Colloidal interactions:
From effective potentials to structure

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C. N. Likos
Faculty of Physics, University of Vienna - Boltzmanngasse 5, A-1090 Vienna, Austria

Summary. — In this paper we present an overview of some key theoretical tools employed for the investigations of the equilibrium structure and thermodynamics of complex fluids. We place our focus on the most common systems of soft-matter science, namely dispersions of colloidal particles, which may be hard or soft, and which may carry electric charge. The concept of the effective Hamiltonian, which plays the key role in these coarse-grained approaches is introduced, and it is given a precise mathematical definition. Its properties as well as key approximations involved in deriving effective potentials are discussed. Thereafter, the ways in which the effective interactions can be combined with tools from the theory of fluids and statistical mechanics are presented, putting emphasis on Density Functional Theory. The general principles are combined with extensive exposures from currently active research fields, and applications to interfacial and wetting behavior of complex mixtures as well as to crystallization and cluster formation are discussed. Appendix A serves as a mini-course on functionals and functional differentiation.

1. Colloidal Soft Matter
2. The coarse-graining strategy: effective interactions
3. Colloidal stabilization
   3'1. Charge stabilization
   3'2. Steric stabilization
4. Classical uniform fluids
5. Nonuniform fluids: density functional theory (DFT)
   5'1. The basic principles of DFT
   5'2. Some useful results
   5'3. Accurate density functionals for soft potentials
   5'4. Fluid-fluid interfaces
   5'5. Wetting
   5'6. Crystallization
   5'7. Cluster crystals
6. Density functional theory for polymer chains
7. Summary and conclusions
8. Appendix A. Functionals and functional differentiation

1. – Colloidal Soft Matter

The term *Soft Matter* describes a very large class of materials whose common characteristic is that they are composed of *mesoscopic* particles, i.e., particles with typical sizes 1 nm–1 µm, dispersed into a solvent whose molecules are much smaller in size (typically of atomic dimensions). In addition, soft-matter systems may contain other, smaller unities such as short polymeric chains, salt dissociated into ions etc. Other terms that are used as synonyms are *complex fluids* (though soft matter is not necessarily fluid) as well as *colloidal suspensions* or *colloidal dispersions*.

The mesoscopic size of the constituent particles is the key in understanding the fact that such systems are indeed soft, i.e., they have a rigidity against mechanical deformations which is many orders of magnitude smaller than that of their atomic counterparts. To illustrate this point, let us consider a perfect crystal having lattice constant $a$, as shown in fig. 1(a). This crystal is sheared by an external force with the result that every lattice plane is displaced parallel to itself by an amount $x$, with respect to the plane immediately below it, as shown in fig. 1(b). Associated with this deformation is an energy per unit area $u(x)$ which, for small values of $x$, is a quadratic function of the deformation, as $x = 0$ is an equilibrium position. In a crystal, this energy depends on the direction of the applied shear and it is given in general by a relation of the form:

$$u(x) = \frac{1}{2} \left( \frac{x}{a} \right)^2 G,$$

where $G$ stands for any one of the several elastic constants of the solid [1]. The shear stress $\sigma$ is defined as the force per unit area of plane and per plane necessary to maintain such a deformation $x$. With $V$ denoting the volume of the crystal, $N$ the number of
lattice planes and taking a cubic crystal for simplicity, this quantity will be given by

\[ \sigma(x) = \frac{1}{NA} \frac{d}{dx} (Vu) = a \left( \frac{du}{dx} \right). \]  

To roughly estimate the critical value \( \sigma_c \) of shear stress which is necessary to make a lattice plane slip, we set the maximum displacement \( x \) equal to \( a/4 \). Then, eqs. (1) and (2) give the result

\[ \sigma_c \approx \frac{d}{dx} G \left( \frac{x^2}{a} \right)^\frac{1}{2} \bigg|_{x=a/4} = \frac{1}{4} G. \]  

On dimensional grounds, the elastic constants of solids (but also those of amorphous systems) have a generic dependence on the typical interaction energy \( \varepsilon \) between the particles and the interparticle separation \( a \) that reads as

\[ G \propto \frac{\varepsilon}{a^3}. \]  

The energy scale \( \varepsilon \) for atomic systems, ranges from \( 10^{-1} \) eV for the noble gases to \( 10 \) eV for the alkali halides and the metals [1]. For typical colloidal crystals, \( \varepsilon \) ranges between \( k_B T \) and \( 100 k_B T \), where \( k_B \) is Boltzmann’s constant and \( T \) is the absolute temperature. As \( k_B T \approx 1/40 \) eV at room temperature, we conclude that the energy scales for atomic and colloidal systems are about the same. Therefore, the major difference in the values of the elastic constants comes from the denominator in eq. (4). As the typical length scales involved in colloidal crystals exceed those of their atomic counterparts by three to four orders of magnitude, the ratio between the elastic constants of colloidal and atomic systems is extremely small:

\[ \frac{G_{\text{colloidal}}}{G_{\text{atomic}}} \approx 10^{-12} - 10^{-9}. \]  

Equations (3) and (5) show that there is an enormous difference in the critical stress required to cleave an atomic and a colloidal crystal. One can shear the latter by moving one’s little finger but one needs to apply extreme shear stresses of the order of \( 10^{11} \) dyn/cm\(^2\) in order to shear the former.

Perhaps the most fascinating aspect of soft-matter science lies in the fact that the physical systems considered in this field are not atomic or molecular in nature: the constituent particles of what are synonymously known as complex fluids are instead macromolecular aggregates, whose spatial extent lies in the domain between 1 nm and 1 \( \mu \)m. Although there is an abundance of naturally occurring soft-matter systems (one only needs to think about proteins, viruses, and DNA molecules), a large variety of complex fluids are man-made [2, 3]. It is hardly exaggerated to state that the overwhelming majority of the products of the food, pharmaceutical, detergent and chemical industries

\(^{(1)}\) Though, physically, the plane slips when \( x = a/2 \), for such large displacements the assumption that \( \sigma(x) \) is a linear function of \( x \) breaks down and we have to limit this analysis to smaller \( x \) values.
are indeed complex fluids. Therefore, there is an overwhelming need for an understanding of the mechanisms by which the physical characteristics of the constituting particles of the fluid are having an influence on the macroscopic properties of the physical system. This is indeed the central question of the field of statistical physics (equilibrium or otherwise): Given a collection of a huge number of microscopic particles under a small number of fixed external parameters, which are the properties of the macroscopic system?

The question is hard enough to answer even when the constituent particles are simple atoms; the degree of difficulty increases by at least one order of magnitude in the case of complex fluids, in which the internal architecture and fluctuations of the aggregates play an additional role. But this challenging problem offers at the same time a chance to design new materials with unusual structural and rheological properties: only in the field of soft matter do we possess the possibility of changing the properties of the constituent particles externally. For atomic fluids, the particles are nature-given and the freedom to influence their interactions is absent.

A particular category of soft matter systems is known under the name colloidal suspensions; membranes, block copolymer melts, networks of filaments are other ones in the long list. The term “colloid” derives from the Greek words κόλλα (glue) and εἴδος (kind). Its original meaning, “sticky stuff”, coined in the 1860s by Thomas Graham, a pioneer in the field [2], reflects the fact that almost all of the compounds used as glues are indeed colloids. Originally, the term colloids was employed to describe spherical, rigid particles of mesoscopic dimensions, i.e., hard colloids dispersed in a microscopic solvent. Examples of such particles are chemically synthesized polysterene [4,5], silica [6,7] or poly-methyl-methacrylate (PMMA) particles [8,9] that serve as realizations of hard-sphere solutions [10] or charge-stabilized colloidal suspensions, which have long attracted the interest of theorists and experimentalists alike [10-12]. Aspherical rigid particles, such as rods or platelets are also described under the name “colloids”, whereas recently the term has been extended to also include soft particles (polymer chains, polyelectrolytes, star polymers, dendrimers) with mesoscopic dimensions. Colloids are abundant in everyday experience. From mayonnaise to blood and from ink to smoke, soft matter is what we are made of and what we use in countless industrial applications in the chemical, pharmaceutical and food industries. Microemulsions as well as self-organized micelles of soap molecules in aqueous solutions also belong to the same category and are sometimes referred to as association colloids, a class also closely related to the very rich, and currently topical, subject of patchy colloids [13-18].

In this contribution we offer an overview of the theoretical tools employed with the goal of describing and understanding the structural and thermodynamic properties of these complex systems and the connections that can be made to experimentally measurable quantities. In view of the complexity of the solvent/solute system and the vast discrepancy in the length- and time-scales associated with the two components, a coarse-graining approach is necessary: a truly microscopic theory for such highly complex molecules would be prohibitively complicated. Therefore, we sketch the basic principles of the coarse-graining procedure in sect. 2, in which we introduce, in particular, the concept of the effective interaction between complex macromolecular aggregates. In sect. 3, we turn our attention to the issue of colloidal stabilization, and we discuss how one can derive there the effective interactions that stabilize colloids by taking advantage of electric charge or by the self-avoidance of grafted polymers. In sect. 4 we turn our attention to the many-body problem of a uniform fluid made up of colloidal particles and to the current theoretical approaches employed to describe the fluid structure and thermodynamics. In sect. 5, we present the powerful tool of density functional theory,
which offers the suitable theoretical framework for the description of nonuniform fluids and fluid interfaces. In sect. 6, we extend the considerations of density functional theory to the much more complex case of polymer chains and, finally, in sect. 7, we summarize and conclude. In Appendix A, we present a primer in the concept of a functional of a given function, in which the interested reader can also find an exposition to the rules of functional differentiation.

2. – The coarse-graining strategy: effective interactions

Imagine that you want to visit the performance of a celebrated ballet ensemble, whose prima ballerina is world-famous for her extraordinary dancing skills. In this case, you would like to have a seating as close to the scene as possible, at a place where you can resolve every detail of the movement of the artists: the waving of their arms and the elegant, skillful motions of their legs and bodies are indeed important for obtaining the full aesthetic pleasure from the performance. Details of the motion in short length- and time-scales are relevant and quite a bit would be lost if one were seated at the last row, where just a diffuse ensemble of performers could be discerned. The situation is different if one wishes to attend the opening ceremony of the Olympic Games, for instance. Here, it is the collective behavior of a large number of individuals performing coordinated movements that matters. One is interested in seeing, from a more distant perspective, the large-scale shapes and patterns formed by the colorful groups of the performing individuals. The relevant motions take place at time-scales that are longer than the ones involved in moving one’s finger or arm; and the length-scales of interest are correspondingly longer than the size of any single individual participating in the (literally!) many-body process. Here, a choice of first-row seating would be unwise. Much more would be gained if one positioned oneself farther away from the spectacle, so that the eyes automatically perform a “coarse-graining” procedure of the event and the short scales get effortlessly eliminated from the view.

When dealing with soft-matter systems, we are faced with a similar problem of coexistence of various different length- and time-scales. Indeed, almost every complex fluid is a solution or dispersion of large particles in a molecular or atomic solvent. The solvent particles are much smaller and much faster than the dissolved ones. If, in addition, the solute particles are polymeric entities, there is a vast separation in the scales of the individual monomers and the aggregate as a whole. A choice has to be made, therefore, as to which kind of phenomena one is interested in. If the motions of the individual atoms are relevant, then a microscopic description of the system is of order. However, a host of interesting problems pertaining, e.g., to the overall phase or rheological behavior of the suspension, is rather connected to longer time-scales and larger length-scales. Small-angle scattering experiments with thermal neutrons can hardly probe correlations at the monomer scale and they rather deliver information about the structure of the system at the mesoscopic scale. Optical tracer experiments probe the slow, diffusive motion of the macromolecular aggregates, in which the ultrafast motion of the individual atoms is lost. Accordingly, one would like to construct a theoretical tool that encaptures the coarse-graining procedure performed by such experiments: the small and fast degrees of freedom should be eliminated from the problem, with their influence being “hidden” in the form or in the parameters of an interaction potential between the large and slow degrees of freedom only. This approach, if successful, also has the advantage of already performing the first step in bridging the scales: it takes us from the microscopic to the mesoscopic scale and the next step to the macroscopic domain is often not terribly
Fig. 2. – The various length scales at which a star polymer solution can be looked upon, ranging from microscopic to macroscopic and covering in this way about eight orders of magnitude.

complicated. Figure 2 shows a sketch of the procedure specifically for the case of star polymers [19-21].

The coarse-graining procedure has its roots at the McMillan-Mayer theory of solutions [22] and its formulation by Kirkwood and Buff [23], for a review of its applications to colloids see the article by van Megen and Snook [24]. The theoretical tool that expressed the coarse-graining at the mathematical level is called effective interaction. A detailed, statistical-mechanical description of the derivation of the effective interaction and its properties has been given, e.g., in ref. [25]. Here we only sketch the main ideas of the procedure. Suppose that we are dealing with a system whose Hamiltonian contains $M$ “small” degrees of freedom that are to be eliminated and $N$ large ones that are to be kept. Let $V_{11}(r^N)$ be the interaction potential between the large degrees of freedom, $V_{22}(s^M)$ the one between the small ones and $V_{12}(r^N, s^M)$ the cross-interaction term, where $\{r^N\}$ and $\{s^M\}$ denote the coordinates of the large and small particles, respectively. The configurational part of the canonical partition function $Z$ is given by

$$Z = \int dr^N \int ds^M \exp \left\{ -\beta [V_{11}(r^N) + V_{12}(r^N, s^M) + V_{22}(s^M)] \right\}$$

$$= \int dr^N \exp \left[ -\beta V_{11}(r^N) \right] \int ds^M \exp \left\{ -\beta [V_{12}(r^N, s^M) + V_{22}(s^M)] \right\}$$

$$= \int dr^N \exp \left[ -\beta V_{11}(r^N) \right] \tilde{Z}(r^N),$$

where $\beta = (k_B T)^{-1}$, $k_B$ denoting Boltzmann’s constant and $T$ the absolute temperature,
and $\tilde{Z}(r^N)$ is, evidently, the constrained partition function of the small particles under a given configuration $\{r^N\}$ of the big ones. By defining the corresponding constrained free energy $\tilde{F}(r^N)$ as
\begin{equation}
\tilde{F}(r^N) = -k_B T \ln \tilde{Z}(r^N)
\end{equation}
and the effective interaction potential function $V_{\text{eff}}(r^N)$ as
\begin{equation}
V_{\text{eff}}(r^N) = V_{11}(r^N) + \tilde{F}(r^N),
\end{equation}
it is evident from eqs. (6)-(8) above that the partition function of the system can be expressed as a trace over the position coordinates of the large particles only and reads as
\begin{equation}
Z = \int dr^N \exp[-\beta V_{\text{eff}}(r^N)].
\end{equation}
An unavoidable consequence of the partial trace is that the effective Hamiltonian contains not only pair interactions but also the whole sequence of many-body forces. An explicit, diagrammatic expansion in the semi-grand ensemble that brings about the structure of the many-body terms has been carried out in ref. [26]. Usually, however, the pair-potential approximation is employed and indeed there are only few cases for which this has proven inadequate. In other words, we express the effective interaction potential as a sum of pair interactions, explicitly
\begin{equation}
V_{\text{eff}}(r^N) = \sum_{i<j} v_{\text{eff}}(|r_i - r_j|),
\end{equation}
where $r_{i,j}$ denote the positions of the $i,$ $j$-particle. Furthermore, there is an overall extensive and coordinate-independent term in the effective Hamiltonian that also derives from the above-mentioned procedure. This so-called “volume term” does not influence the correlation functions of the large particles, though, that remain unaffected by the procedure of deriving the effective interaction. For the case of neutral mixtures, the volume term is linear in both the total volume and the particle number $N_1$ of the species which is not coarse-grained, thus it simply shifts the pressure and the chemical potential without affecting phase boundaries but it does influence the total thermodynamics nevertheless. Particular case must be taken in treatments regarding, e.g., phase equilibria of charged systems or of any system for which the partial densities of the two species are constrained to one another [26-29].

3. – Colloidal stabilization

Colloidal particles are subject to incessant internal dipole fluctuations, which give rise to the famous van der Waals or dispersion attractions acting between them. As a consequence, any colloidal suspension would undergo irreversible aggregation in solution. To guarantee the stability of the suspension, the colloids must be endowed with some additional repulsion. The two most usual mechanisms are charge- and steric stabilization. In the former case, the colloids are synthesized with ionizable chemical groups on their surface, which, upon solution in a polar solvent (water) dissociate, leaving behind charged spheres and counterions in solution. In the latter, the colloids are grafted with self-avoiding polymer chains, which provide a protective coating. For both cases, the effective
interaction can be derived by means of approximate yet analytical approaches. In what follows, we present these analytical solutions, which are based on the Debye-Hückel theory of screening for charge stabilization and on the Witten-Pincus blob arguments [30] for steric stabilization.

3.1. Charge stabilization. – Let us consider a prototype of a charge-stabilized, aqueous colloidal dispersion, consisting of \( N_0 \) colloidal macroions of valence \( Z_0 \) each and radius \( a \), as well as \( \nu \) ionic species. The latter are comprised by the counterions released by the colloids as well as by additional counter- and co-ions that result from added salt. The solvent (water) is modeled in a continuous fashion and its effect is taken into account solely through its dielectric permittivity, \( \varepsilon = 78 \), which screens the Coulomb interactions between all charged species present. The microions’ steric interactions are completely ignored, i.e., the assumption is made that electrostatics dominates the statistical mechanics of the system; however, the hard-core interaction with the colloid is maintained, i.e., the microions cannot penetrate the colloids at distances \( r < a \) from the centers of the latter.

For every charged species \( \alpha = 0, 1, 2, \ldots, \nu \) we introduce the average density \( \rho_\alpha^{(0)} \) as

\[
\rho_\alpha^{(0)} = \frac{N_\alpha}{V},
\]

where \( N_\alpha \) is the number of ions of species \( \alpha \) in the volume \( V \). Denoting the valency of species \( \alpha \) as \( Z_\alpha \), the stability of the system against explosion and the concomitant existence of the thermodynamic limit requires that the electroneutrality condition

\[
\sum_{\alpha=0}^{\nu} Z_\alpha \rho_\alpha^{(0)} = 0
\]

is fulfilled.

According to the general definition of the effective Hamiltonian, our goal now is to fix the \( N_0 \) macroions at positions \( \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_0} \) and trace out the microion degrees of freedom. As a result of the presence of the fixed macroions, the microions develop space-dependent density profiles, which we denote as \( \rho_\alpha(\mathbf{r}) \), \( \alpha = 1, 2, \ldots, \nu \), where \( \mathbf{r} \) is an arbitrary space vector. Focusing exclusively on the electrostatics, it follows that we are interested in calculating the average electrostatic potential \( \Psi(\mathbf{r}) \), which satisfies the Poisson equation:

\[
\nabla^2 \Psi(\mathbf{r}) = \frac{-4\pi}{\varepsilon} \sum_{i=1}^{N_0} Z_0 \delta(\mathbf{r} - \mathbf{R}_i) - \frac{4\pi}{\varepsilon} \sum_{\alpha=1}^{\nu} Z_\alpha \rho_\alpha(\mathbf{r}).
\]

As it stands, eq. (13) above simply couples the unknown fields \( \Psi(\mathbf{r}) \) and \( \rho_\alpha(\mathbf{r}) \), it is thus insufficient for the calculation of either of the two. An additional relation is needed, and for this purpose one resorts to a mean-field approximation: in a spirit similar to the mean-field solution of the Ising model, one assumes that the local density \( \rho_\alpha(\mathbf{r}) \) at any given point in space is determined as the Boltzmann factor of the average electrostatic potential energy \( Z_\alpha \Psi(\mathbf{r}) \), i.e.:

\[
\rho_\alpha(\mathbf{r}) = \rho_\alpha^{(0)} \exp \left\{ - \frac{Z_\alpha \Psi(\mathbf{r})}{k_B T} \right\}, \quad \alpha = 1, 2, \ldots, \nu,
\]
where we have made use of the boundary condition that as \( r \to \infty \), \( \Psi(r) \to 0 \) and thus the ion densities must approach their bulk values there.

Equations (13) and (14) above constitute, together, the Poisson-Boltzmann Approximation (PBA). Though the PBA can be solved numerically under appropriate boundary conditions, it is still too complicated to allow for an analytical solution. Progress can be made if two additional approximations are introduced. First, instead of considering \( N_0 \) fixed macroions, we reduce the problem to a simpler one: we consider only one of the \( N_0 \) counterions fixed at the origin and we smear out the remaining ones into a uniform background of density \( \rho_0^{(0)} \) \(^{(2)}\). Accordingly, all inhomogeneous quantities become functions of \( r \), and eq. (13) takes the form

\[
\nabla^2 \Psi(r) = -\frac{4\pi}{\varepsilon} Z_0 \delta(r) - \frac{4\pi}{\varepsilon} Z_0 \rho_0^{(0)} \Theta(r - a) - \frac{4\pi}{\varepsilon} \sum_{\alpha=1}^{\nu} Z_\alpha \rho_\alpha(r),
\]

with the Heaviside step function \( \Theta(x) \). Second, we linearize the exponential of eq. (14), and approximation valid for regions of space in which the electrostatic energy does not massively exceed the thermal energy \( k_B T \), i.e.

\[
\rho_\alpha(r) = \rho_\alpha^{(0)} \left[ 1 - \frac{Z_\alpha}{k_B T} \Psi(r) \right] \Theta(r - a), \quad \alpha = 1, 2, \ldots, \nu.
\]

Combining eqs. (15) and (16), and making use of the electroneutrality condition, eq. (12), we arrive at the equations that determine the electrostatic potentials \( \Psi_I(r) \) and \( \Psi_{II}(r) \) at the regions \( r < a \) and \( r > a \), respectively, and which constitute the linearized Poisson-Boltzmann or Debye-Hückel theory:

\[
\nabla^2 \Psi_I(r) = -\frac{4\pi}{\varepsilon} Z_0 \delta(r) \quad (r < a),
\]

\[
\nabla^2 \Psi_{II}(r) = \kappa^2 \Psi_{II}(r) \quad (r > a),
\]

with the inverse Debye screening length \( \kappa \), which is related to the densities and valencies of all counterionic species via

\[
\kappa^2 = \frac{4\pi}{\varepsilon k_B T} \sum_{\alpha=1}^{\nu} Z_\alpha^2 \rho_\alpha^{(0)}.
\]

The Debye-Hückel theory must now be solved under the boundary conditions of continuity of the potential and the electric field \( \mathbf{E} = -\nabla \Psi(r) \) on the colloidal surface, \( r = a \) \(^{(3)}\).

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\(^{(2)}\) The careful reader might object that the density should exclude the one macroion fixed at the origin but \( (N_0 - 1)/V \to N_0/V \) as \( N_0 \) and \( V \) go to infinity.

\(^{(3)}\) If we assume the colloidal charge \( Z_0 \) to be uniformly distributed as a surface charge density \( \sigma = Z_0/(4\pi a^2) \) on the colloidal surface instead of being a point charge at \( r = 0 \), the electric field at \( r = a \) has a jump equal to \( 4\pi \sigma/\varepsilon \). The reader should verify that this changes nothing as regards the electrostatic potential \( \Psi_{II}(r) \) outside the colloid. The modification of the potential \( \Psi_I(r) \) that results inside the colloid is physically irrelevant, since neither the microions nor the macroions can penetrate this region.
The final expressions for the electrostatic potential $\Psi_{I,II}(r)$ read as

\begin{align}
\Psi_I(r) &= \frac{Z_0}{\varepsilon r} - \frac{Z_0}{\varepsilon a} + \frac{Z_0}{\varepsilon a(1 + \kappa a)}, \\
\Psi_{II}(r) &= \frac{Z_0}{\varepsilon} \frac{e^{\kappa a}}{1 + \kappa a} e^{-\kappa r}. \tag{20}
\end{align}

The electrostatic potential outside the colloid, therefore, has the form of a screened Coulomb interaction produced by a “point charge” of magnitude $Z_0 e^{\kappa a}/(1 + \kappa a)$, the “enhancement” of the bare charge $Z_0$ being due to the finite size of the colloidal particle. To better appreciate the physical meaning of the screened potential of eq. (21), it is behooving to look at the density profile of the microions that it produces, and which is readily available from eq. (16). For clarity, we restrict ourselves to the case of a single counterionic species (i.e., $\nu = 1$), we denote the counterion density as $\rho_c(r)$, its average value as $\rho_c(0)$, and the counterion valency as $Z_c$. Then, from eqs. (16) and (21) we obtain the excess of counterion charge density over its bulk value, $\Delta Z_c \rho_c(r) \equiv Z_c \rho_c(r) - Z_c \rho_c^{(0)}$, as

\begin{equation}
\Delta Z_c \rho_c(r) = -\frac{Z_0^2 Z_0 \rho_c^{(0)}}{\varepsilon k_B T(1 + \kappa a)} e^{-\kappa(r-a)} \frac{r}{r} \Theta(r-a). \tag{22}
\end{equation}

The total of excess charge contained in this distribution can be obtained easily as

\begin{equation}
Q_{ex} = 4\pi \int_a^\infty \rho_c^2(r) dr = -Z_0, \tag{23}
\end{equation}

i.e., at infinite distances from the colloid, the counterions completely screen its charge. We can now readily give a physical interpretation to the above results: each macroion polarizes the counterions around it, creating a counterion charge density given by eq. (22). What appears as a background $\rho_c^{(0)}$ is due to the smearing out of the macroions that we performed along the way. Since all colloids are identical, each one of them is “dressed” with a counterion profile of eq. (22); in other words, we can now take the background $\rho_c^{(0)}$ and split it equally into $N_0$ bits, each of which has the form of eq. (22), and each of which is centered around a different macroion. The combined entity of macroion and its own counterion cloud appears as a point charge $Z_0 e^{\kappa a}/(1 + \kappa a)$ screened by the cloud, and the total charge around a given macroion within a sphere of radius $r$ around it, $Q(r)$, is calculated as

\begin{equation}
Q(r) = Z_0 + 4\pi \int_a^r x^2 \Delta Z_c \rho_c(x) dx = Z_0 \frac{e^{\kappa a}}{1 + \kappa a} (1 + \kappa r) e^{-\kappa r}. \tag{24}
\end{equation}

By virtue of Gauss’ law, the electric field generated by this charge distribution is

\begin{equation}
E(r) = \frac{Z_0}{\varepsilon} \frac{e^{\kappa a}}{(1 + \kappa a)} \frac{(1 + \kappa r)}{r^2} e^{-\kappa r} \hat{r}. \tag{25}
\end{equation}
Fig. 3. – A sketch of an impenetrable colloidal particle of radius $a$ with an embedded, off-center charge $Z_0$ at a distance $b$ from its center. The coordinate system used in the text is also shown, with the position vector $r$ in space and the polar angle $\theta$. Regions I and II denote, respectively, the parts of space inaccessible and accessible to the mobile counter- and salt-ions.

Associated with this field is the electrostatic potential $\Phi(r)$ via $E(r) = -\nabla \Phi(r)$ and we readily obtain from eq. (25):

$$\Phi(r) = \frac{Z_0}{\varepsilon} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r},$$

identical to eq. (21) above.

Finally, we complete the picture by considering now each counterion cloud as "tightly bound" to each own colloid, i.e., as being unaffected by neighboring colloids. This is the final approximation but it arises naturally in the spirit of the Debye-Hückel approach, and it is consistent with the more general superposition approximation [31, 32] encountered in other branches of colloidal science. Under this assumption, and since a colloid does not feel any force from its own cloud, the total potential energy that it experiences is the sum of interaction energies with all other screened "point charges". Since each of the colloids figures in the theory with a size-corrected charge $Z_0 e^{\kappa a}/(1 + \kappa a)$, the celebrated Debye-Hückel pair interaction potential between charged colloids obtains as

$$V_{DH}(r) = \frac{Z_0^2}{\varepsilon} \frac{e^{2\kappa a}}{(1 + \kappa a)^2} \frac{e^{-\kappa r}}{r}.$$

Despite its intrinsic limitations to the weak coupling regime ($Z_0 \Psi(r) < k_B T$), the Debye-Hückel theory is attractive in terms of its physical transparency and its analytical character. Moreover, it works remarkably well, in comparison to experimental data, especially when treating the colloidal charge as a free parameter. An additional advantage of the Debye-Hückel theory, however, is the fact that it can be generalized to any distribution of charges embedded within the colloid, not just a single charge at the center. The physical situation is depicted in fig. 3, showing one impenetrable colloid of radius $a$ at the origin with an embedded point charge $Z_0$ at a distance $b < a$ from the center. At the exterior, the colloid is screened by a bath of neutralizing counterions and possible
additional salt. The problem of the calculation of the screened electrostatic potential for this case has been addressed by Hoffmann et al. [33]; here, we give the essential information and we refer the reader to the original publication for more details.

Evidently, it is advantageous to choose the direction that connects the colloid center with the point charge as the z-axis, in which case we can take advantage of the ensuing azimuthal symmetry of the problem. Following the same notation for the electrostatic potentials inside and outside the colloid as above, we see that in the Debye-Hückel approximation they obey the equations

\[
\nabla^2 \Psi_I(r) = -\frac{4\pi}{\varepsilon} Z_0 \delta(r - b\hat{z}), \quad (r < a),
\]

(28)

\[
\nabla^2 \Psi_{II}(r) = \kappa^2 \Psi_{II}(r), \quad (r > a),
\]

(29)

After some algebra and matching the boundary conditions at the colloidal surface, the physically relevant solution outside the colloid reads as [33, 34]

\[
\Psi_{II}(r) = \frac{Z_0}{\varepsilon} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r} + \frac{Z_0}{\varepsilon a} \sum_{l=1}^{\infty} (2l + 1) \left( \frac{b}{a} \right)^l \sqrt{\frac{1}{\kappa r} K_{l+1/2}(\kappa r) K_{l-1/2}(\kappa a)} P_l(\cos \theta),
\]

(30)

with the modified spherical Bessel functions of the third kind, \( K_{l+n/2}(z) \), where \( n = 1, 3 \), and the Legendre polynomials \( P_l(\cos \theta) \). Asymptotically, the Bessel functions all behave as \( K_{l+n/2}(z)/\sqrt{z} \sim e^{-z}/z \) as \( z \to \infty \), so that the overall radial asymptotic behavior of the solution is also in this case of the Yukawa form. However, it is modulated in the polar direction according to the corresponding Legendre polynomial \( P_l(\cos \theta) \), and this modulation persists at all distances. Further, eq. (30) above trivially reduces to the previously derived result for the case of spherical symmetry (\( b = 0 \)), whereas the eccentricity of the embedded charge, \( b/a < 1 \), appears raised to successively higher powers in the \( l \)-series, thus the number of terms to achieve sufficient convergence grows with it. The linearity of the theory guarantees the validity of superposition of the solution in the case of more embedded charges, in which case the Legendre polynomials at the right hand-side of eq. (30) above get replaced by the spherical harmonics \( Y_{lm}(\theta, \phi) \) and the summation runs over \( l \) as well as over \( -l \leq m \leq l \) [33]. The effective interaction potential between two such identical or nonidentical colloids with inhomogeneous charge patterns has been recently worked out in detail and in full generality, motivated by ongoing work on the novel class of inverse patchy colloids [34].

3'2. Steric stabilization. – A repulsive barrier against the van der Waals attraction can also be set up by chemically grafting a number \( f \) of self-avoiding polymer chains on the colloidal surface. In this way, a so-called spherical polymer brush results and \( f \) will be referred to as the brush functionality. In what follows, we will focus on the case for which the chain length vastly exceeds the colloidal radius. To physically appreciate the mechanism that brings about colloidal stabilization, and which is nothing else than an entropic repulsion between the chains, we will begin with the simple case \( f = 1 \). In fact, we will even omit the colloidal particle altogether in this case and simply consider two long polymer chains, each of the two being composed of \( M \) mutually repulsive monomers. In the scaling limit, \( M \gg 1 \), the precise nature of the monomer-monomer repulsion becomes immaterial and the resulting effective repulsion between the chains obtains a universal form.
There are two key properties that self-avoiding polymer chains possess. First, their size $R$, expressed, e.g., through their gyration radius or the expectation value of their end-to-end distance, is a power law of their degree of polymerization $M$:

\begin{equation}
R = CaM^\nu,
\end{equation}

where $C$ is a model-dependent constant, $a$ is the monomer size and $\nu = 0.588 \cong 3/5$ is a universal exponent arising from the properties of self-avoiding random walks (SARW) in three dimensions, which describe the statistics of polymer chains in good solvents (\textsuperscript{4}). Apart from establishing a power law dependence, eq. (31) also implies the self-similar character of SARW’s: indeed, if monomers are regrouped in units of “blobs”, each blob containing $g$ monomers, it follows that the chain can be seen as a succession of $M_b = M/g$ blobs, each having a size $D \propto ag^\nu$. Accordingly, the radius of the chain of blobs, $R_b$, will scale as $R_b \propto DM_b^\nu = ag^\nu(M/g)^\nu = aM^\nu$. In other words, and comparing with eq. (31), we see that the chain size remains \textit{invariant} under such a regrouping of monomers into coarser objects.

Associated with the huge number of conformations $Z_M$ that a SARW can assume is an entropy $S_M = k_B \ln Z_M$ and thus a free energy $F_M = -k_B T \ln Z_M$. It can be shown [30, 35] that the latter depends on $M$ as

\begin{equation}
Z_M \propto \tau^M M^{\gamma - 1},
\end{equation}

where $\tau$ is a non-universal parameter that depends on the short-range details of the random walk and $\gamma = 7/6$ is a universal exponent (\textsuperscript{5}). If now the end-monomers of two such chains are held fixed at a distance $r \sim a$ from one another, the combined picture is almost identical to a single polymer chain (or a SARW) with $2M$ monomers. Accordingly, its partition function, $Z(a)$, will be given by $Z(r \sim a) \cong Z_{2M}$ and using eq. (32) we obtain

\begin{equation}
Z(r \sim a) \propto \tau^{2M} (2M)^{\gamma - 1}.
\end{equation}

Since the effective interaction is customarily normalized to zero at infinite separation, we are interested in the ratio $Z(a)/Z(\infty)$. The denominator is the partition function of two $M$-monomer chains held infinitely apart from one another and thus equal to $Z_M^2$. Combining the above results we obtain

\begin{equation}
V_{\text{eff}}(r \sim a) \cong k_B T(\gamma - 1) \ln M.
\end{equation}

However, on dimensional grounds, the effective potential must depend only on the ratio $r/R$, since these are the only two relevant length scales of the problem, given the fact that the monomer length $a$ can be arbitrarily rescaled so that $R$ remains invariant. Accordingly, eq. (34) must take the form

\begin{equation}
V_{\text{eff}}(r \sim a) \cong \frac{\gamma - 1}{\nu} k_B T \ln(R/r),
\end{equation}

(\textsuperscript{4}) The cases of the so-called $\Theta$-solvent ($\nu = 1/2$) and the poor solvent ($\nu = 1/3$) are beyond the scope of this contribution.

(\textsuperscript{5}) For the usual random walk, i.e., without self-avoidance, $\gamma = 1$. 

(\textsuperscript{5})
where we have used eq. (31) to eliminate \( M \) in favor of \( R \), and neglected the constant \( C \). The argument can now be repeated for arbitrary separations \( r \), since the definition of the monomer length \( a \) is, by and large, a matter of choice/definition. Naturally, the regrouping of monomers into bigger monomers can only be followed as long as the new monomer has a size of order \( R \). Finally, we obtain the effective interaction between the end-monomers of two overlapping polymer chains in good solvent as

\[
V_{\text{eff}}(r) \approx -\gamma - \frac{1}{\nu} k_B T \ln(r/R), \quad (r < R).
\]

This logarithmic repulsion is, clearly, of entropic origin: since each chain is self-avoiding, when they overlap each of the two restricts the total amount of configurations available to the other. The entropic nature of \( V_{\text{eff}}(r) \) is manifested by the fact that it scales with \( k_B T \), i.e., that there is no other energy scale present in the problem. If we now assume two colloidal particles of size \( b \ll R \), each of them carrying a single chain grafted on its surface, it is straightforward to see that the arguments presented above carry over, and that therefore an effective logarithmic repulsion of the form of eq. (36) acts between the two.

An enormous enhancement of the stabilization effect follows if the colloids are grafted with \( f \gg 1 \) chains instead of a single one. To establish this in a quantitative fashion, we first need to understand the properties of a single colloid of size \( b \) grafted with \( f \) very long chains, see fig. 4. The grafting creates conditions of very high crowding for the polymer chains and it thereby drastically restricts their conformations. A very useful model to understand this is the Daoud-Cotton model of polymer blobs [36]. This is a generalization of the idea of the de Gennes blob, which can be sketched as follows: suppose you have a polymer chain of undisturbed size \( R \), which is brought into confinement in a cylindrical channel of diameter \( a \ll D \ll R \), a being the monomer size. The resulting chain can be thought of as a one-dimensional close-packed arrangement of blobs of diameter \( D \).
Within each blob, one has the usual SARW in which the effects of confinement are not felt, because the size is still smaller than the distance between the confining walls. However, as the successive blobs are arranged in a linear fashion, there is no SARW of blobs; SARW’s are restricted to the monomers within each blob. According to eq. (32) above, the free energy of a polymer chain scales as $-Mk_BT$, where $M$ is the number of objects that perform the SARW. The confined chain has no such free energy because the blobs are forced to order in a linear fashion, and therefore the entropy associated with all possible blob conformations vanishes. Therefore, the confined chain has a free energy which is higher in comparison to the value for its unconfined counterpart by an amount equal to $M_bk_BT$, $M_b$ being the number of blobs that it has formed. This is usually expressed in a concise fashion by the statement [30]: There is a cost of $k_BT$ per blob upon confinement.

Our first task is therefore to count the number of blobs $M_b$ that are formed by a chain contained into a single spherical colloidal brush of functionality $f$, and obtain the free energy difference, $F_{\text{brush}}(f)$, between the free energy of the brush and that of $f$ free chains as

$$F_{\text{brush}}(f) \equiv f k_B T M_b.$$  

The calculation of the crucial quantity $M_b$ for chains carrying $M$ monomers each is a combination of geometrical and physical considerations [30]. In conjunction with fig. 4, we see that the blob size $\xi(r)$ is growing with the distance from the colloidal center. In fact, since we have $f$ blobs of diameter $\xi(r)$ covering the surface of a sphere of radius $r$, it follows that $\xi^2(r) \propto r^2/f$ or

$$\xi(r) \sim r/\sqrt{f}.$$  

Within a blob of size $\xi(r)$ there are $g(r)$ monomers performing a SARW, thus this number scales as $g(r) \sim \xi^{1/\nu}(r)$. The local monomer density $c(r)$ is expressed as

$$c(r) = \frac{f g(r)}{4\pi r^2 \xi(r)} = \left( \frac{ab}{Dr} \right)^{-4/3} a^{-3},$$

where we have introduced the average distance between the grafting points, $D$, as well as the geometrical relation $D \approx b/\sqrt{f}$. The total number of monomers contained within a radius $R$ of the brush is $fM$, therefore we obtain the “conservation law”

$$f M = 4\pi \int_0^R r^2 c(r) \, dr \Rightarrow \quad R \approx a f^{1/5} M^{3/5}.$$  

The grafting of $f$ chains does not alter the exponent $\nu$ of the SARW as far as the $M$-dependence of the brush size is but it provides an additional stretching factor $f^{1/5}$ with respect to the size each of the chains would have if it had not been grafted. This stretching, which is of course caused by the confinement of each chain into cone-shaped regions that give rise to the blobs, is another way of physically understanding the loss of free energy anticipated in eq. (37) in the language of blobs.
With these preliminaries in place, we can now count the total number of blobs. The radii of the blobs of successive layers, $\xi_1, \xi_2, \ldots, \xi_{Mb}$, from the center can be calculated easily from geometrical considerations:

\begin{align*}
  \xi_1 &= \frac{b}{\sqrt{f}}; \\
  \xi_2 &= \frac{b + \xi_1}{\sqrt{f}}; \\
  \xi_3 &= \frac{b + \xi_1 + \xi_2}{\sqrt{f}},
\end{align*}

and so on. This establishes that each successive layer of blobs has a size larger than the preceding one by the factor $\left(1 + 1/\sqrt{f}\right) \equiv \left(1 + \delta\right)$, and thus

\begin{equation}
  \xi_k = (1 + \delta)^{k-1} \xi_1, \quad k = 2, 3, \ldots, Mb.
\end{equation}

It follows that the number of monomers $g_k \sim (\xi_k/a)^{1/\nu}$ within the blob of size $\xi_k$ is given by

\begin{equation}
  g_k = (1 + \delta)^{(k-1)/\nu} \left(\frac{\xi_1}{a}\right)^{1/\nu} = x^{k-1} \left(\frac{D}{a}\right)^{1/\nu}, \quad k = 2, 3, \ldots, Mb,
\end{equation}

where

\begin{equation}
  x \equiv (1 + \delta)^{1/\nu} \approx 1 + \frac{\delta}{\nu},
\end{equation}

given that $\delta = 1/\sqrt{f} \ll 1$. The monomer number per chain, $M$, is now obtained as

\begin{equation}
  M = \left(\frac{D}{a}\right)^{1/\nu} \sum_{k=1}^{Mb} x^{k-1} = \left(\frac{D}{a}\right)^{1/\nu} x^{Mb-1} \frac{1}{x-1} \approx \frac{\nu}{\delta} \left(\frac{D}{a}\right)^{1/\nu} x^{Mb},
\end{equation}

where we have used eq. (46) and the fact that $x^{Mb} \gg 1$ for long chains ($Mb \gg 1$). Carrying out some straightforward algebra, and making use of the relation $D = b/\sqrt{f}$ we find from eq. (47)

\begin{equation}
  M_b = \nu f^{1/2} \ln \left[\left(M/\nu\right)f^{1/3}(a/b)^{1/\nu}\right].
\end{equation}

Equation (48) expresses, together with eq. (40), a remarkable result, namely that the number of blobs per chain depends only on the ratio $R/b$ of the chain extent over the colloidal radius but not on the monomer length $a$, i.e.:

\begin{equation}
  M_b = f^{1/2} \ln(R/b) - \nu f^{1/2} \ln \nu.
\end{equation}

This is a clear manifestation of the above-mentioned property of long polymer chains, i.e., of the fact that the monomer length is a scale that drops out of sight and that only the overall size $R$ of the chain matters (self-similarity).
The total number of blobs $M_f$ of the star is now just $f$ times $M_b$ and therefore (cf. eq. (37)):

$$F_{\text{brush}}(f) = f^{3/2}k_B T \ln(R/b) - \nu f^{3/2}k_B T \ln \nu.$$  

The final step in establishing the form of the effective interaction between two such brushes kept apart at separation $r \sim b$ follows along the same lines as those put forward for the case $f = 1$. Indeed, two such brushes at separation $r$ look like a single brush with $2f$-arms. Dropping the $r$-independent term from eq. (50) above, it follows that

$$V_{\text{eff}}(r) \approx -f^{3/2}k_B T \ln(r/R) \quad (r < R).$$

In comparison with eq. (36), we see that the logarithmic form of the repulsion is a general and remarkable property of polymers, stemming essentially from their self-avoidance and self-similarity. In addition, the grafting of a large number of chains brings forward a spectacular enhancement of the repulsions by a factor $f^{3/2}$. To have a full picture of the effective interactions of such star-like brushes, $V_{\text{eff}}(r)$ must be supplemented by its functional form for separations $r > R$, a task which has been fulfilled by a combination of theory, simulation and experiment [20]. Considerable work in the last fifteen years has taken place on the basis of this class of effective interactions, which has led to an increase of our understanding of their equilibrium [21] and glassy [37] properties.

4. – Classical uniform fluids

In what follows, we are now assuming that coarse-graining has taken place in a complex fluid, so that its description has been reduced to a much more tractable description that involves an effective Hamiltonian with (pairwise-additive) effective interactions. We are then interested in the many-body problem of $N$ such effective point particles in the system, whose interactions incorporate the effects of the degrees of freedom that have dropped out of sight.

All the information on the equilibrium properties of a many-body system is encoded, in increasing degree of detail, into the thermodynamic potentials (e.g., its Helmholtz free energy or the grand potential) at given conditions and at its $n$-body correlation functions ($n < N$). The latter describe, in general, the joint probability density of finding $n$ particles in the system in elementary volumes $d^3r_i$ centered around the points $r_1, r_2, \ldots, r_n$, in space. Seldom is knowledge of the system in such detailed required for any practical purposes. In practice, one is interested in the thermodynamics as well as in correlation functions up to the pair level, i.e., $n \leq 2$. Accordingly, we define two operators, $\hat{\rho}^{(1)}(\mathbf{r})$ and $\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}')$, called one- and two-particle density operators, respectively, as follows:

$$\hat{\rho}^{(1)}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i),$$

and

$$\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) - \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_i).$$
where \( r_{i,j} \) are the instantaneous particle coordinates and \( r, r' \) denote arbitrary observation points in space. The one- and two-particle densities \( \rho^{(1)}(r) \) and \( \rho^{(2)}(r, r') \) are the expectation values of the corresponding operators in the chosen ensemble. Evidently, \( \rho^{(1)}(r) \) is proportional to the probability density of finding any particle of the system around \( r \), whereas \( \rho^{(2)}(r, r') \) is proportional to the probability density of finding simultaneously any particle of the system around \( r \) and a different particle of the system around \( r' \).

The translational invariance of \( \mathcal{H}_{\text{eff}} \) implies that the one-particle density of the system is a position-independent constant which is simply equal to the average particle density.

\[
\rho^{(1)}(r) = \rho = \frac{N}{V},
\]

where \( N \) stands for the number of particles enclosed in the macroscopic volume \( V \).

Accordingly, in a fluid, the two-particle density depends only on the magnitude of the difference of its arguments:

\[
\rho^{(2)}(r, r') = \rho^{(2)}(|r - r'|).
\]

In the theory of classical fluids, a quantity of central importance for the investigation of the pair structure of the system is the radial distribution function \( g(|r - r'|) \) defined through:

\[
\rho^{(2)}(|r - r'|) = \rho^2 g(|r - r'|).
\]

Physically, the quantity \( \rho g(|r - r'|) \) is proportional to the conditional probability density of finding a particle at position \( r' \) given that another particle is located at position \( r \).

The typical shape of \( g(|r - r'|) \) for a dense liquid is shown in fig. 5(a).

Another important quantity is the structure factor \( S(k) \) of a fluid defined as a three-dimensional Fourier transform of the total correlation function \( h(r) = g(r) - 1 \):

\[
S(k) = 1 + \rho \int d^3 r h(r) e^{-i k \cdot r},
\]

which depends only on the magnitude \( k \) of the wavevector \( k \) since \( h(r) \) is a radially symmetric function \(^{(7)}\). A typical structure factor for a dense liquid is shown in fig. 5(b). It can be shown \([38]\) that the scattering intensity from a liquid sample at momentum transfer \( k \) is proportional to \( S(k) \). This makes the structure factor an important diagnostic tool for testing the accuracy of liquid-state theories, in which this quantity is usually calculated by means of some approximation. Note, though, that the scattering intensity is directly proportional to \( S(k) \) only when we consider scattering from point particles. When we deal with large particles, such as colloids, then the form factor \( P(k) \) of the

\(^{(6)}\) Unless explicitly stated otherwise, the thermodynamic limit, \( N, V \to \infty \) with \( N/V = \rho \), constant, will be assumed throughout.

\(^{(7)}\) We denote the integration in \( d \) spatial coordinates but eq. (57) as well as eq. (59) that follows hold in arbitrary spatial dimensions.
Fig. 5. – Typical shapes of (a) the radial distribution function $g(r)$ and (b) the structure factor $S(k)$ of a dense, classical liquid. The length scale $a$ is set by the density, $a = \rho^{-1/3}$. Notice the successive coordination shells in real space (represented by the maxima of the radial distribution function), reflecting the short-range order of the fluid state.

Particle has to be taken into account and the scattering intensity is proportional to the product $P(k)S(k)$ [39]. Moreover, the quantity $S(k)$ offers a path to thermodynamics, as its $k = 0$ value is proportional to the isothermal compressibility $\chi_T$ of the system [38]:

\begin{equation}
S(0) = \rho k_B T \chi_T.
\end{equation}

For the theoretical approaches to the determination of the pair structure in the fluid state, one important function is the direct correlation function $c(r)$ connected to $h(r)$
through the Ornstein-Zernike relation which has the form

\begin{equation}
    h(r) = c(r) + \rho \int d^3 r' c(|r - r'|) h(r').
\end{equation}

The Ornstein-Zernike relation is exact. As it connects two unknown functions, one more relation or \textit{closure} is needed in order to determine \(g(r)\) and \(c(r)\). Closures are approximate relations which arise from exact diagrammatic expansions of \(g(r)\) in terms of \(c(r)\) but with certain classes of diagrams ignored. The exact relation between \(g(r)\) and \(c(r)\) reads as \[60\]

\[
g(r) = \exp\left[-\beta v(r) + g(r) - 1 - c(r) + B(r)\right],
\]

where \(v(r)\) is the pair potential and \(B(r)\) is the so-called \textit{bridge function}, consisting of the sum of all elementary diagrams that are not nodal. The bridge function is of short range and rather insensitive to the detailed form of the pair potential [40]. All known closures can be thought of as approximate relations for the form of \(B(r)\). Common closures are the Percus-Yevick (PY) and hypernetted chain (HNC) approximations [38]. In the PY closure, the approximation for \(B(r)\) reads as \[61\]

\[
    B_{\text{PY}}(r) = -[g(r) - c(r)] + 1 + \ln[g(r) - c(r)] \quad \text{(PY)},
\]

whereas in the HNC the approximation is made that the bridge function vanishes:

\[
    B_{\text{HNC}}(r) = 0 \quad \text{(HNC)}.
\]

Equations (61) and (62) together with the exact relation (60) yield the common forms of the PY and HNC closures as

\begin{align}
    (63) \\
    c(r) &= g(r) \left[1 - e^{\beta v(r)}\right] \quad \text{(PY)}, \\
    (64) \\
    g(r) &= e^{-\beta v(r) + h(r) - c(r)} \quad \text{(HNC)}.
\end{align}

The Ornstein-Zernike relation, supplied with a closure, leads to the determination of the quantities \(c(r)\), \(g(r)\) and \(S(k)\) for a given interaction potential \(v(r)\) and at given thermodynamic conditions, \textit{e.g.}, density and temperature. Various other quantities of interest, such as the pressure \(P\) or the energy \(U\) can be calculated as integrals involving the radial distribution function:

\begin{align}
    (65) \\
    P &= k_B T \rho - \frac{2}{3} \pi \rho^2 \int_0^\infty r^3 v'(r) g(r) dr,
\end{align}

and

\begin{align}
    (66) \\
    \frac{U}{N} &= \frac{3}{2} k_B T + 2\pi \rho \int_0^\infty r^2 v(r) g(r) dr,
\end{align}

where \(v'(r) = d v(r)/d r\). The free energy \(F\) can then be determined by thermodynamic integration of \(P\) (the \textit{pressure route}) or of \(U\) (the \textit{energy route}) as given in eqs. (65) and (66) above. A third possibility is to use eq. (58) and the thermodynamic definition
of the isothermal compressibility, \( \chi_T = (V \partial^2 F/\partial V^2)^{-1} \). This constitutes the compressibility route. If the exact radial distribution function \( g(r) \) were known, then all three routes would yield identical results for the free energy. Due to the approximations in constructing a closure, however, this is not the case: every route yields a different free energy curve. This is the problem of thermodynamic inconsistency of the closure [38].

The procedure to obtain the structure and thermodynamics of translationally invariant systems (liquids and gases) described above, is known under the name integral equation theories (IET’s). For every possible closure, one has to solve two coupled integral equations. There is by now a large variety of closures in the literature and the accuracy of a given closure depends sometimes on the characteristics of the interaction potential. For example, the PY closure is known to yield very accurate results for short-range, hard interactions, whereas the HNC is accurate for long-range, soft potentials.

The problem of thermodynamic inconsistency mentioned above is usually addressed by modifying the integral equation through the inclusion in the closure of a function which contains one or more additional parameters [40-44]. These parameters are then tuned until thermodynamic consistency is achieved, obtaining in this way not only the thermodynamics but also the pair structure with high accuracy. A particularly simple closure which yields excellent results for purely repulsive potentials was introduced by Rogers and Young [41] and reads as

\[
(67) \quad g(r) = \exp[-\beta v(r)] \left[ 1 + \frac{\exp[\gamma(r)f(r)] - 1}{f(r)} \right],
\]

where

\[
(68) \quad \gamma(r) = h(r) - c(r)
\]

and the function \( f(r) \) is chosen to have the form

\[
(69) \quad f(r) = 1 - \exp(-\alpha r).
\]

Thermodynamic consistency is achieved by varying the parameter \( \alpha \). A comparison between eqs. (67), (69) and (63), (64) shows that the Rogers-Young closure reduces to the PY when \( \alpha = 0 \) and to the HNC when \( \alpha = \infty \).

5. – Nonuniform fluids: density functional theory (DFT)

5.1. The basic principles of DFT. – In the preceding section, we discussed the pair structure and the thermodynamics of homogeneous fluids, also called uniform fluids, to emphasize the fact that their density is independent of the position. Of course, when we say “density”, we refer not to an instantaneous value but rather to a time- or ensemble average. The process of obtaining this quantity can be visualized as follows. Imagine dividing the whole space into increasingly small cells of volume \( \Delta V \) and let \( \Delta N(\mathbf{r}) \) be the number of particles enclosed in the cell centered at the position \( \mathbf{r} \). Consider the ratio \( \Delta N(\mathbf{r})/\Delta V \) in the limit \( \Delta V \to 0 \) and take the ensemble average of it, \( \langle \lim_{\Delta V \to 0} \Delta N(\mathbf{r})/\Delta V \rangle \). In a uniform fluid, the latter quantity is \( \mathbf{r} \)-independent and equal to the usual, homogeneous density \( \rho \) of the system. However, in many situations in condensed matter physics, the systems involved are spatially inhomogeneous, i.e., the density
turns into a spatially dependent field $\rho(\mathbf{r})$ in thermodynamic equilibrium (8). Typical examples are the nonuniform density profiles arising in phase-separated liquids or liquid mixtures, in fluids under the influence of external potentials (confining walls, optical-laser fields, electrostatic or magnetostatic fields) and, in the most extreme case, the vast inhomogeneities appearing when the translational symmetry of the system breaks and the fluid freezes into a crystalline solid. Density functional theory us with a powerful tool to accurately analyze these situations and make nontrivial predictions on a number of properties of the physical systems under consideration (9).

Let us start with a more precise definition of the (inhomogeneous) density $\rho(\mathbf{r})$. Consider a system of $N$ pointlike particles of mass $m$ in the volume $V$ and let $\{\mathbf{r}_i\}$, $i = 1, 2, \ldots, N$ be their positions and $\{\mathbf{p}_i\}$ their momenta. Suppose, without restriction to pair potentials, that $U(\{\mathbf{r}_i\})$ is the potential energy function describing their interactions and that the system is additionally placed under the influence of a one-body external potential $V_{\text{ext}}(\mathbf{r})$. The Hamiltonian $\hat{H}_N$ for the $N$-body system is, therefore (10)

$$\hat{H}_N(\mathbf{p}^N, \mathbf{r}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i).$$

We employ the grand ensemble, in which the chemical potential $\mu$ is fixed and the particle number $N$ is allowed to fluctuate, defining thereby the grand canonical partition function $\Xi$ as

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\mathbf{p}^N \int d\mathbf{r}^N \exp[-\beta(\hat{H}_N - \mu N)],$$

and the associated grand potential $\Omega$ as

$$\Omega(V, T, \mu) = -k_B T \ln \Xi.$$

The expectation value of any operator $\hat{O}(\mathbf{p}^N, \mathbf{r}^N)$ is given in this ensemble as

$$\mathcal{O} \equiv \langle \hat{O}(\mathbf{p}^N, \mathbf{r}^N) \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{1}{N!} \int d\mathbf{p}^N \int d\mathbf{r}^N \hat{O}(\mathbf{p}^N, \mathbf{r}^N) \exp[-\beta(\hat{H}_N - \mu N)].$$

(8) In the presence of time-dependent external fields, the one particle density becomes a spatiotemporal field $\rho(\mathbf{r}, t)$. Recent developments allow for the extention of DFT-approaches also to dynamical problems [45-52].

(9) Here, we will present a concise exposure to the principles of DFT, avoiding proofs of the theorems associated with it. For a more detailed discussion, we refer the reader to the standard work of Evans [53].

(10) In this section, we place a hat above the symbol of a classical operator $\hat{O}$ that depends on the canonical variables of the system, in order to distinguish it from its thermodynamic average.
The so-called one-particle density operator $\hat{\rho}(\mathbf{r})$ is defined as \(^{(11)}\)

\begin{equation}
\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i),
\end{equation}

and the one-particle density $\rho(\mathbf{r})$ is then nothing else but the expectation value of this operator in the sense of eq. (73) above, namely

\begin{equation}
\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle.
\end{equation}

Evidently, $\int d^d r \rho(\mathbf{r}) = \langle N \rangle$, with $\langle N \rangle$ denoting the expectation value of the particle number \(^{(12)}\) in the system for the given $\mu$.

For a given interaction function $U(\{\mathbf{r}_i\})$ and fixed temperature $T$ and chemical potential $\mu$, the definitions above make it clear that $\rho(\mathbf{r})$ is uniquely determined by the external potential $V_{\text{ext}}(\mathbf{r})$. The key property that lends DFT its power lies in the fact that also the opposite is true: a given, equilibrium density profile $\rho_0(\mathbf{r})$ also uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$ that gives rise to it. The proof of this important theorem follows the lines of *reductio ad absurdum* and details can be found in ref. [53]. The implication is, then, that the grand potential $\Omega$ becomes a functional of $\rho_0(\mathbf{r})$, *i.e.*, $\rho_0(\mathbf{r})$ uniquely determines the thermodynamics of the system \(^{(13)}\). Here, we present a short sketch of the steps leading to this fact.

The grand potential $\Omega$ can be expressed as

\begin{equation}
\Omega = \text{Tr} \{ f_0(\hat{H}_N - \mu N + \beta^{-1} \ln f_0) \},
\end{equation}

with the equilibrium phase-space probability density $f_0$:

\begin{equation}
f_0 = \frac{1}{\Xi} \exp \left\{ -\beta(\hat{H}_N - \mu N) \right\},
\end{equation}

and the definition of the trace $\text{Tr}$ as

\begin{equation}
\text{Tr} \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int d\mathbf{p}^N \int d\mathbf{r}^N,
\end{equation}

implying $\text{Tr} f_0 = 1$. Motivated from eq. (76) above, we now define a generalized functional $\Omega[f]$ of any nonnegative function $f(\mathbf{r}^N, \mathbf{p}^N)$ with $\text{Tr} f = 1$ through:

\begin{equation}
\Omega[f] = \text{Tr} \left\{ f(\hat{H}_N - \mu N + \beta^{-1} \ln f) \right\}.
\end{equation}

\(^{(11)}\) This is the same operator as $\hat{\rho}^{(1)}(\mathbf{r})$ of eq. (52) above, but we quote it here again for completeness and we drop the superscript for simplicity in notation.

\(^{(12)}\) We display all integrations in $d$-dimensional space, as the results of this section are general, and we will return to the familiar, $d = 3$-space in practical examples that follow.

\(^{(13)}\) For a crash-course on functionals and functional differentiation, see Appendix A.
After some straightforward algebra, $\Omega[f]$ can be re-expressed as

$$
\Omega[f] = \Omega[f_0] + \beta^{-1} \operatorname{Tr}[f \ln f - f \ln f_0].
$$

Using the Gibbs inequality, $-\ln x \geq 1 - x$, $\forall x > 0$, eq. (80) above leads to $\Omega[f] \geq \Omega[f_0] + \beta^{-1} \operatorname{Tr}[f - f_0]$, and since both functions $f$ and $f_0$ have trace equal to unity:

$$
\Omega[f] \geq \Omega[f_0],
$$

the equality holding only when $f = f_0$. The one-to-one correspondence between $f_0$ and the equilibrium density arises through the property that if two different external potentials $V_{\text{ext}}(r)$ and $V'_{\text{ext}}(r)$ gave rise to the same equilibrium density $\rho_0(r)$, the two corresponding grand potentials, $\Omega$ and $\Omega'$ would satisfy simultaneously the inequalities:

$$
\Omega' < \Omega + \int d^d r \rho_0(r) [V'_{\text{ext}}(r) - V_{\text{ext}}(r)],
$$

$$
\Omega < \Omega' + \int d^d r \rho_0(r) [V_{\text{ext}}(r) - V'_{\text{ext}}(r)],
$$

which lead to an obvious contradiction upon addition, proving the impossibility of the underlying assumption that two different external potentials can lead to the same equilibrium density.

Taking now into account eqs. (70)-(75) above, we see that $\Omega$ can be expressed as

$$
\Omega[\rho_0] = F[\rho_0] + \int d^d r [V_{\text{ext}}(r) - \mu] \rho_0(r),
$$

where the intrinsic free energy $F[\rho_0]$ explicitly depends only on $\rho_0(r)$ and is, evidently, also a unique functional of the one-particle density. In interpreting eq. (84) above, it must be kept in mind that the external potential $V_{\text{ext}}(r)$ that appears there is not arbitrary but rather precisely the external potential that gives rise to $\rho_0(r)$ as the equilibrium profile. Moreover, we can now go one step further: since the functional form of $F$ when seen as a functional of the density is unique for every given interaction energy, the functional $F[\rho]$ for any admissible density profile $\rho(r)$ represents the intrinsic Helmholtz free energy of a system under that external potential which makes $\rho(r)$ be the equilibrium density.

Motivated by the form of eq. (84) above, we now introduce an extended functional $\tilde{\Omega}([\rho], [V_{\text{ext}}])$ of both $\rho(r)$ and $V_{\text{ext}}(r)$ as

$$
\tilde{\Omega}([\rho], [V_{\text{ext}}]) = F[\rho] + \int d^d r [V_{\text{ext}}(r) - \mu] \rho(r).
$$

Evidently, when $\rho(r) = \rho_0(r)$, $\tilde{\Omega}([\rho_0], [V_{\text{ext}}]) = \Omega[\rho_0]$, the grand potential of the system and $F[\rho_0]$ becomes the intrinsic Helmholtz free energy of the same. The computational power associated with DFT comes from a variational principle, inherited from property (81) above, which states that $\tilde{\Omega}([\rho], [V_{\text{ext}}])$ attains its minimum value for the equilibrium density profile $\rho_0(r)$ [53]:

$$
\tilde{\Omega}([\rho], [V_{\text{ext}}]) \geq \tilde{\Omega}([\rho_0], [V_{\text{ext}}]) \equiv \Omega[\rho_0] \quad \text{for} \quad \rho(r) \neq \rho_0(r).
$$
The equilibrium density profile of a system, $\rho_0(r)$, can therefore be determined by minimizing $\tilde{\Omega}([\rho], [V_{\text{ext}}])$ with respect to $\rho(r)$, viz.

$$\frac{\delta \tilde{\Omega}([\rho], [V_{\text{ext}}])}{\delta \rho(r)} \bigg|_{\rho(r)=\rho_0(r)} = 0,$$

or, using eq. (85)

$$\frac{\delta F[\rho]}{\delta \rho(r)} \bigg|_{\rho(r)=\rho_0(r)} = \mu - V_{\text{ext}}(r).$$

The free energy functional $F[\rho]$ is hence the object of central interest in DFT. For each interaction potential there exists a unique functional $F[\rho]$ that determines the equilibrium configuration of the system under the influence of an arbitrary external potential $V_{\text{ext}}(r)$ with the help of eq. (88). For noninteracting particles, we can write down this functional exactly. It is referred to as “ideal free energy” $F_{\text{id}}[\rho]$ and it takes the form (14):

$$F_{\text{id}}[\rho] = k_B T \int d^3 r \rho(r) \left\{ \ln \left[ \rho(r) \Lambda^3 \right] - 1 \right\},$$

with the thermal de Broglie wavelength $\Lambda$. Application of the minimization principle, eq. (88), to an ideal gas then leads to the equilibrium profile

$$\rho_0(r) = \Lambda^{-3} \exp(\beta \mu) \exp[-\beta V_{\text{ext}}(r)],$$

which we recognize as a generalization of the barometric law.

For interacting systems it is customary to separate $F[\rho]$ into the ideal free-energy contribution of eq. (89) and the excess contribution $F_{\text{ex}}[\rho]$ arising from the interactions:

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{ex}}[\rho].$$

The excess free energy is a generating functional for the direct correlation functions of $n$-th order, $c^{(n)}$, which are defined as

$$c^{(n)}(r_1, r_2, \ldots, r_n; [\rho]) = -\frac{\delta^n \beta F_{\text{ex}}[\rho]}{\delta \rho(r_1) \delta \rho(r_2) \cdots \delta \rho(r_n)}.$$ 

The direct correlation function $c(r)$ of a fluid is precisely $c^{(2)}(r_1, r_2; [\rho])$ in the limit of a spatially homogeneous density field. In this case, the translational and rotational invariance of the underlying physical system imply that $c^{(2)}$ depends on $r_1$ and $r_2$ only through the combination $r \equiv |r_1 - r_2|$.

(14) We revert to three spatial dimensions from now on.
5.2. Some useful results. – Let us now use the general principles of DFT discussed above to derive some very useful and general results pertaining to the equilibrium properties of inhomogeneous fluids and their reductions to homogeneous ones. The fact that the intrinsic free energy $F[\rho]$ is a unique functional of the density field $\rho(r)$ has a number of very important mathematical implications. The first is that we can, formally, perform a functional Taylor expansion of this functional around some density field $\rho_i(r)$ as follows:

\[
F[\rho] = F[\rho_i] + \sum_{n=1}^{\infty} \frac{1}{n!} \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_n \frac{\delta^n F[\rho]}{\delta \rho(r_1) \delta \rho(r_2) \cdots \delta \rho(r_n)} \bigg|_{\rho(r)=\rho_i(r)} \times \Delta \rho(r_1) \Delta \rho(r_2) \cdots \Delta \rho(r_n),
\]

where $\Delta \rho(x) = \rho(x) - \rho_i(x)$. Equation (93) is formally exact but the convergence of the series is not guaranteed and very little is known about its mathematical properties. In addition, the functional derivatives of the free energy functional for $n > 2$ are, in general, very poorly known, if at all. Yet, even when the series is truncated at $n = 2$ some very useful results can be obtained from it, especially when the deviation of the density field $\rho(r)$ from its reference state, $\rho_i(r)$ is not too strong. Later on, we will use this expansion to derive the hypernetted chain closure for uniform fluids.

Instead of requiring to knowledge of the functional derivatives of $F[\rho]$ at a reference density $\rho_i(r)$, as eq. (93) above implies, one can resort to a different strategy, which requires knowledge of just the first functional derivative along a path that connects the reference density with the given density $\rho(r)$. Indeed, since $F[\rho]$ is a unique functional of the density, its value is independent of the path along the space of density functions that one follows to reach the profile $\rho(r)$. Consider, therefore, an $\alpha$-parametrized path $\rho_\alpha(r)$ that starts at the reference density $\rho_i(r)$ at $\alpha = 0$ and arrives at the final density $\rho(r)$ at $\alpha = 1$, and which is defined as follows:

\[
\rho_\alpha(r) = \rho_i(r) + \alpha(\rho(r) - \rho_i(r)).
\]

We can now integrate the free energy $F[\rho]$ along the $\alpha$-parameterized path as

\[
F[\rho] = F[\rho_i] + \int_0^1 d\alpha \int d^3 r \frac{\partial \rho_\alpha(r)}{\partial \alpha} \frac{\delta F[\rho]}{\delta \rho(r)} \bigg|_{\rho(r)=\rho_\alpha(r)}.
\]

Notice that eq. (95) requires, as opposed to eq. (93), knowledge of only the first functional derivative of $F[\rho]$ with respect to the density. However, we need to know its value at every point along the $\alpha$-path, i.e., for every member of the family $\rho_\alpha(r)$. This is not a surprise, since the opposite would imply that we would be able to obtain the same information by putting much less effort into the solution of the problem, which is, in general, a goal impossible to achieve \((15)\).

The above considerations find a very useful application for the case in which the system is non-interacting, so that the Helmholtz free energy $F[\rho]$ reduces to its ideal part, $F_{id}[\rho]$. It is advantageous to choose as a reference density that of an empty system,

\((15)\) This is known as the No Free Lunch Theorem.
\( \rho_i(r) = 0 \), implying that \( F_{id}[\rho] = 0 \) as well. Then, eqs. (94)-(95) above take the form:

\[
F_{id}[\rho] = \int_0^1 d\alpha \int d^3r \rho(r) \frac{\delta F_{id}[\rho]}{\delta \rho(r)} \bigg|_{\rho(r) \rightarrow \alpha \rho(r)}.
\]

The functional derivative of the ideal free energy with respect to the density must be evaluated at the profile \( \alpha \rho(r) \), which has to be an equilibrium density all along the \( \alpha \) integration path. This implies that the system must, in every step of the integration, be brought under the influence of a changing external potential, \( V_{ext}^{(\alpha)}(r) \), which makes \( \alpha \rho(r) \) both equilibrium density under its influence. The dependence of the two can be read off from the minimization principle, eq. (88):

\[
\frac{\delta F_{id}[\rho]}{\delta \rho(r)} \bigg|_{\rho(r) \rightarrow \alpha \rho(r)} = \mu - V_{ext}^{(\alpha)}(r).
\]

However, eq. (97) is not suitable for use in the integral of eq. (96), because there we need to know the functional derivative as a functional of the density field, not of the external potential. The crucial step comes from the fact that the equilibrium density can be calculated analytically for a non-interacting system by simply carrying the integration over all particle momenta and coordinates in the framework of usual statistical mechanics, with the result

\[
\alpha \rho(r) = \Lambda^{-3} \exp \left\{ \beta \mu - \beta V_{ext}^{(\alpha)}(r) \right\} \Rightarrow \\
\mu - V_{ext}^{(\alpha)}(r) = k_B T \ln \left[ \alpha \rho(r) \Lambda^3 \right].
\]

From eqs. (96)-(98) it now follows that

\[
F_{id}[\rho] = k_B T \int_0^1 d\alpha \int d^3r \rho(r) \ln \left[ \alpha \rho(r) \Lambda^3 \right],
\]

and carrying out the trivial \( \alpha \)-integration we obtain eq. (89) that expresses the ideal free energy as an explicit functional of the one-particle density.

We now return to the more interesting case of interacting systems. Let us introduce the extended external field \( u(r) \) defined as

\[
u(r) = \beta \left[ \mu - V_{ext}(r) \right].
\]

The grand partition function \( \Xi \) can be regarded as a functional of \( u(r) \) and takes the convenient form

\[
\Xi[u] = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d^{3N} P \int d^{3N} R \exp \left\{ -\beta (\hat{T}_N + \hat{U}_N) \right\} \\
\times \exp \left\{ \int d^3r \hat{\rho}(r) u(r) \right\},
\]
where we have separated in the Hamiltonian \( \tilde{H}_N \) the kinetic and interaction-potential contributions, \( \tilde{T}_N \) and \( \tilde{U}_N \) respectively, from the external field and chemical potential terms. It immediately follows that

\[
\frac{\delta \ln \Xi[u]}{\delta u(\mathbf{r})} = \rho_0(\mathbf{r}),
\]

i.e., the equilibrium density can be obtained from the logarithm of the grand partition function upon taking a functional derivative with respect to the external potential.

Applying the functional derivative once more yields

\[
\frac{\delta \rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_3)} = \langle \hat{\rho}(\mathbf{r}_1) \hat{\rho}(\mathbf{r}_3) \rangle - \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_3) \quad \Rightarrow
\]

\[
\frac{\delta \rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_3)} = \rho^{(2)}_0(\mathbf{r}_1, \mathbf{r}_3) + \delta(\mathbf{r}_1 - \mathbf{r}_3) \rho_0(\mathbf{r}_1) - \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_3),
\]

where we have made use of eq. (53) to introduce into the right-hand side the equilibrium two-particle density \( \rho^{(2)}_0(\mathbf{r}_1, \mathbf{r}_3) \) of the system.

Equation (103) above helps us prove a very important identity, namely a generalization of the Ornstein-Zernike relation, eq. (59), to inhomogeneous systems. For that purpose, we now consider the minimization principle, eq. (88), which, together with eqs. (89), (91) and (92), takes the form

\[
u(\mathbf{r}) = \ln \left[ \rho_0(\mathbf{r}) \Lambda^3 \right] - c^{(1)}(\mathbf{r}; [\rho_0]).
\]

From eq. (104) and the hierarchy of direct correlation functions, eq. (92), it follows that:

\[
\frac{\delta \rho_0(\mathbf{r}_3)}{\delta \rho_0(\mathbf{r}_2)} = \frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{\rho_0(\mathbf{r}_2)} - c^{(2)}(\mathbf{r}_2, \mathbf{r}_3; [\rho_0]).
\]

Considering now the trivial identity

\[
\frac{\delta \rho_0(\mathbf{r}_1)}{\delta \rho_0(\mathbf{r}_2)} = \int d^3r_3 \frac{\delta \rho_0(\mathbf{r}_1)}{\delta u(\mathbf{r}_3)} \frac{\delta u(\mathbf{r}_3)}{\delta \rho_0(\mathbf{r}_2)} = \delta(\mathbf{r}_1 - \mathbf{r}_2),
\]

and introducing into the right-hand side the expressions from eqs. (103) and (105) we obtain, after some straightforward algebra, the equation:

\[
\rho^{(2)}_0(\mathbf{r}_1, \mathbf{r}_2) - \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) = \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) c^{(2)}(\mathbf{r}_1, \mathbf{r}_2; [\rho_0])
\]

\[
+ \rho_0(\mathbf{r}_2) \int d^3r_3 \left[ \rho^{(2)}_0(\mathbf{r}_1, \mathbf{r}_3) - \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_3) \right]
\]

\[
\times c^{(2)}(\mathbf{r}_2, \mathbf{r}_3; [\rho_0]),
\]

which is the generalized Ornstein-Zernike relation for inhomogeneous system. Indeed, going now to a homogeneous system of average density \( \rho \) and taking into account that now \( \rho^{(2)}_0(\mathbf{x}, \mathbf{y}) = \rho^2 g(|\mathbf{x} - \mathbf{y}|) \), \( g(|\mathbf{x} - \mathbf{y}|) = h(|\mathbf{x} - \mathbf{y}|) + 1 \), and \( c^{(2)}(\mathbf{x}, \mathbf{y}; [\rho_0]) = c(|\mathbf{x} - \mathbf{y}|) \) with the uniform direct correlation function \( c(|\mathbf{x} - \mathbf{y}|) \), it can easily be verified that
eq. (107) above reduces to eq. (59) that was introduced earlier in the context of uniform fluids.

We can now take advantage of the powerful DFT-formalism to also derive closure relations for the calculation of the pair structure of uniform fluids, see sect. 4. To this end, we first point out that for the case in which the density is a uniform constant \( \rho \), the first-order direct correlation function \( c_1(\mathbf{r}, \rho) \) becomes a density-dependent constant, which is directly related to the chemical potential of the system. This follows directly from the minimization principle or, equivalently, from eq. (104) which in the case of a vanishing external potential reads as

\[
\beta \mu = \ln(\rho \Lambda^3) - c_1(\rho),
\]

which establishes \(-k_B T c_1(\rho)\) to be equal to the excess chemical potential of the uniform fluid.

Consider now a uniform fluid of density \( \rho \), which is perturbed by a single particle of the same kind as all the rest of it, the said particle being kept fixed at the origin. Accordingly, we obtain a nonuniform fluid under the influence of an external potential \( V_{\text{ext}}(\mathbf{r}) = v(\mathbf{r}) \), where \( v(\mathbf{r}) \) is the interaction potential. According to the famous Percus identity [54], and in agreement also with the definition of the pair correlation function, the resulting inhomogeneous equilibrium density \( \rho_0(\mathbf{r}) \) is related to \( \rho \) and \( g(\mathbf{r}) \) via

\[
\rho_0(\mathbf{r}) = \rho g(\mathbf{r}).
\]

To calculate \( \rho(\mathbf{r}) \) under these conditions, we can apply the Taylor expansion of the free energy, eq. (93), by expanding around the uniform fluid density \( \rho \) and truncating the expansion to second order. This is a reasonable approximation, since the disturbance caused by the particle clamped at the origin is small. Thus, we write

\[
F[\rho] = k_B T \int d^3 r_1 \rho(\mathbf{r}_1) \left\{ \ln \left[ \rho(\mathbf{r}_1) \Lambda^3 \right] - 1 \right\} + F_{\text{ex}}(\rho) - k_B T c_1(\rho) \int d^3 r_1 [\rho(\mathbf{r}_1) - \rho] - \frac{1}{2} k_B T \int\int d^3 r_1 d^3 r_2 c(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho(\mathbf{r}_1) - \rho][\rho(\mathbf{r}_2) - \rho].
\]

The minimum principle, eq. (88), yields, in conjunction with eq. (110) above the equation for the equilibrium profile:

\[
\ln \left[ \rho_0(\mathbf{r}) \Lambda^3 \right] - c_1(\rho) - \int d^3 r' c(|\mathbf{r} - \mathbf{r}'|)[\rho_0(\mathbf{r}') - \rho] = \beta \mu - \beta v(\mathbf{r}),
\]

which, taking into account eqs. (108) and (109), reduces to

\[
\ln g(\mathbf{r}) - \rho \int d^3 r' c(|\mathbf{r} - \mathbf{r}'|)[g(\mathbf{r}') - 1] = -\beta v(\mathbf{r}).
\]

Together with the Ornstein-Zernike relation, eq. (59), the last equation yields the hypernetted chain closure, eq. (64).
5.3. Accurate density functionals for soft potentials. – A great deal of effort has been devoted in the last thirty years, in order to construct approximate functionals \( F_{\text{ex}}[\rho] \), at least for some model interaction potentials that can serve as a reference for more realistic ones. The pioneering work on the construction of approximate functionals is due to Ramakrishnan and Yussouff (RY) \[55\], who proposed a functional Taylor expansion of \( F_{\text{ex}}[\rho] \) around the uniform fluid, truncated at the second order. The decisive merit of the RY-theory is its generality: it can be applied to any interacting system and the functional that ensues is generic in form, with the input dcf of the uniform fluid carrying the signature of the interaction potential. Improvements to the RY-approach were developed, and mostly applied to the hard-sphere system and its freezing transition. These come under the generic name of weighted-density approximations, for a review see ref. \[56\]. A prominent example of a weighted density functional is the geometry-based fundamental-measure theory of Rosenfeld \[57\] and its subsequent extensions and generalizations to more complex systems \[58\]. There exists no reliable geometry-based, Rosenfeld-type functional for soft potentials, however, because the notion of a geometric shape is not well defined for a soft, deformable object.

On the opposite extreme of the hard-sphere interaction potential lies the family of the ultrasoft interaction potentials \( v(r) \). The latter can be generally defined through the property of integrability, which in three dimensions takes the form

\[
\int_0^{\infty} r^2 v(r) dr < \infty.
\]

Equation (113) above is, evidently, not satisfied by the hard-sphere interaction and by the whole family of steeply diverging inverse-power law potentials, \( v(r) = (\sigma/r)^m \). However, the Yukawa interaction, \( v(r) = \epsilon \exp(-\lambda r)/(\lambda r) \), the Gaussian-like interactions between polymer coils \[59\], polyelectrolytes \[60\], and dendrimers in the center-of-mass representation \[61-63\], the interaction potentials between star polymers \[20\] and polymer chains in the midpoint representation \[64\], as well as the effective interactions between microgels \[65, 66\] and polyelectrolyte stars \[67, 68\] do belong to the class of ultrasoft potentials.

It has been shown \[69-75\] that for ultrasoft potentials a very simple and accurate functional for the excess free energy is provided by the so-called mean-field approximation (MFA) or random-phase approximation (RPA), namely

\[
F_{\text{ex}}[\rho] = \frac{1}{2} \int d^3x d^3y \rho(x) \rho(y) v(|x - y|).
\]

The physical motivation behind eq. (115) above lies in the absence of significant short-range correlations between the particles, caused by the ultrasoft divergence of \( v(r) \) as \( r \to 0 \). Accordingly, one approximates the excess free energy of the system just by the interaction energy between the particles. It should be noted that eq. (115) above becomes increasingly accurate as the density of the system grows, because in this case each particle interacts with an increasing number of other ones, thus justifying the mean-field character of the approximation. An implication of eq. (115), in conjunction with eq. (92), is the random-phase approximation for the direct correlation function \( c(r) \), namely

\[
c(r) = -\beta v(r).
\]
The RPA functional can be easily generalized to a ν-component mixture of particles, mutually interacting through the ultrasoft pair potentials \( v_{ij}(r) \) with \( v_{ij}(r) = v_{ji}(r) \), \( i,j = 1,2,\ldots,\nu \). The free energy functional \( F \) depends then on the \( \nu \) density profiles \( \rho_1(\mathbf{r}), \rho_2(\mathbf{r}), \ldots, \rho_{\nu}(\mathbf{r}) \) and takes the form [72]

\[
F[\{\rho_i\}] = k_B T \sum_{i=1}^{\nu} \int d^3r \rho_i(\mathbf{r}) \left\{ \ln [\rho_i(\mathbf{r})\Lambda_i^3] - 1 \right\} + \frac{1}{2} \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} \int d^3x d^3y \rho_i(\mathbf{x}) \rho_j(\mathbf{y}) v_{ij}(|\mathbf{x} - \mathbf{y}|),
\]

with the thermal de Broglie wavelength \( \Lambda_i \) or species \( i \). The variational grand potential for a mixture is simply given by (cf. eq. (85)):

\[
\tilde{\Omega}[\{\rho_i\}, \{V_{\text{ext}}^{(i)}\}] = F[\{\rho_i\}] + \sum_{i=1}^{\nu} \int d^3r \left[ V_{\text{ext}}^{(i)}(\mathbf{r}) - \mu_i \right] \rho_i(\mathbf{r}),
\]

where \( \mu_i \) is the chemical potential of species \( i \) and \( V_{\text{ext}}^{(i)}(\mathbf{r}) \) the external potential acting on it. The equilibrium density profiles are then determined by the simultaneous solution of the \( \nu \) coupled equations (cf. eq. (87)):

\[
\frac{\delta \tilde{\Omega}[\{\rho_i\}, \{V_{\text{ext}}^{(i)}\}]}{\delta \rho_i(\mathbf{r})} = 0, \quad \text{for} \quad i = 1,2,\ldots,\nu.
\]

5.4. Fluid-fluid interfaces. - Here we proceed to a specific application of DFT for an ultrasoft mixture, to provide a taste of the power and elegance of DFT-methods and of the RPA-functional in particular. Archer et al. [74] considered a binary mixture of athermal polymer chains. Taking the chains’ midpoints as effective coordinates, they reduced the problem to a binary mixture of soft particles interacting by means of the pair potentials:

\[
\beta v_{ij}(r) = \frac{5}{18} r^{3/2} \left\{ \begin{array}{ll}
- \ln \left( \frac{r}{\sigma_{ij}} \right) + \frac{1}{2 r_{ij}^3 \sigma_{ij}^2}, & \text{for} \quad r \leq \tau_{ij}, \\
\frac{1}{2 r_{ij}^3 \sigma_{ij}^2} \exp \left[ - \frac{r_{ij}^2}{2 \sigma_{ij}^2} \left( r^2 - \sigma_{ij}^2 \right) \right], & \text{for} \quad r > \tau_{ij},
\end{array} \right.
\]

where \( \sigma_{ii} \) is the corona diameter and \( \tau_{ii} \) is a parameter of order \( 1/R_{ii} \), with \( R_{ii} \) being the radius of gyration of species \( i \) [64] and \( \beta = 1/k_B T \). Here, \( f \) represents, in general, the arm number of star polymers and we focus on \( f = 2 \), so that the star polymer pair potential (119) is equivalent to the effective potential between the central monomers on a polymer chain. For the “cross-parameters” \( \sigma_{12} \) and \( \tau_{12} \), the “mixing rules” employed read as

\[
\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22})
\]

and

\[
\frac{1}{\tau_{12}^2} = \frac{1}{2} \left( \frac{1}{\tau_{11}^2} + \frac{1}{\tau_{22}^2} \right).
\]
Fig. 6. – The RPA-spinodal and binodal lines for the star-polymer mixture (dotted and solid lines) along with the HNC-binodal (dashed line). \(x\) is the concentration of species 2, the smaller component. The straight segments denote HNC-tie-lines between coexisting fluid phases whose coordinates are given by the closed circles at their ends. (From ref. [74]).

In what follows, we will discuss results obtained using the interactions of eq. (119) and the RPA-density functional of eq. (116) for the case \(\sigma_{22}/\sigma_{11} = 2^{−3/5}\) that corresponds to polymer mixtures of polymerization ratio \(N_1 : N_2 = 2 : 1\), a standard test case\(^{(16)}\).

Setting \(\rho_i(r) = \rho_i, i = 1, 2\) in eq. (116) immediately yields the Helmholtz free energy of the mixture, \(F = N f(\rho_1, \rho_2)\). A standard Legendre transformation leads then to the Gibbs free energy per particle, \(g(x, P)\), where \(x = \rho_2/(\rho_1 + \rho_2)\) is the concentration of species 2 and \(P\) the pressure. Stable, homogeneous mixtures are characterized by \(g''(x) \geq 0\) for all \(x\)-values. The occurrence of concave parts in \(g(x, P)\) signals a demixing transition with the coordinates of the coexisting phases given by the common tangent construction. The resulting phase diagram for the system is shown in fig. 6 above, where it can be seen that the system shows a demixing transition at high densities.

The full power of DFT further develops when looking into more subtle, structural quantities in the bulk or at interfaces. Indeed, the form of the RPA-functional, implying \(c_{ij}(r) = -\beta v_{ij}(r)\) allows for an explicit calculation of the complex poles of the structure factors of the two components. These, in turn, deliver information about the decay of the correlation functions \(g_{ij}(r)\) in the bulk system for large \(r\)-values. In fig. 7 we show the phase diagram together with the so-called Fisher-Widom lines that separate two distinct regions: the first, which is surrounding the consolute point of the mixture, is characterized by a monotonic decay of the correlation functions at large \(r\)-values, whereas the second by an oscillatory one. The second region is itself subdivided into two domains, each with

\(^{(16)}\) This arises from the scaling law \(R \sim N^\nu\) connecting the spatial extent \(R\) of a self-avoiding polymer with its degree of polymerization \(N\), using the value \(\nu = 3/5\) of the Flory exponent.
Fig. 7. – The RPA-phase diagram along with the Fisher-Widom line (light solid line) and the Lifshitz lines of the various structure factors. The left hand branch of the FW line lies close to the Lifshitz line for $S_{11}(k)$ (short dashed line) while the right hand branch lies close to the Lifshitz line for $S_{22}(k)$ (long dashed line). The dash-dotted line is the Lifshitz line for the concentration structure factor $S_{cc}(k) = (1 - x)^2 S_{11}(k) + x^2 S_{22}(k) - 2x(1 - x) S_{12}(k)$. The points A-G on the right-hand branch of the binodal are located at total densities $\rho \sigma^3 = 8, 10, 12, 14, 16, 18$ and 20, at which the free interface density profiles will be calculated in what follows. The gray lines are RPA-isobars through the points A-G and their intersections with the left-hand branch of the binodal yield the state points coexisting with A-G. The open circle denotes the RPA-consolute point. (From ref. [74].)

different decay- and oscillation lengths. The Lifshitz lines drawn in fig. 7 denote the locus of points on which the structure factors at $q = 0$ cross from having a local minimum to having a local maximum there.

The presence of two coexisting phases along points on the binodal implies that a free interface between the two will form when the chemical potentials $\mu_i, i = 1, 2$ of the two phases attain appropriate values. DFT allows for a calculation of the density profiles across this interface. Let I and II be the two coexisting phases at the points $(\rho^I, x^I)$ and $(\rho^II, x^II)$. Accordingly, the two components will have bulk densities $\rho^\alpha_i = (1 - x^\alpha) \rho^\alpha$ and $\rho^\alpha_2 = x^\alpha \rho^\alpha , \alpha = I, II$, respectively. The density profiles across the free interface can be calculated by eq. (118) with $V_{\text{ext}}^{(i)}(r) = 0$, under the boundary conditions:

\begin{align}
\lim_{z \to -\infty} \rho_1(z) &= \rho^I_1, \\
\lim_{z \to -\infty} \rho_2(z) &= \rho^I_2, \\
\lim_{z \to +\infty} \rho_1(z) &= \rho^II_1, \\
\lim_{z \to +\infty} \rho_2(z) &= \rho^II_2,
\end{align}

i.e., forcing bulk phase I at $z \to -\infty$ and bulk phase II at $z \to \infty$. 
Fig. 8. – The fluid-fluid interface density profiles of species 1, calculated at states A-G in the phase diagram, see fig. 7. State A lies near the critical point and state G, for which the interface is much sharper, far away from the critical point. These states correspond to total bulk densities $\rho_\sigma^3_1 = 8, 10, 12, 14, 16, 18$ and $20$ in the phase rich in species 2. (From ref. [74].)

Defining the shifted chemical potentials $\bar{\mu}_{1,2} \equiv \mu_{1,2} - 3\ln(\Lambda_{1,2}/\sigma_{11})$, the explicit equations to be self-consistently solved for the density profiles, under the above-mentioned boundary conditions, read as:

\begin{align}
(126) & \quad k_B T \ln \left[ \rho_1(z)\sigma_{11}^3 \right] + \int d^3r' \left[ \rho_1(z')v_{11}(|r' - r|) + \rho_2(z')v_{12}(|r' - r|) \right] = \bar{\mu}_1, \\
(127) & \quad k_B T \ln \left[ \rho_2(z)\sigma_{11}^3 \right] + \int d^3r' \left[ \rho_1(z')v_{12}(|r' - r|) + \rho_2(z')v_{22}(|r' - r|) \right] = \bar{\mu}_2,
\end{align}

where, in Cartesian coordinates, $r = (x, y, z)$, $r' = (x', y', z')$ and the profiles depend only in the third component of the position vector. The imposition of the boundary conditions forces then the occurrence of an interface. In figs. 8 and 9 we show the density profiles for species 1 and 2 and for a number of different coexistence points, denoted A-G in fig. 7. It can be seen that in the neighborhood of the consolute point the profiles are smooth, whereas as one moves away from it, density oscillations develop. The latter are most strongly visible for species 1 and they are present at the interface between the species 1-poor and the species 1-rich phase, on the species 1-rich side, see fig. 8. The density oscillations for species 2 are much weaker and can be seen in the insets of fig. 9. On the basis of the density profiles of the free fluid-fluid interface, the surface tension between the coexisting phases, $\gamma$, can be calculated, as

\begin{equation}
(128) \quad \gamma = \int_{-\infty}^{\infty} dz [P + \omega(z)],
\end{equation}
where $P$ is the pressure at coexistence and $\omega(z)$ is the grand potential density obtained from eqs. (116) and (117) with the inhomogeneous density profiles of the free interface (17) $\rho_i(z)$ and $V_{\text{ext}}^{(i)}(r) = 0$, $i = 1, 2$.

5.5. *Wetting*. Another way to impose inhomogeneous density profiles in a fluid is to bring it in contact with a planar wall (18). When a phase-separating mixture is forced to approach its binodal line in the presence of a planar wall, a variety of wetting phenomena can take place. In particular, the coexisting phase lying at the opposite side of the binodal can form a macroscopically thick layer on the wall before the binodal is reached. In this case, one says that the phase wets the wall and the layer thickness diverges on the binodal (complete wetting). The wetting scenarios, which form indeed a distinct class of surface phase transitions, depend sensitively on the nature of interparticle and particle-wall interactions [76].

For the binary polymer system at hand, a hard wall can be placed at $z = 0$. The effective potentials of the central monomers of the chain with the walls, $V_{\text{ext}}^{(i)}(z)$, have been calculated by Jusufi et al. [64]. Whereas $V_{\text{ext}}^{(i)}(z)$ diverge for $z < 0$, for $z \geq 0$ they

---

(17) For homogeneous density profiles, it holds $\Omega = -PV$ and the integrand of eq. (128) vanishes.

(18) Of course, there are infinitely many ways to bring a fluid under geometric confinement by using spherical, cylindrical, arbitrarily shaped or topographically patterned walls. Here we limit ourselves to wetting on a single, planar wall.
Fig. 10. – The phase diagram obtained from the RPA (as in figs. 6 and 7). The two filled circles show the location of the prewetting line. The upper point on the binodal is the wetting point where the prewetting line meets the binodal tangentially and the lower point is the consolute point at the end of the prewetting line. The inset shows the prewetting line at greater magnification. The horizontal path labeled A is that along which the density profiles in fig. 11 are calculated. (From ref. [74].)

take the form

\[ \beta V_{\text{ext}}^{(i)}(z) = \Theta \begin{cases} -\ln \left( \frac{2z}{\sigma_{ii}} \right) - \frac{1}{4 \sigma_{ii}^2} - 1 \left( \psi_i - \frac{1}{2} \right) + \zeta_i, & \text{for } 0 \leq z \leq \sigma_{ii}/2, \\
\zeta_i \text{erfc}(\kappa_i z)/\text{erfc}(\kappa_i \sigma_{ii}/2), & \text{for } z > \sigma_{ii}/2, \end{cases} \]  

where \( \text{erfc}(x) = 1 - \text{erf}(x) \) is the complementary error function, \( \psi_i = (1 + \kappa_i^2 \sigma_{ii}^2/2)^{-1} \) is a parameter chosen to guarantee the continuity of the local osmotic pressure in the interior of the polymer, and

\[ \zeta_i = \frac{2\sqrt{\pi} \psi_i}{\kappa_i \sigma_{ii}} \text{erfc} \left( \frac{\kappa_i \sigma_{ii}}{2} \right) \exp \left( \frac{\kappa_i^2 \sigma_{ii}^2}{4} \right). \]  

The parameters \( \kappa_i \) and \( \Theta \) have the values \( \kappa_i = 1.16/\sigma_{ii} \) and \( \Theta = 1.30 [64] \).

The inhomogeneous density profiles imposed by the presence of the wall can be now calculated by solving the equations:

\[ k_B T \ln \left[ \rho_1(z) \sigma_{11}^3 \right] + \int \text{d}^3r' [\rho_1(z')v_{11}(|r' - r|) + \rho_2(z')v_{12}(|r' - r|)] = u_1(z), \]  

\[ k_B T \ln \left[ \rho_2(z) \sigma_{11}^3 \right] + \int \text{d}^3r' [\rho_1(z')v_{11}(|r' - r|) + \rho_2(z')v_{22}(|r' - r|)] = u_2(z), \]
Fig. 11. – The density profiles of species 1, the larger particles, adsorbed at a wall described by the potential (129), calculated along a path of constant total density, \( \rho_1^3 = 7.0 \), i.e., path A in fig. 10. From left to right the profiles refer to \( x = 0.9, 0.95, 0.9, 0.88, 0.879, 0.878955, 0.878951 \) and 0.8789505, where \( x \) is the concentration of species 2 and \( x_{\text{coex}} = 0.87895019 \). The thickness of the adsorbed film increases continuously as \( x \to x_{\text{coex}} \), indicating complete wetting. The inset shows the density profiles of species 2 for the same values of \( x \). Note that species 2 is depleted from the region adjoining the wall. (From ref. [74].)

where \( u_i(z) \equiv \bar{\mu}_i - V_i(\text{ext})(z) \). Consider, then, moving along a path of constant total density \( \rho \) and decreasing \( x \), such as path A in fig. 10. The resulting density profiles are shown in fig. 11. It can be seen that, as the binodal is approached, a thick film of a species 1-rich phase wets the wall, which diverges on the binodal: the system shows complete wetting.

The wetting behavior can be quantitatively analyzed by using the density profiles from DFT and looking at the adsorption of species 1 on the wall, defined as

\[
\Gamma_1 = \int_0^\infty dz \left[ \rho_1(z) - \rho_1 \right],
\]

where \( \rho_1 = \rho_1(z \to \infty) \), i.e., the density of species 1 in the bulk.

In fig. 12 we show adsorption curves at various different total densities \( \rho \), varying the concentration \( x \). It can be seen that there is a jump in the adsorption curves, which occurs before the coexistence curve is reached (at \( x = x_{\text{coex}} = 0 \)). In other words, there is a line of first-order wetting transitions traced by the points on the phase diagram for which the adsorption has a discontinuity. This so-called prewetting line is a short segment that is shown in the inset of fig. 10. The lower end of the prewetting line, marked by the lower thick circle in the inset of fig. 10, is the wetting critical point. This is a true surface critical point, similar in nature to the bulk critical points known from the theory of classical fluids. The upper end of the prewetting line, marked by the upper thick circle
Fig. 12. – Plots of the adsorption of species 1, $\Gamma_1$, versus the logarithm of the deviation from bulk coexistence $\ln(x - x_{\text{coex}})$, at constant total density $\rho$, for paths intersecting ((a)-(c)) and passing just below (supercritical) (d) the prewetting line. The jumps in (a)-(c) indicate the first-order prewetting transition. (From ref. [74].)

in the inset of fig. 10, is the so-called wetting point and lies on the binodal. For paths of constant $\rho$ lying higher than the location of the wetting, the adsorption of species 1 on the wall always remains finite, all the way to the binodal. For paths running below the wetting point, the adsorption always diverges on the binodal and a macroscopic, thick film of species 1 forms on the wall. If the path runs above the wetting critical point, intersecting the prewetting line, then there is an adsorption jump on the latter. If not, i.e., if the path runs below the wetting critical point, then the adsorption $\Gamma_1$ grows smoothly as the binodal is approached and diverges right on it.

The above discussion demonstrates both the rich variety of surface-induced phase transitions and wetting behavior and the power of DFT to analyze these. The wetting scenarios can be modified at wish, leading to a disappearance of the prewetting line or to its displacement on the opposite side of the binodal, by suitable modifications of the wall potentials $V_{\text{ext}}^{(i)}(z)$.

5’6. Crystallization. – The density inhomogeneities discussed in the preceding sections pale in comparison with the ones arising in a crystalline solid. In this case, whereas the one-particle density is extremely high in the neighborhood of the lattice sites, the strong localization of the particles around the latter causes the density at the interstitial regions to be extremely low. The peak value of the density on the lattice site, compared to its value in the mid-point between the nearest neighbors can differ by as many as 50 orders of magnitude! It is without a doubt a most challenging task for DFT to be able to make quantitative predictions on the structure and stability of crystalline solids, which spontaneously form under the appropriate thermodynamic conditions (density and temperature).
and without the presence of external potentials. The prototype system for crystallization is the hard-sphere fluid, for which a number of functionals that predict crystallization have been developed [56]. Hard spheres freeze into a face-centered cubic (fcc) lattice at packing fraction $\eta \approx 0.49$ [77-82]. Coulomb systems, and in particular the one-component plasma (OCP) are another common example of systems for which density functionals leading to freezing have been developed [83]. Contrary to hard spheres, the OCP freezes into a body-centered cubic (bcc) lattice at sufficiently strong Coulomb couplings.

To demonstrate the power of DFT and to stay within the realm of the RPA-functional for ultrasoft potentials, we discuss here a recent study on the freezing transition of Yukawa systems [84]. These consist of point particles that interact by means of the purely repulsive potential:

$$v(r) = \frac{\epsilon \exp(-\lambda r)}{\lambda r},$$

where $\epsilon > 0$ is an energy parameter and $\lambda$ is the inverse decay length: for large values of $\lambda$ the potential is strongly screened. Equation (134) describes the screened Coulomb interaction of pointlike charged entities. Evidently, the potential of eq. (134) fulfills the condition (113).

The one-particle density $\rho(\mathbf{r})$ of the crystals possesses evidently the discrete translational and point symmetries dictated by the underlying Bravais lattice; the latter is spanned by the Bravais lattice vectors set $\{\mathbf{R}_i\}$. The localization of the particles around crystal sites is adequately parametrized by modeling the density by a sum of normalized Gaussian profiles centered around the lattice sites, viz.

$$\rho(\mathbf{R}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\mathbf{R}_i} \exp\left[-\alpha (\mathbf{r} - \mathbf{R}_i)^2\right].$$

The parameter $\alpha$ expresses the degree of localization of the “Gaussian orbitals” around the lattice sites: whereas for $\alpha = 0$ a uniform profile results, for $\alpha \to \infty$ the Gaussians reduce to Dirac-delta peaks.

With the modeling of eq. (135), the free energy becomes, at given average density and temperature and for any given Bravais lattice, a function of $\alpha$. The latter is used as a variational parameter and the minimum of $F[\rho]$ at fixed average density is sought. For the case of nonoverlapping Gaussians, the ideal free energy of eq. (89) can be extremely well approximated by the analytical expression

$$F_{\text{id}}(\alpha) = N k_B T \left[ \frac{3}{2} \ln \left( \frac{\alpha A^2}{\pi} \right) - \frac{5}{2} \right].$$

The RPA-excess free energy functional of eq. (114) has to be slightly modified for the case at hand, in the sense that all terms with $\mathbf{R}_i = \mathbf{R}_j$ in the density products must be excluded to avoid self-interaction terms. It then takes the form

$$F_{\text{ex}}(\alpha) = \frac{1}{2} \sum_{i \neq j} \frac{1}{(2\pi)^3} \int d^3k \exp(i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)) \hat{v}(k) \exp[-k^2/(2\alpha)],$$

where $\mathbf{R}_i = \mathbf{R}_i - \mathbf{R}_j$, and $\hat{v}(k)$ is the Fourier transform of the pair potential. Whereas the ideal term, eq. (136), grows with $\alpha$ and thus favors delocalization, the excess term,
eq. (137), attains its minimum for $\alpha \to \infty$ and favors localization\(^{(10)}\). The competition between the two gives rise to a stable minimum at $\alpha \neq 0$, corresponding to a mechanically stable fluid\(^{(20)}\).

Given the free energy of the crystals from DFT, one can combine it with the free energy of the fluid, calculated, e.g., by the methods described in sect. 4, to draw the phase diagram of the system. A simpler (but less accurate) way is to determine from DFT the so-called Lindemann ratio $L$: this is the ratio of the root-mean-square of the displacement of a particle from its lattice site over the nearest-neighbor distance and directly follows from the value of the localization parameter $\alpha$. Empirically, crystals melt when $L$ exceeds 10%. In this way, the phase diagram of fig. 13 can be obtained for the Yukawa system. Clearly, DFT can predict freezing as well as the polymorphic fcc $\to$ bcc structural phase transformation that takes place as the density grows.

5.7. Cluster crystals. – As a final example of the resounding success that DFT has had in predicting accurately a novel type of crystallization, we present here a summary of recent results on the class of cluster crystals. These are periodically modulated fluids but, contrary to usual crystals, the lattice sites are occupied by multiple particles, $n_c \geq 1$, so that the number of particles, $N$ and the number of sites of the crystal, $N_c$, are related

\(^{(10)}\) It can be easily seen that for $\alpha \to \infty$ this term reduces to \((1/2) \sum_{i \neq j} \psi(|R_i - R_j|)\), the lattice sum of the crystal that corresponds to the internal energy of $N$ particles lying motionless on the lattice sites.

\(^{(20)}\) Usually, this minimum occurs at a value of $\alpha$ large enough to justify the approximations involved in deriving eq. (136).
by the proportionality relation:

\begin{equation}
N = n_c N_s.
\end{equation}

Though multiple occupancy appears as physically impossible at first sight, it is perfectly reasonable for effective particles, such as the centers of mass of suitable macromolecules [85,86], for which the effective interaction \( V_{\text{eff}}(r) \) remains finite even at \( r = 0 \). It has been shown [27,70,87] that a necessary and sufficient condition for the emergence of cluster crystals is that the Fourier transform of \( V_{\text{eff}}(r) \), call it \( \tilde{V}_{\text{eff}}(k) \), has negative Fourier components – these form the so-called \( Q^k \)-class of interaction potentials [70].

This arises from the fact that for such systems eqs. (114) and (115) hold. Accordingly, and making use of the Ornstein-Zernike relation, the structure factor \( S(k) \) of a fluid of density \( \rho \) and temperature \( k_BT = \beta^{-1} \), is given by

\begin{equation}
S(k) = \frac{1}{1 + \beta \rho \tilde{V}_{\text{eff}}(k)}.
\end{equation}

With \( k_* \) denoting the wave number for which \( V_{\text{eff}}(k) \) attains its most negative value, \(-|\tilde{V}_{\text{eff}}(k_*)|\), it directly follows from eq. (139) above that \( S(k) \) develops a pole along the whole line

\begin{equation}
k_BT = |\tilde{V}_{\text{eff}}(k_*)|/\rho,
\end{equation}

which is known as the \( \lambda \)-line of the system. Concomitantly, the fluid is unstable towards periodic modulations with wave number \( k_* \). The resulting crystals are dominated by this instability at all densities, so that the resulting lattice constant \( a \) is density-independent and the occupancy \( n_c \) is proportional to the density [87]. In fig. 14 we show a snapshot of such a crystal from computer simulations, in which the effective “GEM4” interaction between the particles has the form [88, 89]:

\begin{equation}
V_{\text{eff}}(r) = \varepsilon \exp\{-r/\sigma\}^4,
\end{equation}

with the energy scale \( \varepsilon \) and the length scale \( \sigma \).

The density functional approach to the problem of freezing of cluster crystals proceeds in the standard way, by expressing the free energy of the system as \( F[\rho] = F[\rho] + F_{\text{ex}}[\rho] \), the former being given by eq. (89) and the latter by eq. (114), which is suitable and very accurate for soft potentials. The essential difference with the crystallization of single-occupancy crystals lies in the parametrization of the periodic one-particle density of the solid, which now takes the form (cf. eq. (135)):

\begin{equation}
\rho(\mathbf{r}) = n_c \left( \frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}_j} \exp \left[ -\alpha (\mathbf{r} - \mathbf{R}_j)^2 \right],
\end{equation}

allowing for multiple occupancy \( n_c \geq 1 \), which is now an additional variational parameter of the free energy, on top of the localization parameter \( \alpha \). The details of the DFT approach to cluster crystals can be found in ref. [87]; here, we restrict ourselves to a summary of the key features and results of this approach.
Introducing the Fourier transform of the periodic density, which is a discrete sum over reciprocal lattice vectors $\{K\}$ of the lattice:

\begin{equation}
\rho(r) = \rho \sum_K \exp\{-K^2/(4\alpha)\} e^{iK \cdot r}, \tag{143}
\end{equation}

allows us to express the excess free energy of the crystal in the form

\begin{equation}
F_{ex}(\rho, T; \alpha, n_c) = \frac{N \rho}{2} \sum_K \tilde{V}_{eff}(K) \exp\{-K^2/(2\alpha)\}. \tag{144}
\end{equation}

Here, the crystal’s average density $\rho = N/V$ as well as the temperature $T$ are fixed thermodynamic parameters, while $\alpha$ and $n_c$ are variational quantities with respect to which the free energy must be minimized. The fact that $n_c$ does not appear explicitly on the right-hand side of eq. (144) is somewhat deceiving: this quantity does depend on cluster occupancy, since the latter affects the lattice constant of the crystal and hence the values of the RLV’S. Considerable simplification, which leads to analytical and universal results for all interaction potentials $V_{eff}(r)$ in the $Q^\pm$-class can be achieved by keeping only the leading term of the shortest nonvanishing RLV’s in the sum at the right-hand side of eq. (144). Within this approximation, the freezing line on the density-temperature plane is given by the equation

\begin{equation}
k_B T = 16\pi^2 \gamma_T |\tilde{V}_{eff}(k_*)| \exp\{-4\pi^2 \gamma_T\} \rho, \tag{145}
\end{equation}

where $\gamma_T = 0.018$ is the smaller of the two solutions of the implicit equation:

\begin{equation}
\gamma^{-1} = -4\pi^2 \left[\ln(\gamma\pi) + 1 + \frac{2\ln 2}{3}\right]. \tag{146}
\end{equation}
The phase diagram of the particular model of eq. (141) is shown in fig. 15, where the approximate freezing line of eq. (145) is compared with the result of the full DFT calculation. The Lindemann $L$ ratio along the whole freezing line as well as the maximum of the peak of the structure factor $S_{\text{max}}$ of the fluid at freezing attain universal values for all $Q^\pm$-potentials, in particular:

$$L = 0.189$$

and

$$S_{\text{max}} = 3.542.$$  

Finally, the cluster occupancy $n_c$ has a linear dependence on density:

$$n_c = \frac{8\sqrt{2}\pi^3}{K_2^2} \rho.$$  

The accuracy of all predictions of the DFT approach has been spectacularly confirmed in comparison with computer simulations [90,91]. Among the novel properties of the cluster crystals, most prominent are their diffusive character, caused by hopping of particles among lattice sites [92,93]; the existence of a cascade of isostructural phase transitions at low temperatures [94,95] and their associated self-similar phonon spectra [94]; as well as their highly unusual response to shear [96] and pressure flows [97], associated with thixotropic behavior and flow quantization. Microscopic realizations of cluster crystals have been proposed [86] and confirmed by monomer-resolved simulations [98]. Finally,
we emphasize that the scenarios of cluster crystallization put forward above remain essentially unaffected if a small hard core is added at the center of the soft particles [99], and the effects of an increasingly large core have been analyzed in the same context in the recent work of Ziherl and Kamien [100]. An alternative, geometric point of view of soft crystals in general has been put forward about a decade ago, again by Ziherl and Kamien [101, 102].

6. – Density functional theory for polymer chains

In this section, we generalize the principles of DFT to polymeric systems, i.e. solutions of (linear) polymer chains. The principles of polymer DFT have been pioneered by Yethiraj and Woodward [103], and a comprehensive review on the same has appeared relatively recently [104]. Representative applications of polymer DFT to confined systems, polymer brushes and even polyelectrolytes can be found in refs. [105-108].

We consider in what follows a solution that contains \( N \) polymer chains, each chain carrying \( M \) sequentially connected monomers. Whereas in the preceding section the position of each particle could be fully described by a single position vector, for the case of polymer chains this is, evidently, not sufficient. The one-particle density \( \rho(r) \) of eq. (75) has to be replaced now by a generalized function of \( M \) spatial coordinates:

\[
(150) \quad \rho(r) \rightarrow \rho_M(r_1, r_2, \ldots, r_M) \equiv \rho_M(R),
\]

where we introduced as a shorthand the super-vector \( R \equiv (r_1, r_2, \ldots, r_M) \). The meaning of \( \rho_M(R) \) is the following: consider a succession of three-dimensional vectors \( r_j \), \( j = 1, 2, \ldots, M \) in space. Then, \( \rho_M(R) \) is proportional to the probability density of finding monomer 1 of some chain at position \( r_1 \) and monomer 2 of the same chain at position \( r_2 \), ..., and monomer \( M \) of the same chain at position \( r_M \), for any chain. For a uniform polymer solution this probability density is, evidently, space-independent but this changes once external fields act on the polymers.

To make the correspondence with the usual DFT complete, we need to express the quantity \( \rho_M(R) \) as an expectation value of an operator, in full analogy with eq. (74). Let the solution contain \( N \) polymer chains of \( M \) monomers each and denote with \( x_{ji} \) the position coordinate of the \( j \)-th monomer that belongs to the \( i \)-th chain. Accordingly, the indices \( j \) and \( i \) span the ranges \( j = 1, 2, \ldots, M \) and \( i = 1, 2, \ldots, N \). In agreement with the interpretation of the quantity \( \rho_M(r_1, r_2, \ldots, r_M) \) given above, we can now introduce the operator \( \hat{\rho}_M(r_1, r_2, \ldots, r_M) \) as:

\[
(151) \quad \hat{\rho}_M(r_1, r_2, \ldots, r_M) = \sum_{i=1}^{N} \prod_{j=1}^{M} \delta(r_j - x_{ji}),
\]

and define \( \rho_M(r_1, r_2, \ldots, r_M) \) as its equilibrium expectation value:

\[
(152) \quad \rho_M(r_1, r_2, \ldots, r_M) = \langle \hat{\rho}_M(r_1, r_2, \ldots, r_M) \rangle,
\]

where \( \langle \cdots \rangle \) denotes an average over the dynamical degrees of freedom \( \{x_{ji}\} \), in which each configuration is weighted according to the Boltzmann factor dictated by the Hamiltonian \( \mathcal{H}(\{x_{ji}\}) \) of the system. From eqs. (151) and (152) above the normalization of
\[ \rho_M(r_1, r_2, \ldots, r_M) \text{ in the grand canonical ensemble easily follows:} \]

\[ \int d^3r_1 \int d^3r_2 \ldots \int d^3r_M \rho_M(r_1, r_2, \ldots, r_M) = \langle N \rangle. \]  

The polymer version of DFT follows along parallel lines with the one for simple fluids sketched in sect. 5. In particular, we consider the grand canonical ensemble and fix the temperature \( T \) and the chain chemical potential \( \mu_M \), while at the same time we introduce an external potential \( \Psi_M(R) \) that acts on the monomers and introduces in the Hamiltonian a coupling \( V_{\text{ext}} \) of the form

\[ V_{\text{ext}}(\{x_{ji}\}) = \int d^3M R \Psi_M(R) \hat{\rho}_M(R). \]

In addition, being a one-body potential, \( \Psi_M(R) \) can be decomposed as

\[ \Psi_M(R) = \sum_{j=1}^M \psi(r_j). \]

Let \( \rho_0(R) \) be the equilibrium density of the polymer solution. Following the same arguments as those in sect. 5, it can be shown that the grand potential \( \Omega \) of the system is a unique functional of the equilibrium density and that it takes the form (cf. eq. (84)):

\[ \Omega[\rho_0] = F[\rho_0] + \int d^3M R \left[ \Psi_M(R) - \mu_M \right] \rho_0(R), \]

and where the intrinsic Helmholtz free energy functional \( F \) does not contain any reference to the external potential. Accordingly, and in analogy with eq. (85), we define an extended functional \( \tilde{\Omega} \) of both the density field \( \rho_M(R) \) and the external potential \( \Psi_M(R) \) as

\[ \tilde{\Omega}[\rho_M, \Psi_M] = F[\rho_M] + \int d^3M R \left[ \Psi_M(R) - \mu_M \right] \rho_M(R). \]

For a given external potential, the equilibrium density field \( \rho_0(R) \) minimizes \( \tilde{\Omega}[\rho_M, \Psi_M] \) over all fields \( \rho_M(R) \) and yields as a result the grand potential \( \Omega = \tilde{\Omega}[\rho_0, \Psi_M] \). Thus, the equilibrium density can be calculated by requiring (cf. eq. (87)):

\[ \frac{\delta \tilde{\Omega}[\rho_M, \Psi_M]}{\delta \rho_M(R)} \bigg|_{\rho_M(R)=\rho_0(R)} = 0. \]

Up to this point, there is a one-to-one correspondence to the case of monomeric liquids, which indeed trivially obtains from the above results by setting \( M = 1 \). However, for \( M > 1 \) important differences in the form of the associated functionals arise between monomeric and polymeric fluids. The intrinsic Helmholtz free energy functional can still be split into an ideal and an excess part:

\[ F[\rho_M] = F_{\text{id}}[\rho_M] + F_{\text{ex}}[\rho_M]. \]
The ideal term in eq. (159) above describing a solution of polymer chains which consist of noninteracting monomers. However, the connectivity of the chains enters as a crucial element of the problem and it modifies the form of the ideal free energy functional (cf. eq. (89)) into

\begin{equation}
F_{id}[\rho_M] = k_B T \int d^3 R \rho_M(R) \left\{ \ln \left[ \rho_M(R) \Lambda^{3M} \right] - 1 \right\} + \int d^3 R \rho_M(R) V_b(R),
\end{equation}

which includes explicitly the contribution from the bonding potential $V_b(R)$, to which we will be returning in what follows.

The excess free energy functional also carries the signature of the connectivity, on top of taking into account the non-bonded (e.g., steric, van der Waals or electrostatic) interactions between the monomers. To better elucidate the subtle issues related to the excess free energy of polymeric systems in the DFT context, let us first define a density field that is a reduced quantity with respect to the full density $\rho_M(R)$ and is defined as

\begin{equation}
\rho(r) = \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_M \sum_{j=1}^{M} \delta(r - r_j) \rho_M(r_1, r_2, \ldots, r_M).
\end{equation}

Evidently, $\rho(r)$ contains much less information than its chain counterpart, $\rho_M(R)$, since it is proportional to the probability density of finding any monomer of any chain at the spatial coordinate $r$. Accordingly, this one-particle density is normalized to the expectation value of the number of monomers in the solution, as opposed to the number of chains (cf. eq. (153)):

\begin{equation}
\int d^3 r \rho(r) = M \langle N \rangle.
\end{equation}

Without the connectivity, $F_{ex}$ would be, evidently, just a functional of $\rho(r)$, not of the full density field $\rho_M(R)$. The way that connectivity modifies this dependence has been established on the basis of work by Chandler and Pratt [109] and further elaborations by Zhou and Stell [110]. In particular, the excess free energy is given as the sum of the excess contribution from a collection of disconnected monomers and one additional term that involves the multibody-cavity correlation function [104]. Enormous simplification can be achieved, however, if one employs Wertheim’s thermodynamic perturbation theory in its lowest order approximation [111], which allows also the aforementioned contribution from the multibody-cavity correlation function to be expressed in terms of $\rho(r)$ alone [105]. Under these circumstances, we obtain a functional $F_{ex}[\rho]$, although we emphasize that this is not the same as the excess functional of a collection of disconnected monomers but it contains the Wertheim-theory corrections. The functional derivative of the excess functional with respect to $\rho_M(R)$ follows through the chain rule

\begin{equation}
\frac{\delta F_{ex}[\rho]}{\delta \rho_M(r_1, r_2, \ldots, r_M)} = \int d^3 r \frac{\delta F_{ex}[\rho]}{\delta \rho(r)} \frac{\delta \rho(r)}{\delta \rho_M(r_1, r_2, \ldots, r_M)}.
\end{equation}
Using eq. (161), it is straightforward to show that eq. (163) yields the result:

\[
\frac{\delta F_{\text{ex}}[\rho]}{\delta \rho_M(r_1, r_2, \ldots, r_M)} = \sum_{j=1}^{M} \frac{\delta F_{\text{ex}}[\rho]}{\delta \rho(r_j)}.
\]

Combining now eqs. (155), (157), (159), (160) and (164), together with the equilibrium condition, eq. (158), we obtain a self-consistent expression for the equilibrium density \( \rho_0(R) \) that reads as

\[
\rho_0(R) = \Lambda^{-3M} \exp \left[ \beta \mu_M - \beta V_b(R) - \beta \sum_{j=1}^{M} \lambda(r_j) \right],
\]

where

\[
\lambda(r_j) = \frac{\delta F_{\text{ex}}[\rho]}{\delta \rho(r_j)} + \psi(r_j).
\]

It must be noted that the functional derivative at the right-hand side of eq. (166) above is calculated at the equilibrium density profile \( \rho_0(R) \), of which the reduced density field \( \rho(r) \) is a functional by virtue of its definition, eq. (161). Accordingly, eq. (165) is a self-consistent equation, in which the equilibrium density field \( \rho_0(R) \) appears on both sides of it.

Clearly, eq. (165) is of little practical importance, as its solution would require the self-consistent (iterative) determination of a function of \( 3M \) variables, a task that becomes prohibitively complicated for long chains (\( M \gg 1 \)). However, the information that is contained in the function \( \rho_0(R) \) is at the same time too detailed. In practice, we are not interested in knowing the probability density of finding a chain in the particular conformation \( R = (r_1, r_2, \ldots, r_M) \); it suffices to know the much simpler probability density of finding any monomer at position \( r \), which is embodied in the density field \( \rho(r) \) defined in eq. (161). Accordingly, to determine the corresponding equilibrium one-particle density \( \rho_0(r) \), we have to apply eq. (161) on both sides of the equilibrium condition, eq. (165). The calculation becomes manageable for linear chains with sequentially bonded monomers because in this case the Boltzmann factor of the bonding potential \( V_b(R) \) factorizes into a product of functions that contain only successive particle coordinates, i.e.

\[
\exp \left[ -\beta V_b(R) \right] = \prod_{j=1}^{M-1} g(|r_j - r_{j+1}|),
\]

with some function \( g(z) \) that typically vanishes for sufficiently large values of its arguments. The self-consistent equilibrium condition for the one-point density, \( \rho_0(r) \) now takes the form

\[
\rho_0(r) = \Lambda^{-3M} \exp \left[ \beta \mu_M - \beta \lambda(r) \right] \sum_{j=1}^{M} I(1 \rightarrow j) I(j \leftarrow M),
\]
in which the two propagators have the form

\begin{equation}
I(1 \rightarrow j) = \int d^3 r_1 \cdots \int d^3 r_{j-1} e^{-\beta \lambda |r_i|} g(|r_1 - r_2|) \cdots e^{-\beta \lambda |r_{j-1}|} g(|r_{j-1} - r|),
\end{equation}

and

\begin{equation}
I(j \leftarrow M) = \int d^3 r_M \cdots \int d^3 r_{j+1} e^{-\beta \lambda (r_M)} g(|r_{M-1} - r_M|) \cdots e^{-\beta \lambda (r_{j+1})} g(|r_{j+1} - r|).
\end{equation}

The above expressions allow for a transparent geometrical interpretation. Topologically, the chain can be thought of as a straight line with filled circles (the integration variables) and an open circle (the field variable). The former are labeled \(r_1, \ldots, r_{j-1}, r_j+1, \ldots, r_M\), whereas the missing variable \(r_j\) has been replaced by the field point \(r\), which is not integrated upon. The propagator \(I(1 \rightarrow j)\) starts from the left end of the chain, at position \(r_1\) and reaches the field variable at the site \(j\) of the straight line through successive integrations over the intermediate variables. The same procedure is followed by the propagator \(I(j \leftarrow M)\) but in the opposite direction, from the right end of the chain, located at \(r_M\), to the field variable \(r\) which lies at the site \(j\). The two propagators have no integration variable in common, thus they factorize in eq. (168). Further, due to the sequential bonding of the monomers of the linear chain, each propagator has a telescopic structure. Indeed, we first introduce a trivial renaming:

\begin{align}
I(1 \rightarrow j) &\equiv G^{(j)}(r), \\
I(j \leftarrow M) &\equiv G^{(M-j+1)}(r),
\end{align}

with the implication that the propagator \(G^{(\alpha)}(r)\) contains \(\alpha - 1\) integrations. The hierarchy of these propagators can be evaluated according to the recurrence relation:

\begin{equation}
G^{(\alpha)}(r) = \int d^3 x e^{-\beta \lambda (r)} G^{(\alpha-1)}(x) g(|r - x|), \quad (\alpha > 1)
\end{equation}

with the initial value

\begin{equation}
G^{(1)}(r) = 1.
\end{equation}

Equation (168) can thus be written as

\begin{equation}
\rho_0(r) = \Lambda^{-3M} \exp \left[ \beta \mu_M - \beta \lambda(r) \right] \sum_{j=1}^{M} G^{(j)}(r) G^{(M-j+1)}(r),
\end{equation}

and it forms, together with eqs. (173) and (174) a self-consistent scheme.

For a given external potential \(\psi(r)\), an initial guess of the equilibrium density field \(\rho(r)\) is made. Given also a suitably chosen excess free energy functional \(F_{ex}[\rho]\), the effective one-body potential field \(\lambda(x)\) for this density profile is calculated using eq. (166). The recurrence relations, eqs. (173) and (174), are used to calculate all propagators, which, by means of eq. (175) lead to a new density profile. The cycle is iterated until convergence between the input- and output density profiles to its equilibrium value, \(\rho_0(r)\), is achieved. For very long chains, \(M \gg 1\), this scheme can be quite cumbersome,
due to the computational effort needed to calculate all distinct propagators $G^{(\alpha)}(r)$, $\alpha = 2, 3, \ldots, M$ at every iteration step. Here, however, a simplifying assumption can be made, namely that for very long chains end-effects are negligible and the density profile is dominated by the large number of propagators with indices away from the ends. Accordingly, all propagators are set equal to one another, $G^{(\alpha)}(r) = G(r)$ $\forall \alpha$, and the self-consistency condition takes the form (cf. eq. (175)):

$$\rho_0(r) = MA^{-3M} \exp[\beta \mu_M - \beta \lambda(r)] G^2(r),$$

with $G(r)$ being determined from the equation (cf. eq. (173)):

$$G(r) = \int d^3x e^{-\beta \lambda(x)} G(x) g(|r - x|).$$

The polymer-DFT outlined above has found numerous applications for confined polymer solutions. Typically, weighed-density excess functionals with the Wertheim corrections for the connectivity are employed for the short-range, steric part of the monomer-monomer non-bonded interactions. Hereby, whereas the tangent hard-sphere model is the usual choice for the bonding potential, giving rise to a Boltzmann factor [105]:

$$\exp[-\beta V_b(R)] = \Lambda^{3M-3} \prod_{j=1}^{M-1} \frac{\delta(|r_j - r_{j+1}| - \sigma)}{4\pi\sigma^2},$$

where $\sigma$ is the hard-monomer diameter. As representative examples, we mention here the investigations of inhomogeneous polymer mixtures [105], of the surface structure and correlation functions of freely jointed Lennard-Jones fluids [107], as well as extensions to polymer brushes [106] and to polyelectrolyte chains [108].

7. – Summary and conclusions

We have presented a concise overview of the fundamentals of coarse-graining and of the methods employed to reduce the complexity of colloidal systems by means of eliminating certain classes of degrees of freedom and thus reducing the systems to simpler ones, in which the effective particles interact by means of suitably defined effective interactions. The review has been by no means exhaustive, as a host of common and highly interesting systems, ranging from polyelectrolytes, soft mixtures and dendrimers and going all the way to, e.g., anisotropic and the currently popular active particles have not been touched upon. Nevertheless, the spirit and the definitions according to which proper coarse-graining, as opposed to ad hoc models, is being performed has been put forward. In this way, the connection with the underlying microscopic models and properties of the systems remains intact, and it allows for a true bridging of the gap between the atomic and the macroscopic length scales in equilibrium. Issues related with coarse-graining for dynamics have only been briefly mentioned, since the topic is covered by other contributions to this volume, most thoroughly in the contribution of this Volume authored by Gerhard Nägele.

On the basis of the effective interaction, the equilibrium structure and thermodynamics of the system can be investigated by means of different theoretical and computational
techniques. Here, we limited ourselves to an exposition of one of the most powerful and celebrated approaches, namely Density Functional Theory, including some modern applications to ultrasoft systems and mixtures thereof. Computer simulations are another major tool but for these aspects the reader is referred to the contribution authored by Daan Frenkel in this book. The aim of this paper was to combine a pedagogical presentation of fundamental results with and exposure of aspects related to current research. As such, it could be of use to beginning graduate students who wish to learn not only the notions but also the “how to” of coarse-graining and density functional theory, but also to experienced researchers as a point of reference for recent work on the properties of soft colloids.

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Appendix A.

Functionals and functional differentiation

The notion of a function of a finite number of variables is familiar from elementary calculus. A function \( f(x_1, x_2, \ldots, x_n) \) is a mapping or a rule that assigns a single number (or a vector) to an ordered array of variables \((x_1, x_2, \ldots, x_n)\). The following are examples of functions of one, two, and \( n \) variables, respectively:

\[
(A.1) \quad f(x) = x^2; \quad g(x_1, x_2) = \sin(x_1 + x_2); \quad h(x_1, x_2, \ldots, x_n) = \sum_{i=1}^{n} \exp(x_i).
\]

A functional is a generalization of this idea. The argument of a functional is a whole function \( f(x) \) of one or many variables and a number \( I[f] \) is assigned to it. A simple example of a functional is

\[
(A.2) \quad I[f] = \int_{-1}^{1} f(x)dx.
\]

Here, the result of the integration depends on the whole function \( f(x) \), hence \( I \) is a functional of \( f(x) \), denoted by the square brackets, \( I[f] \). There are numerous examples of functionals already encountered in undergraduate Physics lectures. Two particular examples are the action \( S[\mathcal{L}] \) of a classical particle, which is a functional of the Lagrangian \( \mathcal{L}(q, \dot{q}) \), which is itself a function of the generalized coordinate \( q \) and velocity \( \dot{q} \). Another is the total energy of an electromagnetic field, i.e.

\[
(A.3) \quad W(t; [E, B]) = \frac{1}{8\pi} \int d^3r [\|E(r, t)\|^2 + \|B(r, t)\|^2],
\]

which is again a functional of the full spatiotemporal electric and magnetic fields \( E(r, t) \) and \( B(r, t) \) and at the same time a function of the time \( t \).

\(^{(2)}\) Parts of this Appendix have been inspired by the discussion in ref. [112].
In statistical mechanics, functionals are again omnipresent. One known example from statistical field theory is the famous Landau-Ginzburg Hamiltonian $\mathcal{H}_{\text{LG}}[\phi, J]$:

$$\mathcal{H}_{\text{LG}}[\phi, J] = \int d^d r \left[ \frac{K}{2} |\nabla \phi(r)|^2 + \frac{\mu}{2!} \phi^2(r) + \frac{\lambda}{4!} \phi^4(r) + J(r)\phi(r) \right], \quad (A.4)$$

which describes the fluctuations of a coarse-grained scalar field $\phi(r)$ in an external potential $J(r)$ in $d$-dimensional space and assigns a statistical weight $W[\phi, J]$, which scales proportionally to $\exp\{-\beta \mathcal{H}_{\text{LG}}[\phi, J]\}$, to each particular field realization. The partition function $Z_{\text{LG}}[J]$ of the model emerges upon integrating over all realizations of the field and it is, of course, a functional of the external field $J(r)$:

$$Z_{\text{LG}}[J] = \int D\phi \exp\{-\beta \mathcal{H}_{\text{LG}}([\phi, J])\}. \quad (A.5)$$

The free energy functional $F[\rho]$ that plays the central role in density functional theory is just another example, for which a whole, spatially dependent function $\rho(r)$ is mapped onto a single scalar quantity $F[\rho]$. In density functional theory (and in statistical field theory), more complicated situations can arise, in which a functional depends not only on the density field $\rho(r)$ but is also a function of a whole collection of spatial coordinates $(r_1, r_2, \ldots, r_n)$. Indeed, the $n$-body direct correlation function $-k_B T c^{(n)}$, which is defined as the $n$-th functional derivative of the excess free energy functional $F_{\text{ex}}[\rho]$ with respect to the density is precisely a function of $n$ spatial coordinates and a functional of $\rho(r)$. It is customary to denote such “mixed” objects as

$$c^{(n)} = c^{(n)}(r_1, r_2, \ldots, r_n; [\rho]), \quad (A.6)$$

i.e., to use parentheses in order to emphasize their character as functions of the variables $(r_1, r_2, \ldots, r_n)$ and additional square brackets to remind their functional dependence on the entire density field $\rho(r)$. The notation in eq. (A.6) above thus means: for each field $\rho(r)$, $c^{(n)}$ is a different function of $(r_1, r_2, \ldots, r_n)$. A very simple, concrete example of such a mixed object is given below:

$$G(s; [\rho]) = \int d^3 r f(\rho(r)) K(r, s), \quad (A.7)$$

which is a function of $s$ and a functional of $\rho(r)$ for a given integration kernel $K(r, s)$. Note that the quantity $f(\rho(r))$ appearing in the integrand is a function of $\rho(r)$, in the sense that its value depends only on the local value of the field at the position $r$ and not on the entire density profile. Formally, local functions of the density can still be looked upon as functionals through the choice $K(r, s) = \delta(r - s)$ in eq. (A.7) above.

We now proceed with the definition of the functional derivative of a functional $F[\rho]$ with respect to the density. This quantity ought to tell us what happens to $F$ if we change the profile $\rho(r)$ locally at the position $r_k$. In analogy with the usual derivative, its functional counterpart is defined as

$$\frac{\delta F[\rho]}{\delta \rho(r_k)} \equiv \lim_{\alpha \to 0} \lim_{\epsilon \to 0} \frac{F[\rho(r) + \epsilon \Delta_\alpha(r - r_k)] - F[\rho(r)]}{\epsilon} = G(r_k; [\rho]), \quad (A.8)$$

where $\Delta_\alpha(r - r_k)$ is a family of $\alpha$-parametrized functions with the property

$$\lim_{\alpha \to 0} \Delta_\alpha(r - r_k) = \delta(r - r_k). \quad (A.9)$$
An alternative definition of the functional derivative can be very useful for practical purposes. Here, one first discretizes space into a regular lattice by introducing a discrete set of points \( r_1, r_2, \ldots, r_N \) with elementary volume \( a^d \) each, where \( d \) is the space dimension. Accordingly, the density field is discretized by a set of values \( \rho_k \equiv \rho(r_k) \) and a functional \( F[\rho] \) can be considered as a function of \( N \) variables, \( F(\rho_1, \rho_2, \ldots, \rho_N) \). The functional derivative is now defined as
\[
\frac{\delta F[\rho]}{\delta \rho(r_k)} = \lim_{a \to 0} \frac{1}{a^d} \frac{\partial F(\rho_1, \rho_2, \ldots, \rho_N)}{\partial \rho_k}.
\]

Evidently, the result of a functional differentiation depends on the entire profile \( \rho(r) \) and on the position \( r_k \) on which the local density variation is taken. It is, therefore, a mixed object, a function of \( r_k \) and a functional of \( \rho(r) \), as the notation manifests.

The simplest functionals to differentiate are the local ones mentioned above. For those, it follows directly from the definition (A.8) that the functional derivative is closely related to the usual derivative, viz.
\[
\frac{\delta f(\rho(r))}{\delta \rho(r_k)} = \delta(r - r_k) \left. \frac{df(s)}{ds} \right|_{s=\rho(r)}.
\]

As a corollary we obtain the useful identity
\[
\frac{\delta \rho(r)}{\delta \rho(r_k)} = \delta(r - r_k).
\]

Another useful rule for functional differentiation is the generalization of the chain rule of usual differentiation. Suppose that \( F \) is a functional of the function \( g \), \( F = F[g] \), and that the function \( g \) is itself a functional of \( f \), \( g = g(r; [f]) \). Now suppose that \( f \) changes. This will cause \( g \) to change and this change will propagate to \( F \). It is therefore legitimate to regard \( F[g] \) also as a functional \( F[f] \) and to ask what the functional derivative of \( F \) with respect to \( f \) is. The answer is provided by the functional chain rule below:
\[
\frac{\delta F[f]}{\delta f(r_k)} = \int d^3r \frac{\delta F[g]}{\delta g(r; [f])} \frac{\delta g(r; [f])}{\delta f(r_k)}.
\]

Let now \( I[f] \) be the functional defined in eq. (A.2) and let us additionally define three simple functionals of the density \( \rho(r) \) or some arbitrary field \( \varphi(r) \) as follows:
\[
G[\rho] = \int d^3r \rho(r) \ln \{ \rho(r) \Lambda^3 - 1 \};
\]
\[
F[\rho] = \frac{1}{2} \int \int d^3xd^3y \rho(x)\rho(y)v(|x - y|);
\]
\[
H[\varphi] = \exp \left\{ \int d^3r \varphi(r) J(r) \right\}.
\]
Using the rules given above, the reader is asked to prove the following relations:

\[ \delta I[f(x_0)] \delta f(x_0) = \begin{cases} 1 & \text{if } |x_0| < 1; \\ 0 & \text{otherwise}. \end{cases} \]  \hfill (A.17)

\[ \delta I[f^2(x_0)] \delta f(x_0) = \begin{cases} 2f(x_0) & \text{if } |x_0| < 1; \\ 0 & \text{otherwise}. \end{cases} \]  \hfill (A.18)

\[ \frac{\delta G[\rho(z)]}{\delta \rho(z)} = \ln \left[ \rho(z) \Lambda^3 \right]. \]  \hfill (A.19)

\[ \frac{\delta F[\rho(z)]}{\delta \rho(z)} = \int d^3 x \rho(x) v(|x - z|). \]  \hfill (A.20)

\[ \frac{\delta^2 F[\rho(z)]}{\delta \rho(z) \delta \rho(w)} = v(|z - w|). \]  \hfill (A.21)

\[ \frac{\delta^n F[\rho(z)]}{\delta \rho(r_1) \delta \rho(r_2) \cdots \delta \rho(r_n)} = 0 \quad \text{for } n \geq 3. \]  \hfill (A.22)

\[ \frac{\delta^n H[\varphi]}{\delta \varphi(r_1) \delta \varphi(r_2) \cdots \delta \varphi(r_n)} = J(r_1)J(r_2) \cdots J(r_n)H[\varphi]. \]  \hfill (A.23)

REFERENCES