^+, Ca^{2+} ...)
  solutes: proteins, colloids

- infinite range ($1/r$) of Coulomb potential $\rightarrow$ collective behavior expected: indeed, most successful are extensions of electrostatics (a field theory) to incorporate the effects of counterions (e.g., Poisson–Boltzmann equation)

- two coarse–graining steps:

$$\begin{pmatrix} \text{solvent} \\ \text{solute} \end{pmatrix} \rightarrow \begin{pmatrix} \text{Poisson–Boltzmann eq.} \\ \text{solutes fixed} \end{pmatrix} \rightarrow \begin{pmatrix} \\ \text{effective potential for solutes} \end{pmatrix}$$

2. Polymers in solvent (macromolecular systems):

- linear polymers: sequence of monomers (units), length up to 10^{10} (chromosomes)

- chemical example: alkane hydrocarbons (not in solution)

Number of C atoms	State at room temperatue	Example
1–4	gas	propane
5–15	low–viscosity liquid	gasoline
16–25	high–viscosity liquid	motor oil
20–50	soft solid	paraffin wax
>1000	plastic solid	polyethylene

- *one polymer in solution:* highly flexible on length scales $\gg$ momomer length $\rightarrow$ effective spherical coil

few polymers in solution: effective gas of interacting coils, potential: soft repulsion

medium polymer concentration: Onset of collective effects, effective descriptions with soft two–body potentials fail

high polymer concentration: crosslinking to gels, onset of viscoelastic behaviour (i.e., flows like a fluid on a long time–scale, is elastic like a solid on a short time–scale)

3. Colloidal mixtures:

- 3–component minimum: solvent – colloid 1 – colloid 2 or solvent – colloid – polymer

- interesting for their model character: effective two–component mixtures (if solvent is "averaged out") on larger length scales $\rightarrow$ rescaling of all macroscopic fluid properties (viscosity, surface tension, Reynolds number . . .)
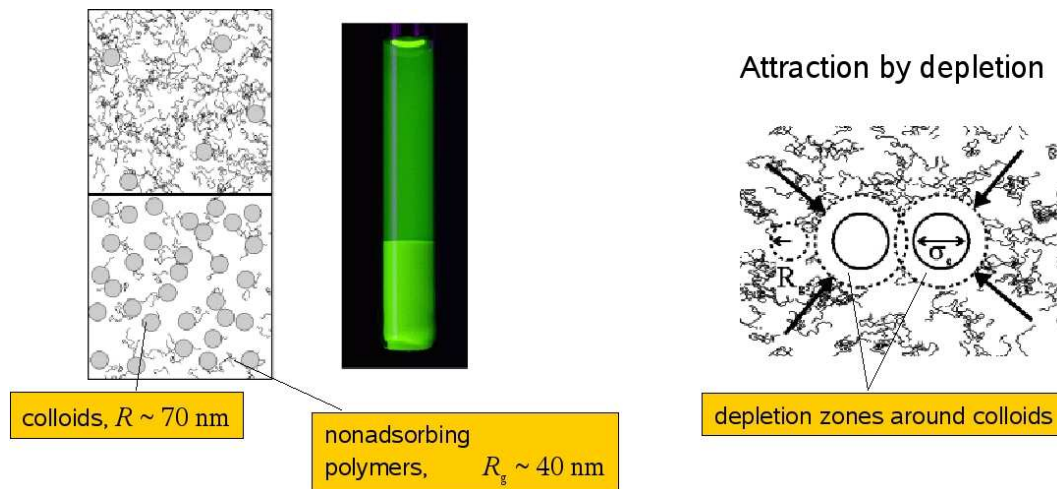
- display phase separation

FIG. 9: Phase separation in the Utrecht colloid–polymer mixture.

II. PRINCIPLES OF THERMODYNAMICS AND STATISTICAL MECHANICS

A. Thermodynamics

Thermodynamics deals quite generally with

- "large" systems in "equilibrium"

- quasistatic processes between equilibrium states

It describes these systems via generalized potentials that depend on system control parameters. These are *extensive* quantities (i.e. $\propto N$ – number of particles – and add up by combining two subsystems). Control parameters can be both *intensive* quantities (i.e. stay constant if a system is just enlarged) and extensive.

Thermodynamic potentials for a given system are specified uniquely in terms of their respective independent control parameters:

1. $U(V, S, N)$ – internal energy (average kinetic + potential energy)

2. $H(S, P, N)$ – enthalpy

3. $F(V, T, N)$ – Helmholtz free energy

4. $G(T, P, N)$ – Gibbs free energy

    _____

5. $\Omega(V, T, \mu)$ – Grand free energy or grand potential

They are linked by Legendre transformations ($H = U + PV$, $F = U - TS$, $G = U - TS + PV$, $\Omega = U - TS - \mu N$) and thus their differentials define the dependent control parameters, e.g.

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_{S,N} \mathrm{d}V + \left(\frac{\partial U}{\partial S}\right)_{V,N} \mathrm{d}S + \left(\frac{\partial U}{\partial N}\right)_{V,S} \mathrm{d}N = -P\mathrm{d}V + T\mathrm{d}S + \mu\mathrm{d}N \qquad (12)$$

For closed systems ($N = $ const.), these definitions (Maxwell relations) can be summarized by the following diagram:
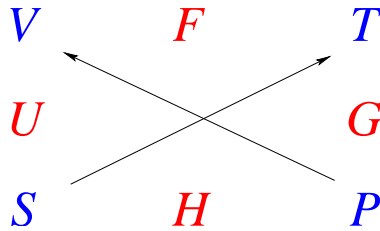
(potentials are flanked by their independent control parameters, derivative of potential w.r.t. one control parameter leads to the dependent control parameter connected with the line, going against the arrow yields a minus sign)

The 2nd law of thermodynamics yields minimization principles for the free energies F, G, Ω (see below).

Observation: $\Omega(\lambda V, T, \mu) = \lambda\Omega(V, T, \mu)$, thus according to Euler's theorem on homogeneous functions

$$\Omega(V, T, \mu) = V\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -PV \ . \qquad (13)$$

One can formulate four laws or axioms upon which thermodynamics is built.

- 0th law - The temperature:

  There exists an equivalence relation between thermodynamic systems $A, B, \ldots$ which we associate with thermodynamic equilibrium. If one empirically tries to describe the corresponding equivalence classes, one finds that they are describable by a system dependent, real number. This is the temperature T (up to a scale factor and a possible zero point).

- **1st law - Conservation of energy:**

  The change in internal energy of a system is given by the work performed on the system and the heat transferred to the system,

$$dU = \delta W \qquad + \qquad \delta Q \qquad\qquad (14)$$
$$\text{mechanical} : -\, pdV$$
$$\text{chemical} : \mu dN$$
$$\text{electromagnetical} \ldots .$$

  The infinitesimal change in internal energy is a total differential, as opposed to the infinitesimal work and heat.

- **2nd law - The entropy postulates:**

  1. $S = S(U, V, N)$ is an extensive state variable.

  2. For the composition of closed systems that may be separated by external constraints:

     S_{eq} [no constraints] $\geq S_{\mathrm{eq}}$ [with constraints]

  3. $S = $ const. for quasistatic, adiabatic transitions ($\delta Q = 0$).

  4. $dS \geq \delta Q/T$ for any process; equality defines an exact differential and holds for quasistatic, adiabatic transitions

  Corollaries: For the equilibrium state of a system

  – under mechanical isolation ($\delta W = 0$) and with $T = $ const., F is minimal

  – with $T, p, N = $ const., G is minimal

  – with $V, T, \mu = $ const., Ω is minimal

  Proof: Since $\delta Q/T \leq \delta S$ (2nd law) $\rightarrow -\delta W \leq -\delta U + T\delta S$ (1st law)

  – $-\delta W \leq -\delta F,$ \qquad mechanical isolation: $\delta F \geq 0$

  – $p\delta V - \mu\delta N \leq \delta(-G + pV),$ \qquad $T, p, N = $ const.: $\delta G \geq 0$

  – $-\mu\delta N \leq \delta(-\Omega - \mu N),$ \qquad $V, T, \mu = $ const.: $\delta\Omega \geq 0$

- **3rd law - On T=0:**

    It is impossible to attain $T = 0$ in a system with a finite number of reversible processes.

    Thus, $\Delta S \to 0$ in any reversible isothermal process as $T \to 0$.

B. Classical statistical mechanics

Microstate

specified by $2Nf$ variables of the phase space
(N particles, f position and velocity dof's
per particle)

$\longleftrightarrow$

Macrostate

$?$

specified by thermodynamic poten-
tial and its control parameters

Gibbs ensembles:

For simplicity, we consider only one species of particles with mass m which interact with a
two–body potential u.

1. Microcanonical ensemble:

   $\delta U = 0$ (no heat or work exchange); $N, V = $ const.

   Definition of internal energy:

   $$U = \mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} u(\mathbf{r}_i - \mathbf{r}_j) \qquad \text{Hamiltonian} \qquad (15)$$

   Basic postulate: All microstates compatible with the above constraints are of equal
   probability in phase space.

   Definition of entropy – link with thermodynamics:

   $$S(U, V, N) = k_{\mathrm{B}} \ln \omega(U, V, N) \qquad (16)$$

   with $k_{\mathrm{B}} = 1.38 \cdot 10^{-23}$ JK^{-1} is Boltzmann's constant and $\omega(U, V, N)$ is the total number
   of microstates compatible with the constraints.

2. Canonical ensemble:

   $\delta W = 0$ (no work exchange), heat exchange with thermal reservoir; $N, V, T = $ const.

   Corollary of basic postulate: microstate at phase state point $\Gamma = \{\mathbf{r}_i, \mathbf{p}_i\}$ has a prob-
   ability p in phase space of

   $$p(\Gamma) = \frac{1}{N! h^{fN}} \frac{\exp(-\beta \mathcal{H}[\Gamma])}{Q_N} \,. \qquad (17)$$

Q_N is the canonical partition function for N particles:

$$Q_N = \frac{1}{N!h^{fN}} \int \exp(-\beta\mathcal{H}[\Gamma])d\Gamma \qquad (\beta = (k_\mathrm{B}T)^{-1}) . \tag{18}$$

The prefactor can be justified thoroughly only by quantum mechanics: h (Planck's constant) must be a constant of dimension Js/m to make Q_N dimensionless, and $N!$ stems from the indistinguishability of particles.

The integral over momenta can be performed immediately, using $\int_0^\infty dx \exp(-ax^2/2) = \sqrt{2\pi/a}$:

$$Q_N = \frac{1}{N!h^{fN}}(2\pi m)^{fN/2} \int d^f\mathbf{r}_1 \ldots d^f\mathbf{r}_N \exp\left(-\beta \sum_{i<j} u(\mathbf{r}_i - \mathbf{r}_j)\right) \tag{19}$$

$$= \frac{1}{N!\lambda^{fN}} Z_N \tag{20}$$

which defines the configuration integral Z_N. ($\lambda = \sqrt{2\pi\beta\hbar^2/m}$ is the de–Broglie wavelength.) The central problem of classical statistical physics and thus of liquid state theory is the evaluation of Z_N.

Definition of free energy – link with thermodynamics:

$$F(V,T,N) = -\beta^{-1} \ln Q_N . \tag{21}$$

3. Grand canonical ensemble:

$\delta W^{\mathrm{mech}} = 0$ (no mechanical work exchange), heat and particle exchange with thermal reservoir; $\mu, V, T = \mathrm{const.}$

Corollary of basic postulate: microstate at phase state point $\Gamma_N = \{\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_N, \mathbf{p}_N\}$ has now a probability p in phase space of

$$p(\Gamma_N) = \frac{1}{\Xi} \exp(N\beta\mu) \; \exp(-\beta\mathcal{H}_N) . \tag{22}$$

Ξ is the grand canonical partition function for a system held at chemical potential μ:

$$\Xi = \sum_{N=0}^{\infty} \exp(N\beta\mu) \, Q_N . \tag{23}$$

Definition of grand free energy – link with thermodynamics:

$$\Omega(V,T,\mu) = -\beta^{-1} \ln \Xi \tag{24}$$

Obviously one could define as many ensembles as there are combinations of independent control parameters.

Phase coexistence:

The possibility of (first–order) phase transitions:

Start with some observations in the grand canonical ensemble:

1. *Particle number fluctuations:*

   expectation values in the g.c.e. of a function $f(N)$ are defined as

   $$\langle f(N) \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} f(N) \, \exp(N\beta\mu) \, Q_N \tag{25}$$

   Let $\bar{N} = \langle N \rangle$ (average number of particles in the system), $\rho = \bar{N}/V$ (particle number density) and $\kappa_T^{-1} = \rho(\partial P/\partial \rho)$ (inverse isothermal compressibility). Then the fluctuations of the particle number N in the g.c.e. ($\equiv$ mean square deviation) are

   $$\frac{1}{\bar{N}}\sqrt{\langle N^2 \rangle - \bar{N}^2} = \frac{\sqrt{\beta^{-1}\rho\kappa_T}}{\sqrt{\bar{N}}} \tag{26}$$

   Exercise: Show this result.

   These fluctuations

   - are small if κ_T finite (i.e. $\partial P/\partial \rho > 0$)

   - may become large if κ_T infinite (i.e. $\partial P/\partial \rho = 0$), as for the critical point or the phase coexistence region

   G.c.e. seems to support the possibility of liquid–gas conversion which corresponds to a macroscopic shift in N.

2. *Minimum principle for Ω:*

   let $\omega = \Omega/V$ and $f = F/V$ – volume densities of the grand free energy and the Helmholtz free energy

   for particles exhibiting hard cores and short–range attractions one can prove explicitly ($T = \text{const.}$)

   $$\Xi = \sum_{N=0}^{\infty} e^{-V\omega(\rho,\mu)} \rightarrow \lim_{V\to\infty} \Xi = e^{-V\omega_0(\mu)} \quad \text{with} \quad \omega_0(\mu) = \min[\omega(\rho,\mu)] \tag{27}$$

   $\Omega = F - \mu N \rightarrow \omega(\rho,\mu) = f(\rho) - \mu\rho$ and $\omega_0(\mu) = \min[f(\rho) - \mu\rho]$, the minimum property entails that $f(\rho)$ is a convex function ($f''(\rho) \geq 0$).

Convexity of $f(\rho)$ is not necessarily guaranteed by the canonical ensemble. Suppose that a certain microscopic model yields a non–convex free energy in the canonical ensemble. Then the minimum property leads to the the *common tangent* or *Maxwell construction*:
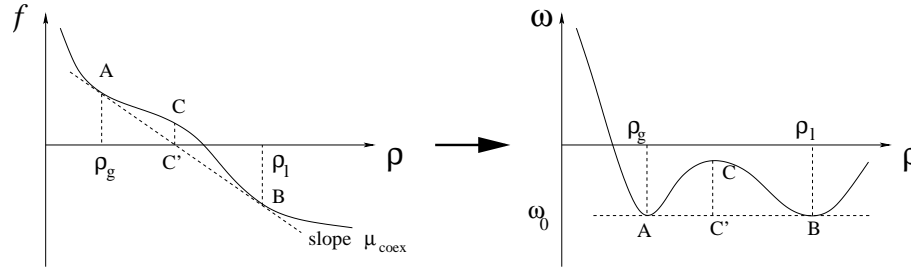
Thus the coexisting gas and liquid states are characterized by equal chemical potential and pressure.

- $f'(\rho_{\mathrm{g}}) = f'(\rho_{\mathrm{l}}) = \mu_{\mathrm{coex}}$

- $\omega(\rho_{\mathrm{g}}, \mu_{\mathrm{coex}}) = \omega(\rho_{\mathrm{l}}, \mu_{\mathrm{coex}}) = -p_{\mathrm{coex}}$

Conclusion: The grand canonical ensemble is indeed the ensemble of choice to study phase transitions.

III. PERTURBATION THEORY FOR GASES

Definition – virial expansion of equation of state:

$$\frac{\beta P}{\rho} = \sum_{l=1}^{\infty} a_l(\beta)(\rho\lambda)^{l-1} \tag{28}$$

$$a_l(\beta): \quad \text{temperature-dependent } l\text{th virial coefficient}$$

Idea: Grand-canonical partition function defines a power expansion in terms of $z = \exp(\beta\mu)$ (fugacity). Seek expansion of $P(z)$ and $\rho(z)$.

A. Classical cluster expansion

J. E. Mayer and M. G. Mayer, Statistical Mechanics *(Wiley, NY, 1940)*

Let $f = 3$ (monatomic gases in three dimensions). Recall definition of grand partition function

$$\Xi = \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3}\right)^N \frac{Z_N(V,T)}{N!} \tag{29}$$

$$Z_N(V,T) = \int d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \exp\left(-\beta \sum_{i<j} u(\mathbf{r}_i - \mathbf{r}_j)\right) \qquad \text{configuration integral} \tag{30}$$

In terms of Mayer f–bond, $\exp[-\beta(u(\mathbf{r}_i - \mathbf{r}_j)] = 1 + f_{ij}$. Advantage: f–bond goes to zero for large distances, qualitative behaviour is as follows:

$\beta = \varepsilon = 1$
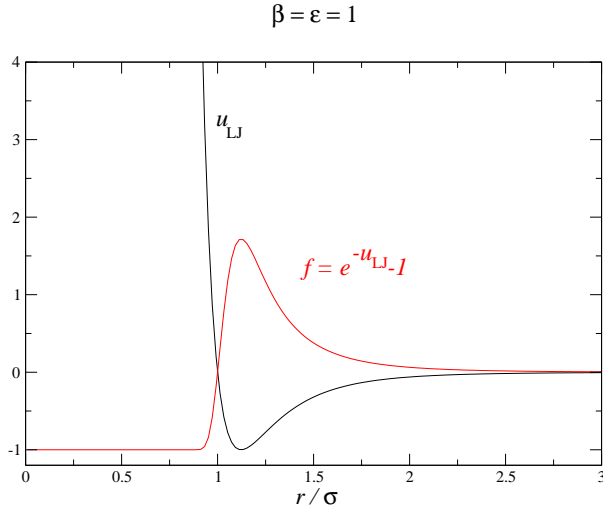
Expand the product of exponentials:

$$Z_N(V,T) \;=\; \int d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \left[1 + (f_{12} + f_{13} + \ldots) + (f_{12}f_{13} + f_{12}f_{14} + \ldots) + \ldots \right] \quad (31)$$

Associate each term in the expansion with a graph.

Definition: An N–particle graph is a collection of N distinct circles numbered $1, 2, \ldots, N$, with lines possibly joining pairs of points (a distinct pair may be joined by only one line).

- Circle $i \equiv$ particle at position $\mathbf{r}_i$

- Line joining the pair $\alpha = (ij) \equiv f_{ij}$

- Graph with lines joining $\alpha, \beta, \ldots, \lambda \equiv \int d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \, f_\alpha f_\beta \ldots f_\lambda$

Note that
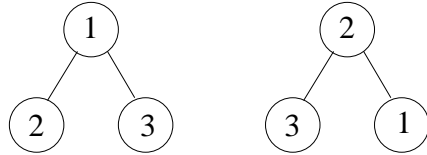
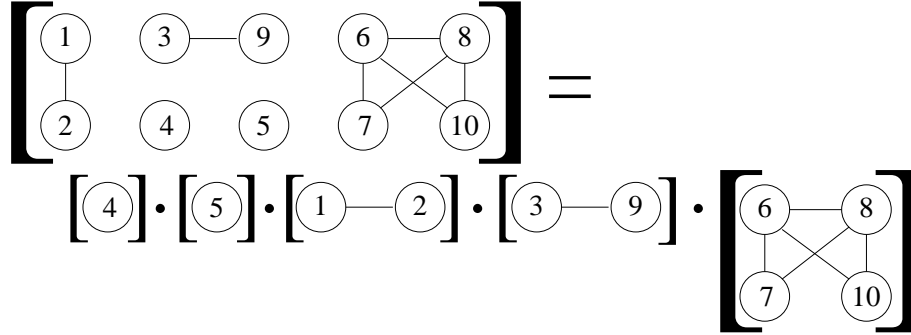are distinct graphs but these are identical:
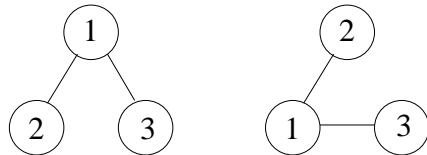
Thus

$$Z_N = (\text{sum of all distinct } N\text{–particle graphs}) \quad (32)$$

23

An arbitray graph may be composed into factors of connected graphs.

Definition: In a connected graphs, every circle is joined to all other circles either directly or indirectly. A connected graph with l circles is called an l–cluster.

Example:

A cluster integral $b_l(V,T)$ is defined as

$$b_l(V,T) = \frac{1}{l!\,\lambda^{3(l-1)}\,V}(\text{sum of all possible } l-\text{clusters}) \tag{33}$$

with the properties

- $b_l(V,T)$ is dimensionless

- $\bar{b}_l(T) = \lim_{V\to\infty} b_l(V,T)$ is a finite number:
  (perform variable change $(\mathbf{r}_1,\ldots,\mathbf{r}_l) \to (\mathbf{r}_m, \mathbf{r}_2 - \mathbf{r}_1, \ldots, \mathbf{r}_l - \mathbf{r}_1)$ with the center–of–mass coordinate $\mathbf{r}_m = (1/l)\sum \mathbf{r}_i$, integrand depends only on relative coordinates and the finite range of f_{ij} makes the integral over relative coordinates finite, integral over $\mathbf{r}_m$ yields factor V which is cancelled by denominator)

24

The first three cluster integrals are:

$$b_1 = \frac{1}{V}\left[\,\text{①}\,\right] = \frac{1}{V}\int d^3\mathbf{r}_1 = 1 \tag{34}$$

$$b_2 = \frac{1}{2!\lambda^3 V}\left[\,\text{①}\!-\!\text{②}\,\right] = \frac{1}{2\lambda^3 V}\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2\, f_{12} = \frac{1}{2\lambda^3}\int d^3\mathbf{r}_{12}\, f_{12} \tag{35}$$

$$b_3 = \frac{1}{3!\lambda^3 V}\left[\;\text{(graphs)} \;+\; \text{(graphs)} \;+\; \text{(graphs)} \;+\; \text{(graphs)}\;\right] \tag{36}$$

Hint: Imagine the numbered circles fixed in space, then draw all possible connections to obtain a connected graph.
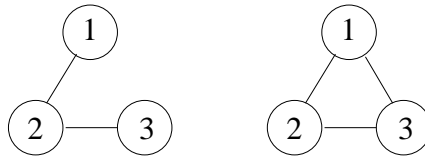
Cluster decomposition of Z_N:

Any $N-$particle graph is a product of m_l $l-$clusters with

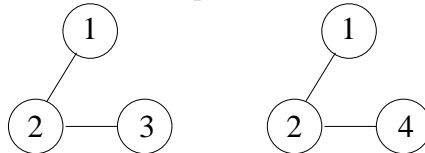$$\sum_{l=1}^{N} l\, m_l = N \tag{37}$$

A given set of integers $\{m_l\}$ does not uniquely specify a graph!

- there are different ways to form an l-cluster

- different particle assignment within cluster possible

Thus, $\{m_l\}$ specifies a *collection* of graphs $\equiv S\{m_l\}$. Then

$$Z_N(V,T) = \sum_{\{m_l\}} S\{m_l\}\Bigg|_{\sum_{l=1}^{N} l\, m_l = N} \tag{38}$$

and pictorially $S\{m_l\}$ is given by

$$S\{m_l\} = \sum_P \left[\bigcirc\right]^{m_1} \left[\bigcirc\!-\!\bigcirc\right]^{m_2} \times \tag{39}$$

$$\left[\;\vcenter{\hbox{(graph)}} + \vcenter{\hbox{(graph)}} + \vcenter{\hbox{(graph)}} + \vcenter{\hbox{(graph)}}\;\right]^{m_3} [\ldots]^{m_4}\ldots$$

- in brackets: polynomials of *unnumbered* graphs (calculated as if graphs are non–commuting to which *numbering* is assigned *at the end*, e.g.

$$\left[\;\vcenter{\hbox{(graph)}} + \vcenter{\hbox{(graph)}}\;\right]^2\Bigg|_{\substack{\text{one specific}\\\text{numbering }P}} = \vcenter{\hbox{(graphs 1,2,3,5,4,6)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}}$$

- P is the set of all independent enumerations of blank circles with particle numbers

  - factor $N!$ – permutations of N objects

  - factor $1/(m_1!\ldots m_N!)$ – permutations of the m_l $l-$clusters are not independent, e.g. $(123) \leftrightarrow (456)$ in example above

  - factor $1/(1!^{m_1} 2!^{m_2} \ldots N!^{m_N})$ – permutations within each $l-$cluster are not independent and is seen by examining the set of all $l-$ clusters (terms within square brackets), e.g.

$$\left.\vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}}\right|_{P = \,2\,\,\,3}^{\,\,1} = \left.\vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}} + \vcenter{\hbox{(graphs)}}\right|_{P = \,3\,\,\,2}^{\,\,1}$$

- $[\ldots]^{m_l} = \left(l!\,\lambda^{3l-3}\,V\,b_l\right)^{m_l}$

Therefore

$$S\{m_l\} = N! \lambda^{3N} \prod_{l=1}^{N} \frac{1}{m_l!} \left(\frac{V}{\lambda^3} b_l \right)^{m_l} \tag{40}$$

and

$$Z_N(V, T) = \sum_{\{m_l\}} N! \lambda^{3N} \prod_{l=1}^{N} \frac{1}{m_l!} \left(\frac{V}{\lambda^3} b_l \right)^{m_l} \Bigg|_{\sum_{l=1}^{N} l\, m_l = N} \tag{41}$$

Complicated in appearance due to the fixed N constraint!

In the grand canonical ensemble N is summed over $\to$ removal of constraint possible. Examine Ξ

$$\Xi(z, V, T) = \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3} \right)^N \frac{Z_N(V, T)}{N!} \tag{42}$$

$$= \sum_{N=0}^{\infty} z^N \sum_{\{m_l\}} \prod_{l=1}^{N} \frac{1}{m_l!} \left(\frac{V}{\lambda^3} b_l \right)^{m_l} \delta_{N, \sum l m_l} \tag{43}$$

$\sum_N$ drops out $\left(\sum_{\{m_l\}} \to \sum_{m_l} \text{ unconstrained} \right)$; interchange $\sum_{m_l}$ and $\prod_l$

$$= \prod_{l=1}^{\infty} \exp \left(\frac{V}{\lambda^3} z^l b_l \right) \tag{44}$$

This is remarkably simple! And it is an example of a more general theorem, useful in qunatum many–body physics and quantum field theory:

Linked Cluster Theorem: The sum of all graphs is the exponential of the sum of all connected graphs.

Note that in $Z_N \to \Xi$: a factor of $z = e^{\beta \mu}$ is attached to each circle.

27

B. Virial equation of state

Thermodynamic limit $V \to \infty$:

$$\bar{b}_l(T) = \lim_{V \to \infty} b_l(V, T) \tag{45}$$

Then

$$\beta P = \ln \Xi(z, T) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \bar{b}_l z^l \tag{46}$$

$$\rho = \frac{\partial P}{\partial \mu} = \beta z \frac{\partial P}{\partial z} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l \, \bar{b}_l z^l \tag{47}$$

Recall definition of the virial coefficients a_l by $\beta P / \rho = \sum a_l (\rho \lambda)^{l-1}$:

Exercise: Show (by eliminating z order by order in P) that:

$$a_1 = \bar{b}_1 = 1 \tag{48}$$

$$a_2 = -\bar{b}_2 \tag{49}$$

$$a_3 = 4\bar{b}_2^2 - 2\bar{b}_3 \tag{50}$$

$$a_4 = -20\bar{b}_2^3 + 18\bar{b}_2\bar{b}_3 - 3\bar{b}_4 \tag{51}$$

$$\ldots$$

Show explicitly to this order that the calculation of the virial coefficients a_l involves only the evaluation of those diagrams in the l–cluster which are at least *doubly connected*. Here, *doubly connected* means that even if you remove one circle together with its adjacent bonds the diagram stays connected. Calculate second and third virial coefficent for the hard–sphere model (analytically) and for the Lennard–Jones model (numerically for $\beta\epsilon = 0.6$ – above coexistence – and $\beta\epsilon = 1.0$ – below coexistence). Compare to the "exact" equations of state. More about diagrammatic methods in Chapter IV D.

C. Phase transitions and zeros in Ξ

Consider again particles with hard cores.

- finite $V \leftrightarrow$ finite maximum number of particles $M(V)$.

- $Z_N(V,T) = 0$ for $N > M(V)$ (since $e^{-\beta u} = 0$)

- $\Xi(z,V) = 1 + zQ_1(V) + \cdots + z^M Q_M(V)$

  polynomial with positive coefficients $\rightarrow$ no real positive roots

- $\dfrac{\partial P(V)}{\partial \rho} = \dfrac{\partial P(V)}{\partial z} / \dfrac{\partial \rho}{\partial z} \geq 0$, since both quotients are ≥ 0

All thermodynamic functions are free of singularities $\rightarrow$ no signal of phase transitions! Thus the thermodynamic limit $V \rightarrow \infty$ must somehow generate nonanalyticities in Ξ if there are phase transitions. Consider now these theorems:

Theorem 1: $P(z) = \lim_{V \to \infty} \frac{1}{V} \ln \Xi(z,V)$ exists for all $z > 0$; it is continuous and non–decreasing; it is also independent on the shape of V (for $\partial V \propto V^{2/3}$).

Theorem 2: Suppose R is a region in the complex z–plane that includes a segment of the positive real axis and contains no roots of Ξ (for *arbitrary* V). In this region, $\ln \Xi /V$ converges uniformly to $P(z)$ (which is analytic) as $V \rightarrow \infty$.

T. D. Lee and C. N. Yang, Phys. Rev. 87, 404 and 410 (1952)

Corollary: Suppose one complex root z^* moves to the real and positive value z_0. Then two domains R_1 and R_2 exis in which Theorem 2 holds independently. At z_0, $P(z)$ is continuous but its first derivative needs not $\rightarrow$ first order phase transition with $z_0 = \exp(\beta \mu_{\mathrm{coex}})$.
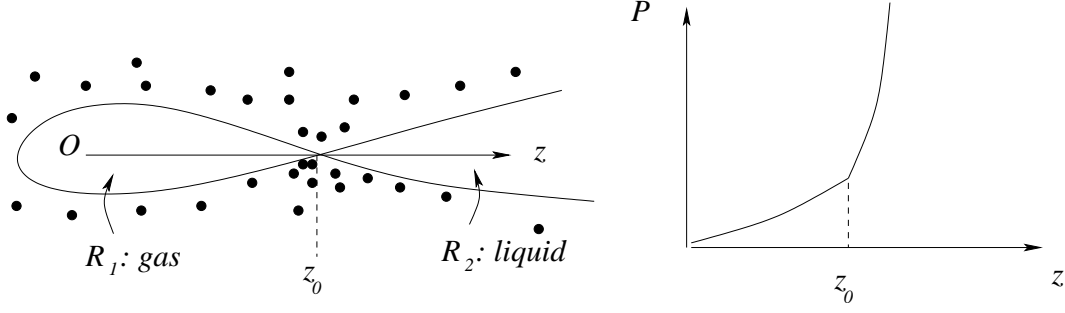
If at z_0, $P'(z)$ is continuous but not $P''(z)$, then we have a second–order phase transition.

Conclusion: At the chemical potential μ_{coex} of coexisting phases, the grand partition function Ξ is zero. The pressure $P = \frac{1}{V}\lim_{V\to\infty} \ln \Xi(\mu_{\text{coex}}, V)$ is finite and its (higher) derivative is discontinuous at μ_{coex}.

Mathematical example: Consider

$$\Xi(z, V) = (1 + z)^V \left(1 + z^{\alpha V}\right) \tag{52}$$

with $V \to V/\sigma^3$ is a dimensionless volume and $\alpha > 0$.

1. The zeros of Ξ:

   - $z_0 = -1$ is a multiple zero outside the physical domain $z > 0$

   - $z_{0,n} = \exp[2\pi i n/(\alpha V)]$ are zeros on the unit circle in the complex $z-$plane. With n fixed and $V \to \infty$, these zeros move to $z = 1$.

   Thus we expect a phase transition at $z = 1$.

2. Equation of state (parametrically in z):

$$\beta P = \lim_{V\to\infty} \ln \Xi/V = \ln(1 + z) + \lim_{V\to\infty} \ln(1 + z^{\alpha V})/V = \begin{cases} \ln(1+z) + \alpha \ln z & (z > 1) \\ \ln(1+z) & (z < 1) \end{cases} \tag{53}$$

$$\rho = z\frac{\partial P}{\partial z} = \begin{cases} \frac{z}{1+z} + \alpha & (z > 1) \\ \frac{z}{1+z} & (z < 1) \end{cases} = \lim_{V\to\infty} \frac{1}{V} z \frac{\partial \ln \Xi}{\partial z} \quad \text{(in each phase domain separately)} \tag{54}$$

3. The power expansion $P(z)$ for small z has radius of convergence $z = 1$! Naive analytic continuation beyond $z = 1$ implies continuation of the "gas" equation of state,

$$\beta P = -\ln(1 - \rho) \,, \tag{55}$$

to the "liquid" domain where actually

$$\beta P = -(1 + \alpha)\ln(1 - \rho + \alpha) + \alpha \ln(\rho - \alpha) \tag{56}$$

holds. (The coexisting densities are $\rho_\mathrm{g} = 1/2$ and $\rho_\mathrm{l} = 1/2 + \alpha$.)
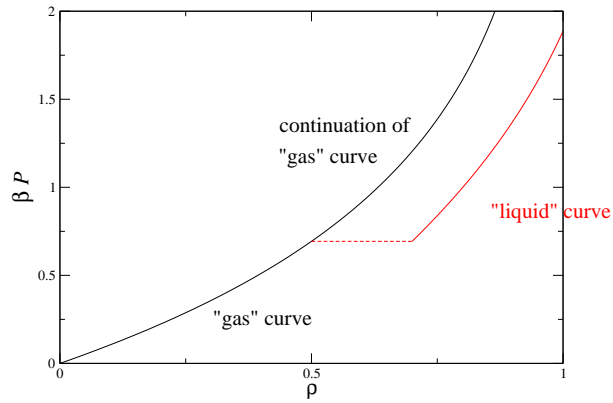
Back to the virial expansion: One may expect that the series expansion $P(z)$ or $P(\rho)$ fails near a phase transition point. However, contrary to the above example, there is no general argument that links the radius of convergence of the virial series to the onset of a phase transition.

IV. THE EQUILIBRIUM THEORY OF FLUID STRUCTURE

Aim: Access physical content of statistical theory through correlation functions:

- *n−particle correlations:*

  fix $n-1$ particles at positions $\mathbf{r}_1, \ldots, \mathbf{r}_{n-1}$, ask for probability to find another particle at position $\mathbf{r}_n$

  "measurable" quantities in experiment and simulation

  "generated" by grand potential

- *n−point direct correlation functions:*

  "functional inverse" of $n-$particle correlations

  "unmeasurable" quantities! but theoretically much more handy

  "generated" by free energy

- theoretical application: density functional theory

A. The $n-$particle correlation functions and reformulations of the equation of state

Notation: $\mathbf{r}_1 \to 1, \mathbf{r}_2 \to 2, \ldots, \mathbf{r}_1' \to 1', \ldots$

1. $n-$particle density $\rho^{(n)}(1, \ldots, n)$:

   $\rho^{(n)}(1, \ldots, n)d(1, \ldots, n)$ – probability of finding n particles of the system with coordinates in the volume element $d\mathbf{r}^n$, irrespective of the positions of the remaining particles (and of all momenta)

   $$\rho^{(n)}(1, \ldots, n) = \langle \hat{\rho}(1, \ldots, n) \rangle \tag{57}$$

   $$\hat{\rho}(1, \ldots, n) = \sum_{i=1}^{N} \sum_{j \neq i}^{N} \ldots \delta(1, i')\delta(2, j') \ldots \tag{58}$$

32

Canonical ensemble: averaging about $\mathbf{r}'_i$:

$$\rho^{(n)}(1,\dots,n) = \frac{1}{Z_N}\frac{N!}{(N-n)!}\int d(n+1)\dots dN \exp[-\beta\sum_{i<j}u(i'-j')]\Big|_{1'=1,\dots,n'=n} \tag{59}$$

Normalization:

$$\int d1\dots dn\,\rho^{(n)} = \frac{N!}{(N-n)!} \tag{60}$$

Grand canonical ensemble: averaging about $\mathbf{r}'_i$ *and* N:

$$\rho^{(n)}(1,\dots,n) = \frac{1}{\Xi}\sum_{N=n}^{\infty}\frac{z^N}{\lambda^{3N}(N-n)!}\int d(n+1)\dots dN \exp[-\beta\sum_{i<j}u(i'-j')]\Big|_{1'=1,\dots,n'=n} \tag{61}$$

Normalization:

$$\int d1\dots dn\,\rho^{(n)} = \langle\frac{N!}{(N-n)!}\rangle \tag{62}$$

in particular

$$\int d1\,\rho^{(1)} = \langle N\rangle \text{ and } \int d1 d2\,\rho^{(2)} = \langle N^2\rangle - \langle N\rangle \tag{63}$$

2. Normalized $\rho^{(n)}(1,\dots,n)$ – n–particle distribution function $g^{(n)}(1,\dots,n)$:

Definition:

$$g^{(n)}(1,\dots,n) = \frac{\rho^{(n)}(1,\dots,n)}{\rho^{(1)}(1)\dots\rho^{(1)}(n)} \tag{64}$$

In particular

$$g^{(1)} = 1 \qquad \text{and} \qquad g^{(2)}(1,2) \overset{\text{bulk}}{=} g(1-2) = \frac{\rho^{(2)}(1-2)}{\rho^2} \tag{65}$$

Since $g(\mathbf{r}_1,\mathbf{r}_2)\to 1$ for $\mathbf{r}_1,\mathbf{r}_2\to\infty$, a useful definition is

$$h(\mathbf{r}_1,\mathbf{r}_2) = g(\mathbf{r}_1,\mathbf{r}_2) - 1 \tag{66}$$

since it vanishes at infinite separation.

3. n–particle fluctuation function $H^{(n)}(1,...,n)$:

Definition: Measures fluctuations in the local density about its average value at n points.

$$H^{(n)}(1,...,n) = \langle\,\Pi_{i=1}^{n}[\hat{\rho}(i) - \rho^{(1)}(i)]\,\rangle\,. \tag{67}$$

Examples:

$$H^{(1)}(1) = 0 , \tag{68}$$

$$
\begin{aligned}
H^{(2)}(1,2) &= \langle \, [\hat{\rho}(1) - \rho^{(1)}(1)][\hat{\rho}(2) - \rho^{(1)}(2)] \, \rangle \\
&= \rho^{(2)}(1,2) + \rho^{(1)}(1)\,\delta(1-2) - \rho^{(1)}(1)\rho^{(1)}(2) \\
&= \rho^{(1)}(1)\rho^{(1)}(2)\,h(1,2) + \rho^{(1)}(1)\,\delta(1-2) \, . \tag{69}
\end{aligned}
$$

Note that $\hat{\rho}(1)\hat{\rho}(2) = \sum_{i'} \delta(1-i') \sum_{j'} \delta(2-j') = \sum_{i'} \delta(1-i') \sum_{j' \neq i'} \delta(2-j') + \sum_{i'} \delta(1-i')\delta(2-j') \equiv \hat{\rho}^{(2)}(1,2) + \hat{\rho}(1)\delta(1-2)$.

Equation of state for the bulk fluid: (bulk: $\rho^{(1)} = \rho$)

- *(Internal) energy equation of state:*

  Remember the definition $U = \langle \mathcal{H} \rangle$ where $\mathcal{H}$ – Hamiltonian. For two–body potentials this is equivalent to

  $$U = U^{\mathrm{id}} + U^{\mathrm{ex}} = U^{\mathrm{id}} + \int d1 d2 \, \langle \frac{N(N-1)}{2} u(1-2)\delta(1,1')\delta(2,2') \rangle \tag{70}$$

  (Pick two particles out of N and average about their potential energy *at fixed distance.* Then integrate over the positions of these two particles.)

  U^{id} – internal energy of ideal gas.

  $$U^{\mathrm{ex}} = \frac{1}{2} \int d1 d2 \, u(1-2) \, \rho^{(2)}(1-2) = V\frac{\rho^2}{2} \int d\mathbf{r} \, u(\mathbf{r})g(\mathbf{r}) \tag{71}$$

  Once $U(\rho, T)$ is known, all other thermodynamic quantities can be deduced immediately.

- *Virial or pressure equation of state:*

  Reminder – virial theorem:

  Definition of virial function for an $N-$particle system:

  $$\mathcal{V}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \tag{72}$$

  where $\mathbf{F}_i$ – total force acting on particle i. Consider the time average

  $$\langle \mathcal{V} \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^{N} \mathbf{r}_i(t) \cdot \mathbf{F}_i(t) \, dt = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^{N} \mathbf{r}_i(t) \cdot m\ddot{\mathbf{r}}_i(t) \, dt$$

  $$= -\lim_{\tau \to \infty} \frac{1}{\tau} \left[\int_0^\tau \sum_{i=1}^{N} m\dot{\mathbf{r}}_i^2(t) \, dt - m(\mathbf{r}_i(\tau) \cdot \dot{\mathbf{r}}_i(\tau) - \mathbf{r}_i(0) \cdot \dot{\mathbf{r}}_i(0)) \right] \tag{73}$$

  1. system volume finite $\to$ virial theorem

  $$\langle \mathcal{V} \rangle_t = -2 \, \langle \sum_{i=1}^{N} \mathbf{p}_i^2/(2m) \rangle_t \tag{74}$$

  2. ergodic theorem: time average = ensemble average

  $$\langle \mathcal{V} \rangle_t = -3 \, \langle N \rangle \, k_{\mathrm{B}} T \quad \text{g.c.e.} \tag{75}$$

35

Total force on particle i can be split into internal force (exerted by all the other particles)

$$\mathbf{F}_i^{\text{int}} = -\sum_{\text{only } j \neq i} \nabla_i u(\mathbf{r}_i - \mathbf{r}_j) \quad \rightarrow \tag{76}$$

$$\langle \mathcal{V}^{\text{int}} \rangle = -\langle \sum_{i \neq j}^{N} \mathbf{r}_i \nabla_i u(\mathbf{r}_i - \mathbf{r}_j) = -\langle \sum_{i < j}^{N} (\mathbf{r}_i - \mathbf{r}_j) \cdot \nabla u(\mathbf{r}_i - \mathbf{r}_j) \rangle$$

and external force (exerted by the confining walls of the system). "Actio = reactio" demands that *on average*

$$\langle \sum_{i=1}^{N} \mathbf{F}_i^{\text{ext}} \rangle = -P \int_{\partial V} dA \mathbf{n} \quad \rightarrow \tag{77}$$

$$\langle \mathcal{V}^{\text{ext}} \rangle = -P \int_{\partial V} dA \mathbf{r} \cdot \mathbf{n} = -P \int_V dV \text{div} \mathbf{r} = -3PV$$

Putting together, we obtain

$$PV = \langle N \rangle k_{\text{B}} T - \frac{1}{3} \langle \mathcal{V}^{\text{int}} \rangle \tag{78}$$

Rewrite the statistical average (as for U):

$$PV = \langle N \rangle k_{\text{B}} T - \frac{1}{3} \int d1 d2 \, \langle \frac{N(N-1)}{2} (1-2) \nabla u(1-2) \delta(1,1') \delta(2,2') \rangle \tag{79}$$

$$= \langle N \rangle k_{\text{B}} T - \frac{1}{6} V \rho^2 \int d\mathbf{r} \, \mathbf{r} \cdot \nabla u(\mathbf{r}) \, g(r) \tag{80}$$

Dividing by $\langle N \rangle$, we obtain the *pressure* or *virial equation*:

$$\frac{\beta P}{\rho} = 1 - \frac{\rho}{6} \int d\mathbf{r} \, \mathbf{r} \cdot \nabla u(\mathbf{r}) \, g(r) \tag{81}$$

- *Compressibility equation of state:*

  Remember the integrated one– and two–particle densities $\int d1 \quad \rho^{(1)} = \langle N \rangle$ and $\int d1 d2 \, \rho^{(2)} = \langle N^2 \rangle - \langle N \rangle$. Thus the squared particle number fluctuations are

$$\langle N^2 \rangle - \langle N \rangle^2 = \int d1 d2 \, \rho^{(2)} + \int d1 \, \rho^{(1)} - \left(\int d1 \, \rho^{(1)} \right)^2 = \frac{\langle N \rangle}{\beta \frac{\partial P}{\partial \rho}} \quad \text{(see (??))} \tag{82}$$

  and the compressibility equation is:

$$\beta \frac{\partial P}{\partial \rho} = \frac{1}{1 + \rho \int d\mathbf{r} \, h(\mathbf{r})} \tag{83}$$

36

B. Fluids in external fields

Liquids:

- homogeneous in the bulk

- inhomogeneous near walls or other boundaries; where different phases meet

- modelling of walls or other obstacles: external potential V^{ext} acting on single particles, description of wetting and adsorption phenomena possible

- theoretical advantages:

  - *functional formulation* of the theory

  - exploitation of *test particle ideas*, e.g.:
    pair distribution function in the bulk $\equiv$ density distribution around fixed particle acting as an external potential

1. Definitions

internal potential energy of fluid particles

$$U_N = \sum_{i<j}^{N} u(\mathbf{r}_i - \mathbf{r}_j) \tag{84}$$

external potential energy

$$V_N = \sum_{i}^{N} V^{\text{ext}}(\mathbf{r}_i) = \int d^3\mathbf{r}\ \hat{\rho}(\mathbf{r})\, V^{\text{ext}}(\mathbf{r})\ , \tag{85}$$

(remember density operator definition (**??**): $\hat{\rho}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$)

Generalizations from bulk:

Grand partition function depends on a position–dependent *intrinsic chemical potential,*

$\psi(\mathbf{r}) = \mu - V^{\text{ext}}(\mathbf{r})$:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N) \left(\frac{z}{\lambda^3}\right)^N \rightarrow \tag{86}$$

$$\sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N) \left(\frac{z}{\lambda^3}\right)^N \exp(-\beta V_N) = \tag{87}$$

$$\sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N) \prod_{i}^{N} \frac{\exp(\beta\psi(\mathbf{r}_i))}{\lambda^3} \tag{88}$$

In the bulk, the grand potential was $\beta\Omega(V, T, \mu) = -\ln\Xi$ the conjugate variable to μ was $-\bar{N}$, or, after division by V, minus the density ρ:

$$\frac{\partial\Omega}{\partial\mu} = -\frac{1}{\Xi}\frac{\partial\Xi}{\partial(\beta\mu)} = -\frac{z}{\Xi}\frac{\partial\Xi}{\partial z} = -\frac{1}{\Xi}\sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N)\, N \, \left(\frac{z}{\lambda^3}\right)^N = -\langle N \rangle \tag{89}$$

Now, in the general inhomogeneous situation, we define the grand potential functional via $\beta\Omega[\psi(\mathbf{r})] = -\ln\Xi[\psi(\mathbf{r})]$, and the conjugate to $\psi(\mathbf{r})$ is found by functional differentiation:

$$\begin{aligned}
\frac{\delta\Omega}{\delta\psi(\mathbf{r})} &= -\frac{1}{\Xi}\frac{\delta\Xi}{\delta(\beta\psi(\mathbf{r}))} \\
&= -\frac{1}{\Xi}\sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N) \sum_i \frac{\delta\psi(\mathbf{r}_i)}{\delta\psi(\mathbf{r})} \prod_i^N \frac{\exp(\beta\psi(\mathbf{r}_i))}{\lambda^3} \\
&= -\langle\hat{\rho}(\mathbf{r})\rangle = -\rho^{(1)}(\mathbf{r}) \ . \tag{90}
\end{aligned}$$

What about higher functional derivatives? First note that repeated application of $\delta/\delta z^*$ on Ξ (with $z^*(\mathbf{r}) = \exp[\beta\psi(\mathbf{r})]$) gives

$$\frac{1}{\Xi}\frac{\delta^n\Xi}{\delta z^*(\mathbf{R}_1)\dots\delta z^*(\mathbf{R}_n)} = \tag{91}$$

$$\frac{1}{\Xi}\sum_{N=0}^{\infty} \frac{1}{N!} \int d1 \dots dN \, \exp(-\beta U_N) \sum_{i_1} \frac{\delta(\mathbf{R}_1 - \mathbf{r}_{i_1})}{\lambda^3} \sum_{i_2 \neq i_1} \frac{\delta(\mathbf{R}_2 - \mathbf{r}_{i_2})}{\lambda^3} \cdots \prod_{i=n+1}^{N} \frac{\exp(\beta\psi(\mathbf{r}_i))}{\lambda^3}$$

$$= \prod_i^n \exp(-\beta\psi(\mathbf{R}_i)) \, \langle\hat{\rho}(\mathbf{R}_1, \dots, \mathbf{R}_n)\rangle$$

$$= \frac{1}{\prod_i^n z^*(\mathbf{R}_i)} \, \rho^{(n)}(\mathbf{R}_1, \dots, \mathbf{R}_n) \ .$$

Thus, one calls the grand partition function Ξ the generating functional for the n–particle densities.

Use this for the second derivative of Ω:

$$
\begin{aligned}
\frac{\delta^2 \Omega}{\delta\psi(\mathbf{R}_1)\delta\psi(\mathbf{R}_2)} &= -\beta z^*(\mathbf{R}_2)\frac{\delta}{\delta z^*(\mathbf{R}_2)}\left(\frac{1}{\Xi}z^*(\mathbf{R}_1)\frac{\delta\Xi}{\delta z^*(\mathbf{R}_1)}\right) \\
&= -\frac{\beta}{\Xi}z^*(\mathbf{R}_1)z^*(\mathbf{R}_2)\frac{\delta^2\Xi}{\delta z^*(\mathbf{R}_1)\delta z^*(\mathbf{R}_2)} - \frac{\beta}{\Xi}\delta(\mathbf{R}_1-\mathbf{R}_2)z^*(\mathbf{R}_1)\frac{\delta\Xi}{\delta z^*(\mathbf{R}_1)} + \\
&\quad \beta\left(\frac{1}{\Xi}z^*(\mathbf{R}_1)\frac{\delta\Xi}{\delta z^*(\mathbf{R}_1)}\right)\left(\frac{1}{\Xi}z^*(\mathbf{R}_1)\frac{\delta\Xi}{\delta z^*(\mathbf{R}_1)}\right) \\
&= -\beta\rho^{(2)}(\mathbf{R}_1,\mathbf{R}_2) - \beta\delta(\mathbf{R}_1-\mathbf{R}_2)\rho^{(1)}(\mathbf{R}_1) + \beta\rho^{(1)}(\mathbf{R}_1)\rho^{(1)}(\mathbf{R}_2) \\
&= -\beta H^{(2)}(\mathbf{R}_1,\mathbf{R}_2) \,. \tag{92}
\end{aligned}
$$

More generally:

$$
\frac{\delta^n(\beta\Omega)}{\delta(\beta\psi(\mathbf{R}_1))\ldots\delta(\beta\psi(\mathbf{R}_n))} = -H^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n) \qquad (n \geq 2) \,. \tag{93}
$$

Exercise: Show this by induction.

Thus, the grand potential Ω is the generating functional for the 1–particle density and the n–particle fluctuations.

Since $V^{\text{ext}}(\mathbf{r})$ is supposed to contain the information about spatial confinement of the fluid, replace V as thermodynamic quantity: $V \to V^{\text{ext}}(\mathbf{r})$, and the (grand canonical) first law of thermodynamics becomes:

$$
\delta U = T\delta S + \int d^3\mathbf{r}\rho(\mathbf{r})\,\delta V^{\text{ext}}(\mathbf{r}) + \mu\delta N \tag{94}
$$

The free energy and the internal energy

In the bulk, the conjugate variabel pair $(\mu, -N)$ lead to the Legendre transform

$$
F(T,V,N) = \Omega(T,V,\mu) + N\mu \,. \tag{95}
$$

Since now $(\mu, -N) \to (\psi(\mathbf{r}), -\rho(\mathbf{r}))$, we can define

$$
\mathcal{F}[\rho(\mathbf{r})] = \Omega[\psi(\mathbf{r})] + \int d^3\mathbf{r}\rho(\mathbf{r})[\mu - V^{\text{ext}}(\mathbf{r})]. \tag{96}
$$

Here, $\rho(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$.

$\mathcal{F}$ and Ω are functions of the temperature T but not of the volume V anymore. Since $V^{\text{ext}}(\mathbf{r})$

is supposed to contain the information about spatial confinement of the fluid, replace V as thermodynamic quantity: $V \to V^{\text{ext}}(\mathbf{r})$. The first law transforms as

$$
\begin{aligned}
\delta U &= T\delta S - P\delta V + \mu \delta N \to \\
\delta U &= T\delta S + \int \frac{\delta \Omega}{\delta V^{\text{ext}}} \delta V^{\text{ext}} + \mu \delta N \\
&= T\delta S + \int d^3\mathbf{r} \rho(\mathbf{r})\, \delta V^{\text{ext}}(\mathbf{r}) + \mu \delta N \; .
\end{aligned}
\tag{97}
$$

The ideal gas

For an ideal gas, the one–particle density in an external field is given by the barometric law

$$
\rho(\mathbf{r}) = \rho_0 \exp[-\beta V^{\text{ext}}(\mathbf{r})] = \lambda^{-3}\exp[\beta(\mu - V^{\text{ext}}(\mathbf{r}))] = \lambda^{-3}\exp[\beta\psi(\mathbf{r})].
\tag{98}
$$

Since $\delta\Omega/\delta\psi = -\rho$, we find

$$
\beta\Omega^{\text{id}}[\psi] = -\lambda^{-3}\int d^3\mathbf{r}\,\exp[\beta\psi(\mathbf{r})].
\tag{99}
$$

Legendre–transforming gives

$$
\begin{aligned}
\beta\mathcal{F}^{\text{id}}[\rho] &= \beta\Omega + \int d^3\mathbf{r}\rho(\mathbf{r})[\beta\psi(\mathbf{r})] \\
&= \int d^3\mathbf{r}\rho(\mathbf{r})[\ln \lambda^3 \rho(\mathbf{r}) - 1] \; .
\end{aligned}
\tag{100}
$$

The ideal gas shows no correlations, i.e.

$$
g^{(n)}(1,\ldots,n) = 1 \; .
\tag{101}
$$

(The n–particle densities factorize into 1–particle densities.)

Direct correlation functions

We saw that $\Omega[\psi]$ generates the one–particle density and the n–point fluctuations by (multiple) functional differentiation $\delta/\delta\psi$. The (multiple) functional differentiation $\delta/\delta\rho$ on $\mathcal{F}$ generates a new class of correlation functions:

$$
C^{(n)}(\mathbf{R}_1,\ldots,\mathbf{R}_n) = -\frac{\delta\,\beta\mathcal{F}[\rho]}{\delta\rho(\mathbf{R}_1)\ldots\delta\rho(\mathbf{R}_n)} \; .
\tag{102}
$$

The minus sign is convention. The ideal part is local (i.e. depends only on one position coordinate)

$$C_{\text{id}}^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = -\frac{\delta \beta \mathcal{F}^{\text{id}}[\rho]}{\delta \rho(\mathbf{R}_1) \ldots \delta \rho(\mathbf{R}_n)} . \tag{103}$$

$$= \begin{cases} -\ln \lambda^3 \rho(\mathbf{R}_1) & (n = 1) \\ \dfrac{(-1)^{n-1}}{\rho^{n-1}(\mathbf{R}_1)} \delta(\mathbf{R}_2 - \mathbf{R}_1) \ldots \delta(\mathbf{R}_n - \mathbf{R}_1) & (n > 1) \end{cases} . \tag{104}$$

The excess part only is usually associated with the terminus direct correlation function:

$$C_{\text{ex}}^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = -\frac{\delta \beta \mathcal{F}^{\text{ex}}[\rho]}{\delta \rho(\mathbf{R}_1) \ldots \delta \rho(\mathbf{R}_n)} \equiv c^{(n)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) . \tag{105}$$

1. $n = 1$: $-C^{(1)}$ is the intrinsic chemical potential

$C^{(1)}$ immediately follows from the definition of $\mathcal{F}$ by Legendre transforming Ω:

$$\mathcal{F}[\rho(\mathbf{r})] = \Omega[\psi(\mathbf{r})] + \int d^3\mathbf{r} \rho(\mathbf{r}) \psi(\mathbf{r}). \tag{106}$$

Thus

$$-\frac{\delta \beta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r})} = -\beta \psi(\mathbf{r}) \tag{107}$$

$$= C^{(1)}(\mathbf{r}) = -\ln \lambda^3 \rho(\mathbf{r}) + c^{(1)}(\mathbf{r}) \tag{108}$$

Thus we have a direct connection of $c^{(1)}$ to ρ:

$$\rho(\mathbf{r}) = \lambda^{-3} \exp\left[\beta \psi(\mathbf{r}) + c^{(1)}\right] \tag{109}$$

This appears to be a neat generalization from the ideal gas where

$$\rho^{\text{id}} = \lambda^{-3} \exp \beta \mu^{\text{id}} \tag{110}$$

holds.

2. $n = 2$ and the Ornstein–Zernike relation

First we show that $-C^{(2)}$ (generated from $\mathcal{F}$) and $H^{(2)}$ (generated from Ω) are the inverse of each other. Note: The inverse of a two–point function is defined by

$$\int d\mathbf{r}'' f(\mathbf{r}, \mathbf{r}'') f^{-1}(\mathbf{r}'', \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{111}$$

Now consider the following

$$
\begin{aligned}
\delta(\mathbf{r} - \mathbf{r}') &= \frac{\delta\psi(\mathbf{r})}{\delta\psi(\mathbf{r}')} \\
&= \int d\mathbf{r}'' \frac{\delta\psi(\mathbf{r})}{\delta\rho(\mathbf{r}'')} \frac{\delta\rho(\mathbf{r}'')}{\delta\psi(\mathbf{r}')} \qquad \text{(functional chain rule)} \\
&= \int d\mathbf{r}'' \left[-\beta^{-1} C^{(2)}(\mathbf{r}, \mathbf{r}'') \right] \left[\beta H^{(2)}(\mathbf{r}'', \mathbf{r}') \right]
\end{aligned}
\tag{112}
$$

Here we used $\rho = -\delta\Omega/\delta\psi$ and $\psi = -\beta^{-1}\delta\mathcal{F}/\delta\rho$ (which follow from the Legendre transformation). Thus the inversion property is purely a consequence from the relation of Ω to $\mathcal{F}$ via the Legendre transformation.

One of the central relations of liquid state theory, the Ornstein–Zernike relation links $c^{(2)}$ with h and directly follows from this inversion relation:

$$
\begin{aligned}
\delta(\mathbf{r} - \mathbf{r}') &= -\int d\mathbf{r}'' C^{(2)}(\mathbf{r}, \mathbf{r}'') H^{(2)}(\mathbf{r}'', \mathbf{r}') \\
&= -\int d\mathbf{r}'' \left[-\frac{\delta(\mathbf{r} - \mathbf{r}'')}{\rho(\mathbf{r})} + c^{(2)}(\mathbf{r}, \mathbf{r}'') \right] \left[\rho(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') + \rho(\mathbf{r}')\rho(\mathbf{r}'') h(\mathbf{r}'', \mathbf{r}') \right] \\
&= \delta(\mathbf{r} - \mathbf{r}') + \rho(\mathbf{r}') h(\mathbf{r}', \mathbf{r}) - \rho(\mathbf{r}') c^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}') \int d\mathbf{r}'' \rho(\mathbf{r}'') c^{(2)}(\mathbf{r}, \mathbf{r}'') h(\mathbf{r}'', \mathbf{r}') .
\end{aligned}
$$

Using the symmetry of $c^{(2)}$ and h in their arguments, we find

$$
h(\mathbf{r}, \mathbf{r}') - c^{(2)}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \rho(\mathbf{r}'') c^{(2)}(\mathbf{r}, \mathbf{r}'') h(\mathbf{r}'', \mathbf{r}')
\tag{113}
$$

(Ornstein-Zernike relation)

Solve for h recursively:

$$
\begin{aligned}
h(1, 2) &= c^{(2)}(1, 2) + \int d3\, c^{(2)}(1, 3)\, \rho(3)\, c^{(2)}(3, 2) + \\
&\quad \int d3d4\, c^{(2)}(1, 3)\, \rho(3)\, c^{(2)}(3, 4)\, \rho(4)\, c^{(2)}(4, 2) + \dots
\end{aligned}
\tag{114}
$$

Physical interpretation:

- total correlation h between 1 and 2 contains a "direct" piece $c^{(2)}(1, 2)$ and an "indirect" piece propagated via intermediate particles: (3), (3,4) …

- plausible assumption (for the bulk at least): range of $c(1,2) = c(1-2) \sim$ range of $u(1-2)$ (interparticle potential)

- layer or peak structure in $h(1-2)$ follows from "indirect" correlations

Example: bulk Lennard–Jones fluid with cutoff $r_c = 4\sigma$ in the interparticle potential:
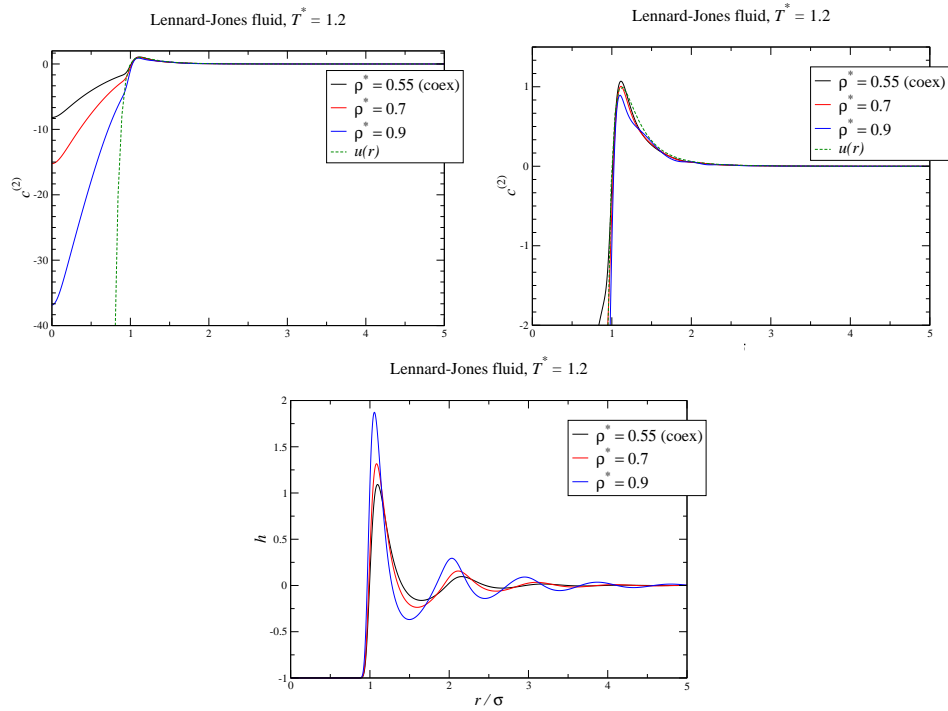

FIG. 10: h and $c^{(2)}$ for a LJ fluid

2. Ornstein–Zernike theory of the critical point

Critical point:

- correlations between particles become universal power–laws (i.e. long–ranged), independent of atomic details

- measurable by scattered intensity of X-rays, neutrons and light → structure factor

Structure factor

We assume quasi–elastic scattering: energy of radiation quanta is much larger than typical excitation energies of the system. Then:
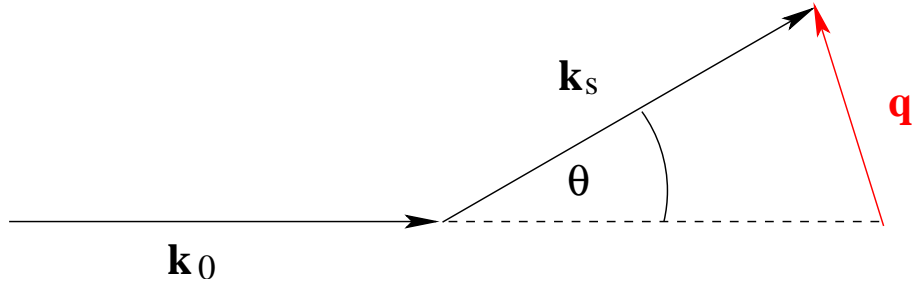
$$k \equiv |\vec{k}_0| \simeq |\vec{k}_s| \tag{115}$$

$$q \equiv |\vec{q}| \simeq \sqrt{2k^2 - 2k^2 \cos\theta} = 2k \sin\frac{\theta}{2} \tag{116}$$

When illuminated by a plane wave, each particle j would scatter it with a direction–dependent amplitude $a_j(\mathbf{q})$ (*scattering amplitude*). Asymptotically the scattered waves are approximately planar, such that the total intensity is given by a coherent superposition of the $a_j(\mathbf{q})$:

$$I(\mathbf{q}) = \langle \left| \sum_j a_j(\mathbf{q}) \right|^2 \rangle \tag{117}$$

Relation between the scattering amplitudes of any two particles in the system:

$$a_j(\mathbf{q}) = a_1(\mathbf{q}) \exp(-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_1)) \tag{118}$$

44

(this is the phase difference of the asymptotic planar waves which have been emitted by the two particles). Hence

$$I(\mathbf{q}) = |a_1(\mathbf{q})|^2 \left\langle \left| \sum_j \exp(-i\mathbf{q} \cdot \mathbf{r}_j) \right|^2 \right\rangle \tag{119}$$

If there are no correlations (ideal gas), then $I^{\mathrm{id}}(\mathbf{q}) = \langle N \rangle |a_1(\mathbf{q})|^2$. The structure factor is now defined by the normalized scattered intensity

$$
\begin{aligned}
S'(\mathbf{q}) &= \rho \frac{I(\mathbf{q})}{I^{\mathrm{id}}(\mathbf{q})} \\
&= \frac{1}{V} \langle \sum_{i,j} \exp(-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \rangle \\
&= \frac{1}{V} \int d\mathbf{R}_1 d\mathbf{R}_2 \, \exp(-i\mathbf{q} \cdot (\mathbf{R}_1 - \mathbf{R}_2)) \, \langle \sum_i \delta(\mathbf{r}_i - \mathbf{R}_1) \sum_j \delta(\mathbf{r}_i - \mathbf{R}_2) \rangle \\
&= \frac{1}{V} \int d\mathbf{R}_1 d\mathbf{R}_2 \, \exp(-i\mathbf{q} \cdot (\mathbf{R}_1 - \mathbf{R}_2)) \, \langle \hat{\rho}(\mathbf{R}_1) \hat{\rho}(\mathbf{R}_2) \rangle \\
&= \frac{1}{V} \int d\mathbf{R}_1 d\mathbf{R}_2 \, \exp(-i\mathbf{q} \cdot (\mathbf{R}_1 - \mathbf{R}_2)) \, \langle \hat{\rho}(\mathbf{R}_1, \mathbf{R}_2) + \delta(\mathbf{R}_1 - \mathbf{R}_2) \hat{\rho}(\mathbf{R}_1) \rangle \\
&= \rho^2 \int d\mathbf{R} \exp(-i\mathbf{q} \cdot \mathbf{R}) \, g(\mathbf{R}) + \rho \\
&= \rho \left(1 + \rho \tilde{h}(\mathbf{q})\right) + \rho^2 \, 2\pi \delta(\mathbf{q}) \,.
\end{aligned}
\tag{120}
$$

The second term only contributes for $\mathbf{q} = 0$, i.e. for forward scattering. Forward scattering is dominated by the beam anyway, so one usually discards this term.

$$S(\mathbf{q}) = \rho \left(1 + \rho \tilde{h}(\mathbf{q})\right) = \tilde{H}(\mathbf{q}). \tag{121}$$

Using the Ornstein–Zernike equation in the bulk,

$$
\begin{aligned}
h(\mathbf{r}) &= c^{(2)}(\mathbf{r}) + \rho \int d\mathbf{r}' c^{(2)}(\mathbf{r}') \, h(\mathbf{r} - \mathbf{r}') \quad \rightarrow \\
\tilde{h}(\mathbf{q}) &= \tilde{c}^{(2)}(\mathbf{q}) + \rho \, \tilde{c}^{(2)}(\mathbf{q}) \, \tilde{h}(\mathbf{q}) \quad \rightarrow \\
1 + \rho \, \tilde{h}(\mathbf{q}) &= \frac{1}{1 - \rho \, \tilde{c}^{(2)}(\mathbf{q})}
\end{aligned}
\tag{122}
$$

and thus

$$S(\mathbf{q}) = \frac{\rho}{1 - \rho \, \tilde{c}^{(2)}(\mathbf{q})} \tag{123}$$

The Ornstein–Zernike assumption

45

The direct correlation function $c^{(2)}(\mathbf{r})$ stays short–ranged near the critical point. I.e., its Fourier transform may be Taylor expanded in $\mathbf{q}$. For isotropic systems

$$\tilde{c}^{(2)}(\mathbf{q}) \equiv \tilde{c}^{(2)}(q) = c_0 + c_2\, q^2 + \dots \tag{124}$$

and therefore

$$\frac{\rho}{S(q)} = [1 - \rho c_0] - \rho c_2\, q^2 + \dots \tag{125}$$

Note that from OZ and the compressibility equation we know

$$1 - \rho c_0 = \frac{1}{1 + \rho \tilde{h}(0)} = \frac{1}{1 + \rho \int d\mathbf{r}\, h(r)} \tag{126}$$

$$= \beta \frac{\partial P}{\partial \rho} \xrightarrow{T \to T_c} 0$$

At the critical point, the structure factor should be divergent: $S(q) \propto q^{-2}$.

Al-ZN alloy : T(crit) = 351.5°C

FIG. 7.4. The q dependence of the structure factor $S(q)$ for several temperatures just above the critical temperature $T_c = 351\cdot5°C$. After the work of Münster and Sagel (1958) on Al–Zn alloy. The 'lattice-gas' model of a simple fluid (cf. §1.1) also provides a useful model for a binary alloy.

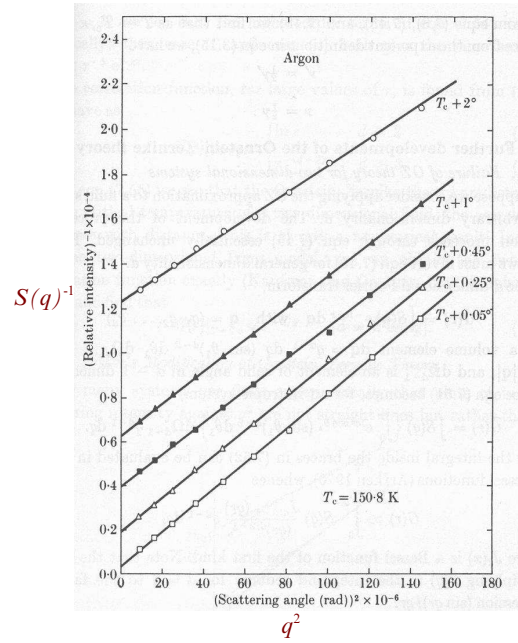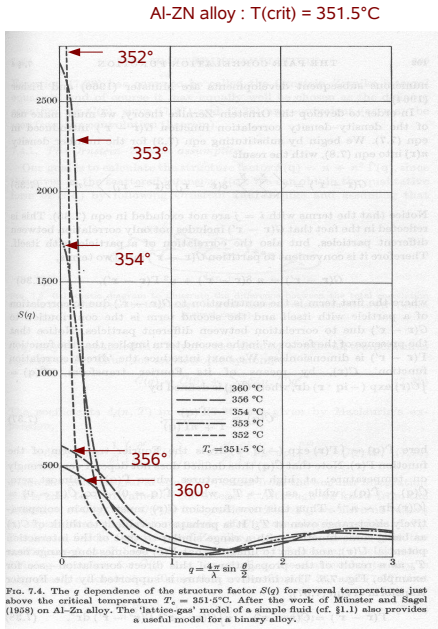FIG. 11: $S(q)$ for an Al–Zn alloy: $q \to 0$ divergence as $T \to T_c$

$S(q)^{-1}$ for Argon: apparent confirmation of the OZ assumption

46

The behavior of $h(r)$ is obtained by back–inversion of the Ornstein–Zernike relation:

$$\tilde{h}(q) = \frac{\tilde{c}^{(2)}(q)}{1 - \rho\,\tilde{c}^{(2)}(q)}$$

$$\approx \frac{c_0}{[1 - \rho c_0] - \rho c_2\, q^2} \tag{127}$$

Introduce a squared length $\xi^2 = -\rho c_2/(1 - \rho c_0)$:

$$\tilde{h}(r) = \frac{1}{(2\pi)^3}\frac{c_0}{1 - \rho c_0}\int d\mathbf{q}\,\exp(i\mathbf{q}\cdot\mathbf{r})\,\frac{1}{1 + \xi^2 q^2} \tag{128}$$

This is a typical Fourier integral:

$$\int d\mathbf{q}\,\exp(i\mathbf{q}\cdot\mathbf{r})\,\frac{1}{1 + \xi^2 q^2} = 2\pi\int_0^\infty dq\,\frac{q^2}{1 + \xi^2 q^2}\int_{-1}^1 dx\,\exp(iqrx)$$

$$= \frac{2\pi}{ir}\int_0^\infty dq\,\frac{q}{1 + \xi^2 q^2}\,[\exp(iqr) - \exp(-iqr)]$$

The integral is symmetric in $q \to -q$. Therefore we can extend it to $q \in (-\infty, 0]$ and close the contour in the upper half plane (for terms $\propto \exp(iqr)$) and in the lower half plane (for terms $\propto \exp(-iqr)$). Such a contribution is then only finite if the integrand has a simple pole in the enclosed area. Thus:

$$\int d\mathbf{q}\,\exp(i\mathbf{q}\cdot\mathbf{r})\,\frac{1}{1 + \xi^2 q^2} = \frac{\pi}{ir}\frac{1}{\xi^2}\left[\oint_{-\infty,\mathrm{up}} dq\,\frac{q\,\exp(iqr)}{\left(q + \frac{i}{\xi}\right)\left(q - \frac{i}{\xi}\right)} - \oint_{-\infty,\mathrm{low}} dq\,\frac{q\,\exp(-iqr)}{\left(q + \frac{i}{\xi}\right)\left(q - \frac{i}{\xi}\right)}\right]$$

$$= \frac{\pi}{ir}\frac{1}{\xi^2}\,(2\pi i)\,\exp(-r/\xi) = \frac{2\pi^2}{\xi^2}\frac{\exp(-r/\xi)}{r} \tag{129}$$

and thus

$$h(r) = \frac{1}{4\pi}\frac{c_0}{(-\rho c_2)}\frac{\exp(-r/\xi)}{r} \tag{130}$$

At $T \neq T_c$, $h(r)$ decays exponentially with a characteristic length ξ, the correlation length. As $T \to T_c$, ξ diverges since $1 - \rho c_0 \to 0$, and therefore at the critical point, the pair correlation function decays independent of c as $h(r) \propto 1/r$ $(T = T_c)$.

Renormalization group predicts at $T = T_c$:

$$h(r) \propto \frac{1}{r^{d-2-\eta(d)}} \tag{131}$$

with $\eta(3) \approx 0.06$. Thus, the OZ assumption of a finite $c^{(2)}$ does not so bad! However, for $d = 2$ the renormalization group predicts $\eta(2) = 1/4$ and thus $h(r) \propto r^{-1/4}$. Compare this

to the OZ prediciton:

Exercise: Show for arbitrary dimension d that

$$h(r) \propto \int_0^\infty S(q) \frac{J_{d/2-1}(r/\xi)}{(r/\xi)^{d/2-1}} q^{d-1} \, dq \tag{132}$$

which implies for $T \to T_c$:

$$h(r) \propto \begin{cases} \ln r \, \exp(-r/\xi) \left[1 + O\left(\frac{1}{\ln r/\xi} \right) \right] & (d = 2) \\ \frac{\exp(-r/\xi)}{r} & (d = 3) \\ \frac{\exp(-r/\xi)}{r^{d-2}} \left[1 + O(r/\xi) \right] & (d > 3) \end{cases} \tag{133}$$

Note that the RG results are recovered if the divergence of the structure factor at $T = T_c$ is modified: $S(q) \propto q^{-2} \to q^{-2+\eta}$.

3. Density Functional Theory

Remember the equilibrium phase space probability of a microstate in the grand canonical ensemble:

$$p_{\mathrm{eq}}(\Gamma) = \frac{1}{\Xi} \exp(-\beta \mathcal{H}_N + N\beta\mu) . \tag{134}$$

Summation over N and integration over position–momentum of N particles is usually termed *classical trace*:

$$\mathrm{Tr}_{\mathrm{cl}}\,(\dots) := \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int (\dots)\, d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N \tag{135}$$

With this new notation

$$\Xi = \mathrm{Tr}_{\mathrm{cl}}\,\exp(-\beta \mathcal{H}_N + N\beta\mu), \qquad \mathrm{Tr}_{\mathrm{cl}}\,p_{\mathrm{eq}} = 1 . \tag{136}$$

We may regard a generalized (non–equilibrium) grand potential $\Omega[p]$ as a functional of a general phase space probability p. From thermodynamics we expect that $\Omega[p_{\mathrm{eq}}] \equiv \Omega$ is a minimum, i.e. $\Omega[p] \geq \Omega[p_{\mathrm{eq}}]$.

- Explicit form of $\Omega[p]$:

$$\Omega[p] = \mathrm{Tr}_{\mathrm{cl}}\,p(\beta^{-1}\ln p + \mathcal{H}_N - N\mu) = \mathrm{Tr}_{\mathrm{cl}}\,p(\beta^{-1}\ln p - \beta^{-1}\ln \Xi p_{\mathrm{eq}}) \tag{137}$$

  Check

$$\Omega[p_{\mathrm{eq}}] = \mathrm{Tr}_{\mathrm{cl}}\,p_{\mathrm{eq}}(\beta^{-1}\ln p_{\mathrm{eq}} - \beta^{-1}\ln \Xi p_{\mathrm{eq}}) = -\beta^{-1}\ln \Xi = \Omega , \tag{138}$$

  as it should be. For the minimum property, consider

$$\Omega[p] - \Omega[p_{\mathrm{eq}}] = \beta^{-1}\left[\mathrm{Tr}_{\mathrm{cl}}\,p\ln p - \mathrm{Tr}_{\mathrm{cl}}\,p\ln p_{\mathrm{eq}}\right] \tag{139}$$

$$= \beta^{-1}\mathrm{Tr}_{\mathrm{cl}}\,p_{\mathrm{eq}}\left[\frac{p}{p_{\mathrm{eq}}}\ln\frac{p}{p_{\mathrm{eq}}} - \frac{p}{p_{\mathrm{eq}}} + 1\right] \tag{140}$$

  This holds since $\mathrm{Tr}_{\mathrm{cl}}\,p_{\mathrm{eq}} = \mathrm{Tr}_{\mathrm{cl}}\,p = 1$. Since $x\ln x \geq x - 1$ $(x > 0)$, we immediately find

$$\Omega[p] - \Omega[p_{\mathrm{eq}}] \geq 0 . \tag{141}$$

- **Theorem 1:**

  For some specific fluid (fixed T), $\mathcal{F}[\rho]$ is a unique functional of the equilibrium density profile.

  Note that the free energy does not depend explicitly on $V^{\text{ext}}(\mathbf{r})$ but only through $\rho(\mathbf{r})$. To see that, remember $V_N = \int d\mathbf{r} \hat{\rho} V^{\text{ext}}$ and $\mathcal{H}_N = K_N + U_N + V_N$ with K_N, U_N – kinetic and potential energy. Then

  $$\mathcal{F} = \Omega[\psi(\mathbf{r})] + \int d^3\mathbf{r} \rho(\mathbf{r})[\mu - V^{\text{ext}}(\mathbf{r})] \tag{142}$$

  $$= \text{Tr}_{\text{cl}} \left[p_{\text{eq}}(\beta^{-1} \ln p_{\text{eq}} + \mathcal{H}_N - N\mu) + p_{\text{eq}}(N\mu - V_N) \right] \tag{143}$$

  $$= \text{Tr}_{\text{cl}} \; p_{\text{eq}}(\beta^{-1} \ln p_{\text{eq}} + K_N + U_N) \tag{144}$$

  Since

  $$p_{\text{eq}}(\Gamma) = \frac{1}{\Xi} \exp(-\beta(K_N + U_N + V_N) + N\beta\mu) \;, \tag{145}$$

  we have $p_{\text{eq}} \equiv p_{\text{eq}}[V^{\text{ext}}]$. Since

  $$\rho(\mathbf{r}) = \text{Tr}_{\text{cl}} \; \hat{\rho} \, p_{\text{eq}} \;, \tag{146}$$

  we have $\rho \equiv \rho[p_{\text{eq}}[V^{\text{ext}}]]$.

  If we can show a one–to–one correspondence $\rho(\mathbf{r}) \leftrightarrow V^{\text{ext}}(\mathbf{r})$, then also $p_{\text{eq}} \equiv p_{\text{eq}}[\rho]$ and thus also $\mathcal{F} \equiv \mathcal{F}[\rho]$.

  Define the Hamiltonians, equilibrium phase space densities and grand potentials

  $$\mathcal{H}_1 = K_N + U_N + V_{N,1}, \qquad \mathcal{H}_2 = K_N + U_N + V_{N,2}$$

  $$p_{\text{eq},1} = p_{\text{eq}}[V_1^{\text{ext}}], \qquad p_{\text{eq},2} = p_{\text{eq}}[V_2^{\text{ext}}]$$

  $$\Omega_1 = \Omega_{\mathcal{H}_1}[p_{\text{eq},1}] \qquad \Omega_2 = \Omega_{\mathcal{H}_2}[p_{\text{eq},2}]$$

  Assume now $\rho[V_1^{\text{ext}}] = \rho[V_2^{\text{ext}}]$. The minimum property of Ω entails

  $$\Omega_2 < \Omega_{\mathcal{H}_2}[p_{\text{eq},1}] = \text{Tr}_{\text{cl}} \; p_{\text{eq},1}(\mathcal{H}_2 - N\mu + \beta^{-1} \ln p_{\text{eq},1}) \tag{147}$$

  $$= \Omega_1 + \text{Tr}_{\text{cl}} \left[p_{\text{eq},1}(V_{N,2} - V_{N,1}) \right] \tag{148}$$

  $$= \Omega_1 + \int d\mathbf{r} \; \rho(\mathbf{r})[V_2^{\text{ext}}(\mathbf{r}) - V_1^{\text{ext}}(\mathbf{r})] \tag{149}$$

  We may exchange subscripts $_{1 \leftrightarrow 2}$:

  $$\Omega_1 < \Omega_2 + \int d\mathbf{r} \; \rho(\mathbf{r})[V_1^{\text{ext}}(\mathbf{r}) - V_2^{\text{ext}}(\mathbf{r})] \tag{150}$$

and add the two inequalities:

$$\Omega_2 + \Omega_1 < \Omega_1 + \Omega_2 \ , \tag{151}$$

which contradicts the assumption $\rho[V_1^{\text{ext}}] = \rho[V_2^{\text{ext}}]$. Thus, different V^{ext} lead to different ρ.

- Theorem 2:

  Let $n(\mathbf{r})$ be some average of the microscopic density associated with a nonequilibrium phase space probability p_n. Then the generalized grand potential functional is

  $$\Omega[n] = \mathcal{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, V^{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r}\, n(\mathbf{r}) \tag{152}$$

  and acquires its minimum at equilibrium, $n = \rho$, with $\Omega[\rho] = \Omega$.

Given the above points, the proof is trivial:

$$\Omega[p_n] = \text{Tr}_{\text{cl}}\, p_n(\beta^{-1} \ln p_n + K_N + U_N \quad + V_N - N\mu) \tag{153}$$
$$= \mathcal{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, V^{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r}\, n(\mathbf{r}) \equiv \Omega[n] \tag{154}$$

We have shown already that $\Omega[p_{\text{eq}}] \leq \Omega[p_n]$, thus also $\Omega[\rho] \leq \Omega[n]$.

These theorems are called the *Hohenberg–Kohn–Mermin theorems*. The practical importance lies in the following:

- There exists a *unique* free energy functional $\mathcal{F}[n]$ due to $(n =)\rho(\mathbf{r}) \leftrightarrow V^{\text{ext}}(\mathbf{r})$. The minimization of the associated $\Omega[n]$ determines the equilibrium density profile ρ:

  $$0 = \left.\frac{\delta \mathcal{F}}{\delta n(\mathbf{r})}\right|_{n(\mathbf{r})=\rho(\mathbf{r})} + V^{\text{ext}}(\mathbf{r}) - \mu \tag{155}$$

  or

  $$\rho(\mathbf{r}) = \rho_0 \exp\left(\beta[\mu^{\text{ex}} - V^{\text{ext}}(\mathbf{r})] + c^{(1)}(\mathbf{r})\right) \ , \tag{156}$$

  which we have seen before.

- Although the precise form of $\mathcal{F}[n]$ is unknown for most systems (except the ideal gas and one–dimensional systems), one may construct trial functionals $\mathcal{F}'[n]$ whose

51

equilibrium density profiles are given by $\delta\Omega'[n]/\delta n|_{n=\rho'} = 0$. That the grand potential is bounded from below, i.e.

$$\Omega[\rho'] \geq \Omega[\rho] \ . \tag{157}$$

is not of help since one does not know the correct functional form of $\Omega[n]$.

Rather it gives the straightforward possibility to define a model system by $\mathcal{F}'[n]$ and exploit its implications through the functional formulation of liquid state physics. Unfortunately, it is difficult to constrain $\mathcal{F}'[n]$ such that it gives an internally consistent model of a fluid with two–body potentials.

C. DFT and integral equations

*This section reflects personal taste in setting up a theory of integral equations. See also J. Phys.: Condens. Matter **17**, 429 (2005).*

Integral equations: Many properties of fluids are contained in three unknown functions, the density profile $\rho(\mathbf{r})$, the pair correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$ and the direct correlation function $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. Only one exact relation between them, the Ornstein–Zernike relation, is available. The theory of integral equations aims at establishing a second and third relation (the *closure relations*) which are partially only approximative.

Link with density functional theory:

- The test particle trick: Let $\rho_V(\mathbf{r})$ be the density profile pertaining to the external potential $V(\mathbf{r})$. A perturbed external potential $V'(\mathbf{r}, \mathbf{r}_0) = V(\mathbf{r}) + u(\mathbf{r} - \mathbf{r}_0)$ corresponds of fixing an addtional test particle at $\mathbf{r}_0$ which exerts the potential $u(\mathbf{r} - \mathbf{r}_0)$ onto the remaining fluid particles. Then the density profile $\rho_{V'}$ which minimizes Ω,

$$\left. \frac{\delta\Omega[\rho]}{\delta\rho} \right|_{\rho(\mathbf{r})=\rho_{V'}(\mathbf{r})} = 0 \tag{158}$$

is equivalent to

$$\rho_{V'}(\mathbf{r}) = \rho_V(\mathbf{r})\, g(\mathbf{r}, \mathbf{r}_0) \ . \tag{159}$$

- Particle insertion and potential distribution theorem: A simplified version of the potential distribution theorem is:

$$\Delta\Omega = \Omega|_{V^{\text{ext}}(\mathbf{r})=V(\mathbf{r})+u(\mathbf{r}-\mathbf{r}_0)} - \Omega|_{V^{\text{ext}}(\mathbf{r})=V(\mathbf{r})} = -\beta^{-1}\, c^{(1)}(\mathbf{r}_0) \ . \tag{160}$$

  The first–order direct correlation function evaluated at $\mathbf{r}_0$ describes minus the grand potential difference between a fluid with a test particle inserted at $\mathbf{r}_0$ and a fluid without the test particle. $-\beta^{-1}c^{(1)}$ gives the free energy profile of a test particle dragged through a liquid subjected to the external potential V.

  Proof:

1. We show

$$\exp(\beta\Delta\Omega) = -\left\langle \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)\right\rangle\Bigg|_{V^{\mathrm{ext}}=V} \tag{161}$$

This is easy:

$$\beta\Delta\Omega = -\ln\frac{\sum_{N=0}^{\infty}\frac{1}{N!}\int d1\ldots dN\ \exp(-\beta U_N)\prod_i^N \lambda^{-3}\exp(\beta[\mu - V(\mathbf{r}_i) - u(\mathbf{r}_i - \mathbf{r}_0)])}{\sum_{N=0}^{\infty}\frac{1}{N!}\int d1\ldots dN\ \exp(-\beta U_N)\prod_i^N \lambda^{-3}\exp(\beta[\mu - V(\mathbf{r}_i)])}$$

$$\to$$

$$\exp(\beta\Delta\Omega) = -\frac{\mathrm{Tr}_{\mathrm{cl}}\ \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)}{\Xi|_{V^{\mathrm{ext}}=V}}$$

$$= -\left\langle \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)\right\rangle\Bigg|_{V^{\mathrm{ext}}=V} \tag{162}$$

2. We show

$$\left\langle \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)\right\rangle\Bigg|_{V^{\mathrm{ext}}=V} = \lambda^3\rho(\mathbf{r}_0)\ \exp(-\beta[\mu - V(\mathbf{r}_0)]). \tag{163}$$

Try to write this expectation value as if the test particle belongs to the fluid from the outset:

$$\left\langle \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)\right\rangle\Bigg|_{V^{\mathrm{ext}}=V} =$$

$$\frac{1}{\Xi|_{V^{\mathrm{ext}}=V}}\sum_{N=0}^{\infty}\frac{N+1}{(N+1)!}\int d1\ldots d(N+1)\ \exp(-\beta U_{N+1})\ \times$$

$$\prod_i^{N+1}\lambda^{-3}\exp(\beta[\mu - V(\mathbf{r}_i)])\frac{\lambda^3}{N+1}\exp(-\beta[\mu - V(\mathbf{r}_0)])\sum_{i=1}^{N+1}\delta(\mathbf{r}_i - \mathbf{r}_0)$$

$$= \lambda^3\ \exp(-\beta[\mu - V(\mathbf{r}_0)])\frac{\mathrm{Tr}_{\mathrm{cl}}\ \hat\rho(\mathbf{r}_0)}{\Xi|_{V^{\mathrm{ext}}=V}}$$

$$= \lambda^3\rho(\mathbf{r}_0)\ \exp(-\beta[\mu - V(\mathbf{r}_0)] \tag{164}$$

Through the identity derived earlier, $-\beta\psi(\mathbf{r}) = -\ln\lambda^3\rho(\mathbf{r}) + c^{(1)}(\mathbf{r})$, we have our final result:

$$\beta\Delta\Omega = -\ln\left\langle \exp\left(-\beta\sum_i u(\mathbf{r}_i - \mathbf{r}_0)\right)\right\rangle\Bigg|_{V^{\mathrm{ext}}=V} = c^{(1)}(\mathbf{r}_0) \tag{165}$$

Note that for $V = 0$ (bulk fluid) the result is quite natural

$$\Delta\Omega \stackrel{N\to\infty}{=} \frac{\partial\Omega}{\partial N} = -\mu\ . \tag{166}$$

54

The connection between μ and $\langle\exp(-\beta u)\rangle$ can be used profitably in simulations (this is called Widom's trick). E.g., for hard spheres $\exp(-\beta u) = \theta(\sigma - r)$ and thus, in order to determine μ, one needs to compute the probability of finding a spherical cavity of radius σ for the equilibrium configuration.

- Functional Taylor expansion of $\mathcal{F}^{\text{ex}}$: In general, the excess free energy functional is unknown. However, through a Taylor expansion with respect to $\rho(\mathbf{r})$, one may gain access to its Taylor coefficients, the $c^{(n)}$'s.

In order to use the test particle trick, we will expand around the "background" density profile $\rho_V(\mathbf{r})$ and then minimize Ω in the presence of the external potential $V' = V + u$. We define

$$\mathcal{F}^{\text{ex}}[\rho(\mathbf{r})] = \mathcal{F}^{(2)}[\rho(\mathbf{r})] + \mathcal{F}^{\text{B}}[\rho(\mathbf{r})] \tag{167}$$

where $\mathcal{F}^{(2)}$ contains the Taylor expansion to second order and $\mathcal{F}^{\text{B}}$ contains the remainder. Let $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_V(\mathbf{r})$:

$$\mathcal{F}^{(2)}[\rho(\mathbf{r})] = F(\rho_V(\mathbf{r})) + \int d\mathbf{r}_1 \underbrace{\left.\frac{\delta\mathcal{F}^{\text{ex}}}{\delta\rho(\mathbf{r}_1)}\right|_{\rho=\rho_V}}_{-\beta^{-1}c^{(1)}(\mathbf{r}_1;\,\rho_V)} \Delta\rho(\mathbf{r}_1) + \tag{168}$$

$$\frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \underbrace{\left.\frac{\delta^2\mathcal{F}^{\text{ex}}}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}\right|_{\rho=\rho_V}}_{-\beta^{-1}c^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\,\rho_V)} \Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)$$

We minimize $\Omega = \mathcal{F} - \int(\mu - V')\rho$ to determine the equilibrium profile $\rho_{V'}$:

$$\ln\frac{\rho_{V'}(\mathbf{r})}{\rho_V(\mathbf{r})} + \beta u(\mathbf{r} - \mathbf{r}_0) = \int d\mathbf{r}' \, c^{(2)}(\mathbf{r},\mathbf{r}';\rho_V)\Delta\rho(\mathbf{r}') - \beta\left.\frac{\delta\mathcal{F}^{\text{B}}}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{V'}}. \tag{169}$$

Exercise: Show this result.

Using the test particle trick, we have

$$\frac{\rho_{V'}(\mathbf{r})}{\rho_V(\mathbf{r})} = g(\mathbf{r},\mathbf{r}_0;\rho_V) \qquad \text{and} \qquad \Delta\rho(\mathbf{r}) = \rho_V(\mathbf{r})\, h(\mathbf{r},\mathbf{r}_0;\rho_V) \tag{170}$$

Thus

$$\ln g(\mathbf{r},\mathbf{r}_0;\rho_V) + \beta u(\mathbf{r} - \mathbf{r}_0) = \int d\mathbf{r}' \, c^{(2)}(\mathbf{r},\mathbf{r}';\rho_V)\, \rho_V(\mathbf{r}')\, h(\mathbf{r}',\mathbf{r}_0;\rho_V) - \beta\left.\frac{\delta\mathcal{F}^{\text{B}}}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_V g}$$

$$\overset{\text{(OZ)}}{=} h(\mathbf{r},\mathbf{r}_0;\rho_V) - c(\mathbf{r},\mathbf{r}_0;\rho_V) - \beta\left.\frac{\delta\mathcal{F}^{\text{B}}}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_V g}. \tag{171}$$

This is a general form of the first closure. If one stops at second order, i.e. $\mathcal{F}^{\mathrm{B}} = 0$ then it is called hypernetted chain (HNC) equation. Thus we will call

$$\mathcal{F}^{(2)} \equiv \mathcal{F}^{\mathrm{HNC}} \; .$$

The second closure is obtained through the $c^{(1)}$–definition

$$\ln \lambda^3 \rho_V(\mathbf{r}) = c^{(1)}(\mathbf{r}) + \mu - V(\mathbf{r}) \tag{172}$$

(A) We may use this relation directly with $c^{(1)}$ obtained from the potential distribution theorem:

$$
\begin{aligned}
-c^{(1)}(\mathbf{r}_0) &= \beta\Omega|_{V^{\mathrm{ext}}(\mathbf{r})=V(\mathbf{r})+u(\mathbf{r}-\mathbf{r}_0)} - \beta\Omega|_{V^{\mathrm{ext}}(\mathbf{r})=V(\mathbf{r})} \tag{173} \\
&= -c_{\mathrm{HNC}}^{(1)}(\mathbf{r}_0) - \int d\mathbf{r}\, \rho_V(\mathbf{r})\, g(\mathbf{r}, \mathbf{r}_0; \rho_V) \left.\frac{\delta \mathcal{F}^{\mathrm{B}}}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_V g} + \left.\beta\mathcal{F}^{\mathrm{B}}[\rho]\right|_{\rho=\rho_V g}
\end{aligned}
$$

with the HNC result (dropping the label ρ_V on the correlation functions)

$$-c_{\mathrm{HNC}}^{(1)}(\mathbf{r}_0) = \int d\mathbf{r}\, \rho_V(\mathbf{r}) \left(\frac{1}{2} h(\mathbf{r}, \mathbf{r}_0) \left[h(\mathbf{r}, \mathbf{r}_0) - c(\mathbf{r}, \mathbf{r}_0) \right] - c(\mathbf{r}, \mathbf{r}_0) \right) \tag{174}$$

Exercise: Show these results.

(B) Take the gradient of the $c^{(1)}$–definition:

$$
\begin{aligned}
\nabla \ln \rho_V(\mathbf{r}) &= \nabla c^{(1)}(\mathbf{r}) - \nabla V(\mathbf{r}) \\
&= \int d\mathbf{r}'\, \frac{\delta c^{(1)}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \nabla' \rho(\mathbf{r}') - \nabla V(\mathbf{r}) \\
&= \int d\mathbf{r}'\, c^{(2)}(\mathbf{r}, \mathbf{r}') \nabla' \rho(\mathbf{r}') - \nabla V(\mathbf{r}) \tag{175}
\end{aligned}
$$

or by using OZ yet again

$$\nabla \ln \rho_V(\mathbf{r}) = \beta\nabla V(\mathbf{r}) + \beta \int d\mathbf{r}'\, \rho_V(\mathbf{r}')\, h(\mathbf{r}, \mathbf{r}')\, \nabla' V(\mathbf{r}') \tag{176}$$

This is called the Yvon–Born–Green (YBG) equation of first order. (It relates $\rho^{(1)}$ to $\rho^{(2)}$ and higher order YBG equations relate $\rho^{(n)}$ to $\rho^{(n+1)}$.)

D. Diagrammatic methods and integral equations

Generalization of the graphical methods introduced for the classical cluster expansion:

- Labelled diagrams:

circle $i \equiv$ particle at position $\mathbf{r}_i$	$\rightarrow$	black γ–circle $i \equiv$ function $\gamma(\mathbf{r}_i)$
		white γ–circle i $\quad\sim$
		$[\text{e.g.,} \ \gamma(\mathbf{r}_i) = z^*(\mathbf{r}_i), \rho(\mathbf{r}_i), \ldots]$
line joining $(ij) \equiv$ Mayer f–bond $f(\mathbf{r}_i - \mathbf{r}_j)$	$\rightarrow$	η–bond $(ij) \equiv$ function $\eta(\mathbf{r}_i, \mathbf{r}_j)$
		$[\text{e.g.,} \ \eta(\mathbf{r}_i, \mathbf{r}_j) = f(\mathbf{r}_i - \mathbf{r}_j), c^{(2)}(\mathbf{r}_i, \mathbf{r}_j), \ldots]$
value of graph: integral over all "circles"	$\rightarrow$	integral over all "black circles"

- Unlabelled diagrams:

  - any labelling of balck circles produces the same graph value $\rightarrow$ labels may be omitted

  - however, different labellings may produce topologically distinct diagrams, see previous example:

  - Definition of unlabelled graph value:

    Simple diagram (value Γ), n white circles, labelled 1, ..., n and m black unlabelled circles

$$\Gamma = \frac{1}{m!} \sum_{P_{\text{td}}} \Gamma_{\text{labelled}} \tag{177}$$

$$[P_{\text{td}} - \text{topologically distinct numbering (labelling) of black circles}]$$

$$= \frac{1}{S} \Gamma_{\text{labelled}} \qquad [any \text{ numbering (labelling)}]$$

    This defines the symmetry number S.

    Example: $S(\Delta) = 6$, $S(\Lambda) = 2$.

– Unlabelled diagrams are topologically distinct: impossible to find a permutation which converts a labelling of diagram 1 into a labellling of diagram 2 → distinct integrals

Some definitions:

Immediately clear: adjacent circles, (independent) paths between circles, intersecting bond

1. multiply or n–tuple connectivity:

   at least n independent paths between any pair of circles
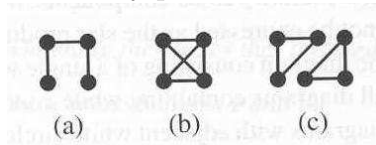
   (a) simply connected, (b) triply connected, (c) unconnected

2. multiply or n–tuple connecting circle:

   removal of circle plus intersecting bonds causes diagram to fall apart into n sub-diagrams

3. (a) articulation circle:

   is a connecting circle, upon removal at least one subdiagram has no white circle

   (b) articulation pair:

   is a connecting pair of circles, upon removal the same effect

4. nodal circle:

   is a connecting circle through which all paths between two selected white circles pass

   Examples:
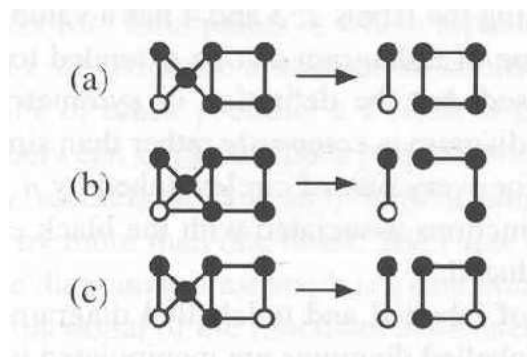
effect of removal of (a) articulation circle, (b) articulation pair, (c) nodal circle

58

5. star product $*$:

   linking together two diagrams at white circles with same label.

   Example:
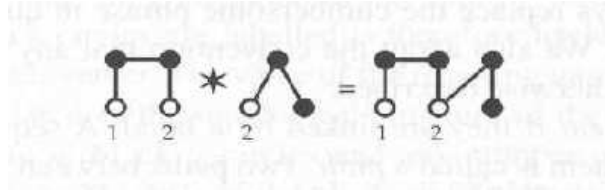
6. star–irreducible diagram:

   is impossible to star–decompose into two subdiagrams (except for the trivial case single white circle)

   Examples for star–reducible diagrams: with white connecting circles or with adjacent white circles

Useful lemmas for manipulating diagrams:

T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, *537 (1961).*

1. A general exponentiation theorem:

   G – set of topologically distinct and star–irreducible diagrams

   H – G plus all possible star products within G (

   $$\sum_{\alpha \in H} \Gamma_\alpha = \exp\left(\sum_{\alpha \in G} \Gamma_\alpha\right) - 1$$

   $G = \{\Gamma\}$ (single diagram):
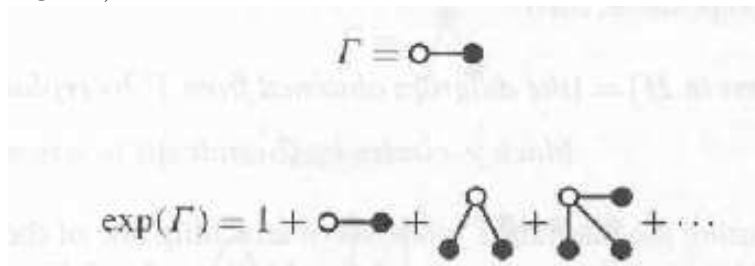
   Examples:

- No white circles:

  $\Gamma = \{$all connected graphs$\} \to \exp(\Gamma) = 1 + \Gamma + \{$all disconnected graphs$\}$

- One white circle:

  $\Gamma = \{$all connected graphs, white circle is no articulation circle$\} \to \exp(\Gamma) = 1 + \Gamma + \{$all connected graphs, white circle is articulation circle$\}$

- Two white circles:

  $\Gamma = \{$all connected graphs, white circles are no articulation pair$\} \to \exp(\Gamma) = 1 + \Gamma + \{$all connected graphs, white circles are articulation pair$\}$

We have seen this already for the special case of diagrams having only black circles: $\sum_{\text{disconnected}} = \exp(\sum_{\text{connected}})$. (In that case the star product of two connected diagrams is simply the disconnected diagram composed of these two connected diagrams.

2. Functional derivative:

Let Γ contain no white circle.

(a)

$$\frac{\delta\Gamma}{\delta\gamma(\mathbf{r}_1)} = \sum[\text{all distinct diagrams obtained by whitening one circle } (\text{label } \mathbf{r}_1)]$$

(b)
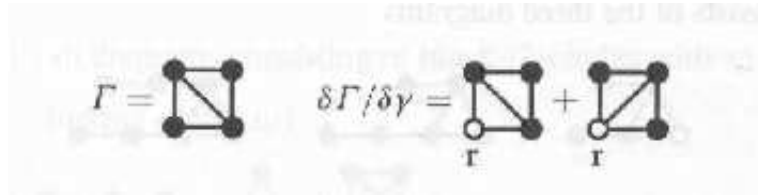
$$\frac{\delta\Gamma}{\delta\eta(\mathbf{r}_1, \mathbf{r}_2)} = \frac{1}{2}\sum\left[\begin{array}{c}\text{all distinct diagrams obtained by whitening two circles } (\text{label } \mathbf{r}_1, \mathbf{r}_2) \\ \text{and erasing the connecting bond}\end{array}\right]$$
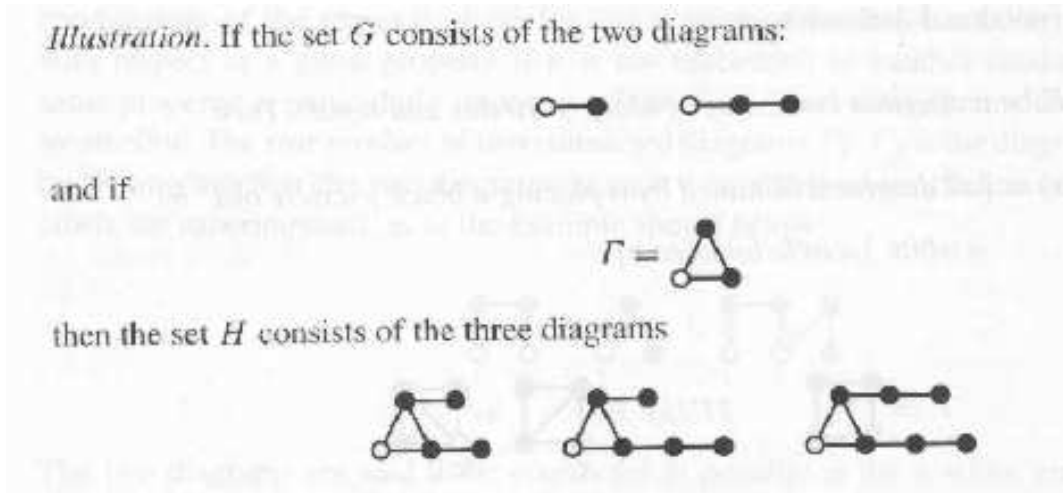

60
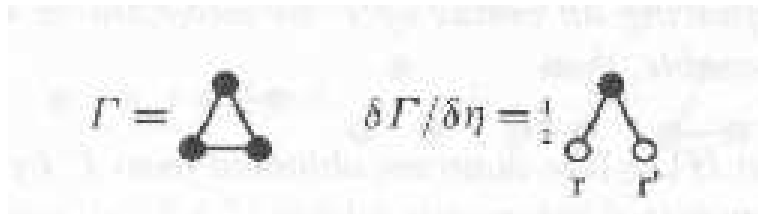
3. Decorating a diagram Γ:

Let Γ be a connected diagram.

(a) Let G be a set of distinct, connected diagrams which contain one white circle (label $\mathbf{r}_1$). The value of the set is $\mathcal{G}(\mathbf{r}_1)$. The decoration of Γ with the set G leads to a set H:

$$\begin{matrix} \text{diagrams where every black circle of } \Gamma \\ \text{is replaced by a diagram of } G \text{ in all possible ways} \end{matrix} \in H$$

The actual lemma states that if one knows the value $\mathcal{G}(\mathbf{r}_1)$ one can insert it right away into each black circle of Γ to obtain the value of all decorated diagrams:

$$\sum \left[\begin{matrix} \text{diagrams where every black circle of } \Gamma \\ \text{is replaced by } \mathcal{G}(\mathbf{r}) \end{matrix} \right] = \sum_{i \in H} \Gamma_i$$

Illustration. If the set G consists of the two diagrams:

and if

$$\Gamma = $$

then the set H consists of the three diagrams

(b) Let G' be a set of distinct, connected diagrams which contain two white circles (label $\mathbf{r}_1$ and $\mathbf{r}_2$). The value of the set is $\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2)$. The decoration of Γ with the set G' leads to a set H':

$$\begin{matrix} \text{diagrams where every bond of } \Gamma \\ \text{is replaced by a diagram of } G' \text{ in all possible ways} \end{matrix} \in H'$$
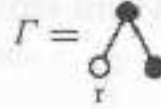
The actual lemma states again that we can use $\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2)$ right away:

$$\sum \left[\begin{matrix} \text{diagrams where every bond of } \Gamma \\ \text{is replaced by } \mathcal{G}(\mathbf{r}_1, \mathbf{r}_2) \end{matrix} \right] = \sum_{i \in H'} \Gamma_i$$
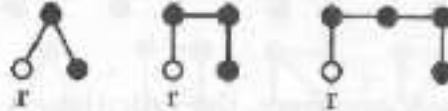
Illustration. If the set G consists of the two diagrams:
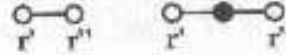
and if

$$\Gamma = \text{(diagram)}$$
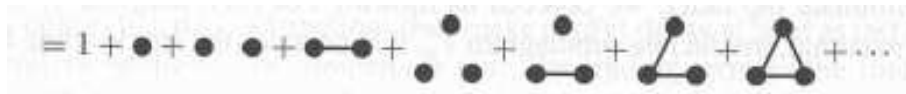
then the set H consists of the three diagrams

These lemmas are useful for topological reduction, i.e. the reduction of a certain set of diagrams (H or H') to a single diagram Γ with new $\mathcal{G}$–circles or $\mathcal{G}$–bonds.

Diagrammatic expansions

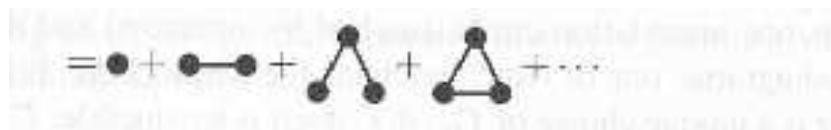- Grand partition function Ξ and grand potential Ω:

  We showed already explicitly:

  $$\Xi = \exp\left(\sum[\text{all connected graphs with } z\text{–circles and } f\text{–bonds}]\right)$$

  $$= 1 + \bullet + \bullet\ \ \bullet + \bullet\!-\!\bullet + \cdots$$

  For the general inhomogenous case, replace $z = \exp(\beta\mu)$ by $z^*(\mathbf{r}) = \exp(\beta[\mu - V^{\text{ext}}(\mathbf{r})]) = \exp(\beta\psi(\mathbf{r}))$. Since $-\beta\Omega = \ln\Xi$,

  $$-\beta\Omega = \sum[\text{all connected graphs with } z^*\text{–circles and } f\text{–bonds}]$$

  $$= \bullet + \bullet\!-\!\bullet + \cdots$$

62

- Density profile $\rho(\mathbf{r}_1)$ and direct correlation function $c^{(1)}(\mathbf{r}_1)$:

We have

$$\rho(\mathbf{r}_1) = -\frac{\delta\Omega}{\delta\psi(\mathbf{r}_1)} = -z^*(\mathbf{r}_1)\frac{\delta\Omega}{\delta z^*(\mathbf{r}_1)} \tag{178}$$

and

$$\rho(\mathbf{r}_1) = z^*(\mathbf{r}_1)\,\exp(c^{(1)}(\mathbf{r}_1)) \tag{179}$$

We apply lemma 2 to obtain $\delta\Omega/\delta z^*$:

$$\rho(\mathbf{r}_1) = \sum \left[\begin{array}{c}\text{all connected graphs with one\ white circle (labelled } z^*(\mathbf{r}_1)),\\ \text{black } z^*\text{–circles and } f\text{–bonds}\end{array}\right]$$

$$= \underset{z^*(\mathbf{r}_l)}{\bigcirc} + \underset{z^*(\mathbf{r}_l)}{\bigcirc\!\!-\!\!\bullet} + \underset{z^*(\mathbf{r}_l)}{\triangle} + \underset{z^*(\mathbf{r}_l)}{\curlyvee} + \underset{z^*(\mathbf{r}_l)}{\triangle} + \cdots$$

These diagrams contain articulation circles (upon whose removal the diagrams fall apart). These articulation circles may be black or white. The white ones can be removed by considering the diagrammatic expansion of $c^{(1)}$.

$$c^{(1)}(\mathbf{r}_1) = \frac{1}{z^*(\mathbf{r}_1)}\sum\left[\begin{array}{c}\text{all connected graphs with } f\text{–bonds, black } z^*\text{–circles}\\ \text{and a white circle (labelled } z^*(\mathbf{r}_1))\ \text{which is not an articulation circle)}\end{array}\right]$$

$$= \underset{z^*(\mathbf{r}_l)}{\bigcirc} + \underset{z^*(\mathbf{r}_l)}{\bigcirc\!\!-\!\!\bullet} + \underset{z^*(\mathbf{r}_l)}{\triangle} + \underset{z^*(\mathbf{r}_l)}{\triangle} + \cdots$$

By the exponentiation lemma, $\exp(\sum\dots)$ contains all the diagrams of $\sum\dots$ (also contained in $\rho(\mathbf{r}_1)$) plus all possible star products. These star products just give all diagrams which have a white articulation circle (the remainder of $\rho(\mathbf{r}_1)$).

The black articulation circles are removed as follows:

$$c^{(1)}(\mathbf{r}_1) = \frac{1}{\rho(\mathbf{r}_1)}\sum\left[\begin{array}{c}\text{all connected graphs (no connecting circles) with } f\text{–bonds,}\\ \text{black } \rho\text{–circles and a white circle (labelled } \rho(\mathbf{r}_1))\end{array}\right]$$
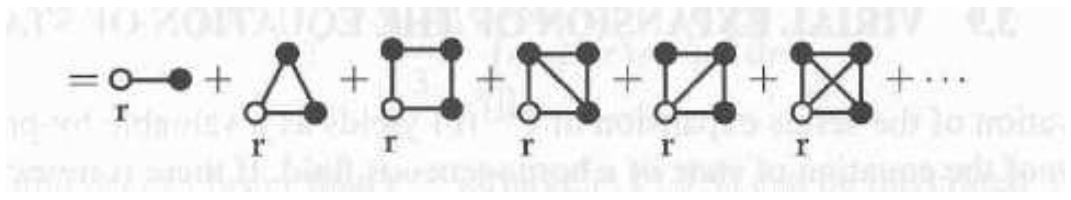
We have neither articulation (removal: at least one subdiagram with no white circle) nor nodal (removal: two selected white circles in different subdiagrams) circles. The equality means that all the diagrams with black articulation circles are generated by decorating all irreducible diagrams with diagrams of $\rho(\mathbf{r}_1)$ (which have no restrictions on the appearance of articulation circles). See lemma 3. Thus we have switched from a z^*–expansion to the conjugate ρ–expansion.

In the bulk, $c^{(1)} = -\beta\mu^{\text{ex}}$. Thus

$$\mu^{\text{ex}} = -\sum_{i=1}^{\infty} b_{i+1}^{\text{ir}} \rho^i \tag{180}$$

$$\beta p^{\text{ex}} = \int_0^{\rho} d\rho' \, \rho' \frac{\partial \mu^{\text{ex}}}{\partial \rho'} = -\sum_{i=2}^{\infty} \frac{i-1}{i} b_i^{\text{ir}} \rho^i \tag{181}$$

and we recover the virial coefficient $a_l = -l/(l-1)\, b_l^{\text{ir}}$ as essentially the irreducible l–cluster integral b_l^{ir}. We had shown this before only up to a_4.

- The direct correlation function $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$:

  Since $c^{(2)} = \delta c^{(1)}/\delta\rho$, we may apply lemma 2 and whiten one black circle:

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all nodal–free connected graphs with} \;\; f\text{–bonds,} \\ \text{black} \;\; \rho\text{–circles and two} \;\; \text{white circles (labelled } \rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \end{array} \right]$$
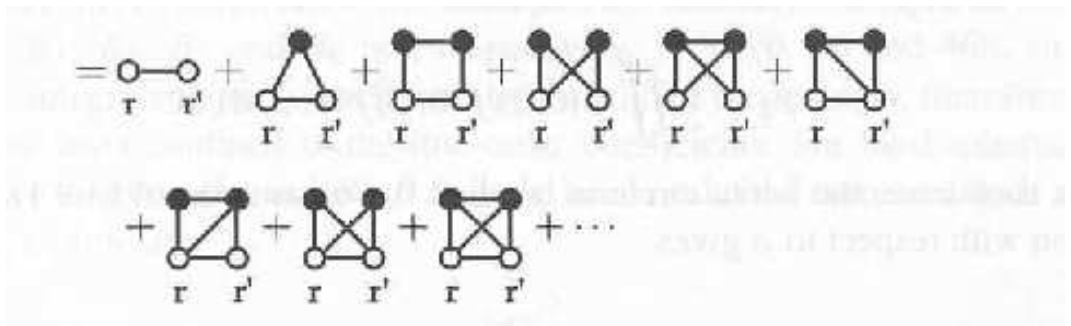
Except for the diagram with only two white circles, all diagrams are at least doubly–connected. The absence of nodal points (the absence of chain–like structures) in the expansion of $c^{(2)}$ confirms the previously gained intuition that the direct correlation
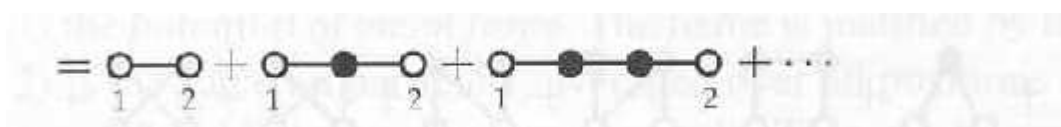
64

function essentially has the range of the interparticle potential, i.e. the range of the f–bond.

Diagrammatic expansions of pair functions and the closure relation

- The pair correlation function h

From OZ we have:

$$h(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all chain graphs with two terminal white circles} \\ \text{(labelled } \rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)\text{), black } \rho\text{–circles and } c^{(2)} \text{ bonds} \end{array} \right]$$
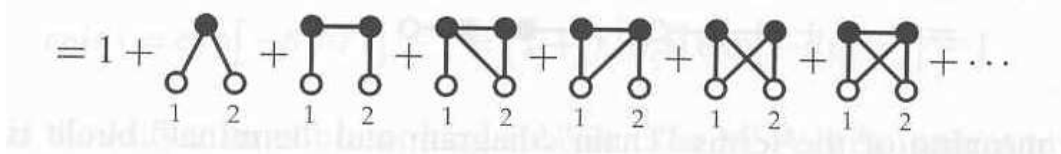

To express this as expansion with f–bonds, insert the previously obtained expansion for $c^{(2)}$ into the bonds. The diagrammatic series for h is then similar to that for $c^{(2)}$, but now black nodal circles are allowed:

$$h(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all connected graphs with } f\text{–bonds, black } \rho\text{–circles} \\ \text{and two white, non–connecting circles (labelled } \rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \end{array} \right]$$

We have no articulation circle (removal: at least one subdiagram with no white circle) since the black connecting circles are nodal (removal: here two subdiagrams, each with a white circle).

- The cavity distribution function y

Consider the following graphical expansion:

$$y(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all connected graphs with } f\text{–bonds, black } \rho\text{–circles and} \\ \text{two } non\text{–}adjacent, \text{ non–connecting white circles } (\rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \end{array} \right]$$

Compare to h:

  - lowest order: 1 instead of $f(\mathbf{r}_1 - \mathbf{r}_2)$

- higher order: h–expansion encompasses any y–graph plus the same graph with an f–bond between the white circles
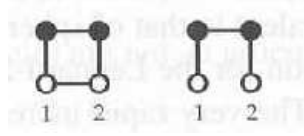
Thus

$$h(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_1 - \mathbf{r}_2) + (y(\mathbf{r}_1, \mathbf{r}_2) - 1)(1 + f(\mathbf{r}_1 - \mathbf{r}_2)) \leftrightarrow \qquad (182)$$

$$g(\mathbf{r}_1, \mathbf{r}_2) = e(\mathbf{r}_1 - \mathbf{r}_2)\, y(\mathbf{r}_1, \mathbf{r}_2) \qquad (183)$$

with definition of an e–bond:

$$e(\mathbf{r}_1 - \mathbf{r}_2) = f(\mathbf{r}_1 - \mathbf{r}_2) + 1 = \exp[-\beta u(\mathbf{r}_1 - \mathbf{r}_2)] \qquad (184)$$

Properties:

- no f–bond between white circles $\rightarrow y$ continuous even for discontinuous potentials like hard–spheres

- interpretation: pair distribution function for particles 1 und 2 (associated with the white circles) with *no* interaction among themselves and *full* interaction with all other particles

  (hard spheres: 1 and 2 are *cavities*)

- The general closure

Note that the expansion of y contains graphs in which the two white circles form an articulation pair. These graphs are star–reducible:
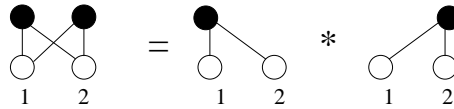
Thus we can eliminate them with the exponentiation theorem and find:

$$\ln y(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all connected graphs with } f\text{–bonds, black } \rho\text{–circles and} \\ \text{two } non\text{–}adjacent, \text{ non–connecting white circles } (\rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \\ \text{which form } no\ articulation\ pair \end{array} \right]$$

We want to reconstruct $\ln y$ in a different way. A subset of $\ln y$ is given by $h - c^{(2)}$:

- h contains all diagrams of $\ln y$ plus diagrams with an f–bond between the white circles plus diagrams without an f–bond between the white circles where these are an articulation pair

- $c^{(2)}$ contains all the diagrams with an f–bond between the white circles: see Ornstein–Zernike

- $c^{(2)}$ contains all the articulation pair diagrams: these are star–composed of two diagrams which may contain a nodal circle $\rightarrow$ the star–composition has at least two independent paths between the white circles. That fits into the definition of $c^{(2)}$.

- $c^{(2)}$ contains *some* of the diagrams of $\ln y$, namely the ones which do not have a nodal circle (i.e. which have more than one path between the white circles)

Thus:

$$[h - c^{(2)}](\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all connected graphs with } f\text{–bonds, black } \rho\text{–circles and two} \\ non\text{–}adjacent, \text{ non–connecting white circles } (\rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \\ \text{and with at least one nodal circle} \end{array} \right]$$

We define the remainder in $\ln y$ as the bridge function b:

$$-b(\mathbf{r}_1, \mathbf{r}_2) = [\ln y - (h - c^{(2)})](\mathbf{r}_1, \mathbf{r}_2) \tag{185}$$

$$= \frac{1}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \sum \left[\begin{array}{c} \text{all connected graphs with } f\text{–bonds,} \\ \text{black } \rho\text{–circles } which\ are\ no\ nodal\ circles \text{ and} \\ \text{two } non\text{–}adjacent, \text{ non–connecting white circles } (\rho(\mathbf{r}_1) \text{ and } \rho(\mathbf{r}_2)) \\ \text{which form } no\ articulation\ pair \end{array} \right]$$

The lowest–order (in density) bridge diagram is $\propto \rho^2$, i.e. it has two black circles:
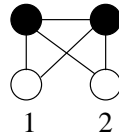
Putting everything together, we find the exact closure

$$\ln g(\mathbf{r}_1, \mathbf{r}_2) + \beta u(\mathbf{r}_1 - \mathbf{r}_2) = [h - c^{(2)} - b](\mathbf{r}_1, \mathbf{r}_2) \tag{186}$$