

General strategies for coarse graining in soft materials

Carlo Pierleoni
University of L'Aquila, Italy



MULTISCALE MODELING AND SIMULATIONS OF HARD AND SOFT MATERIALS
2009, ICTS, Bangalore 7-16 December 2009



[International Centre for Theoretical Sciences](#), TIFR,
Mumbai [International Centre for Materials Science](#),
JNCASR, Bangalore



Outline

- Introduction to soft matter and coarse graining
- Structure of the effective hamiltonian for the effective one component system
- Depletion interactions in hard sphere mixtures
- Density functional theory for classical systems
- Applications: the electric double layer
charged stabilized colloids
- Integral equations approach and the inversion theorem
- Brief review of polymer physics
 - single chain
 - polymer solutions
- Coarse-graining strategy for polymer solutions
- Semidilute solutions of linear chains in good solvent conditions
- Star polymers in good solvent
- Diblock copolymer solutions

What is Soft Matter?

A large class of material composed by *mesoscopic* particles (10^{-9}m - 10^{-6}m) dispersed in a solvent of much smaller molecules (typical atomic size). Synonyms of Soft matter are *complex fluids*, *colloidal suspensions* and *colloidal dispersions*.

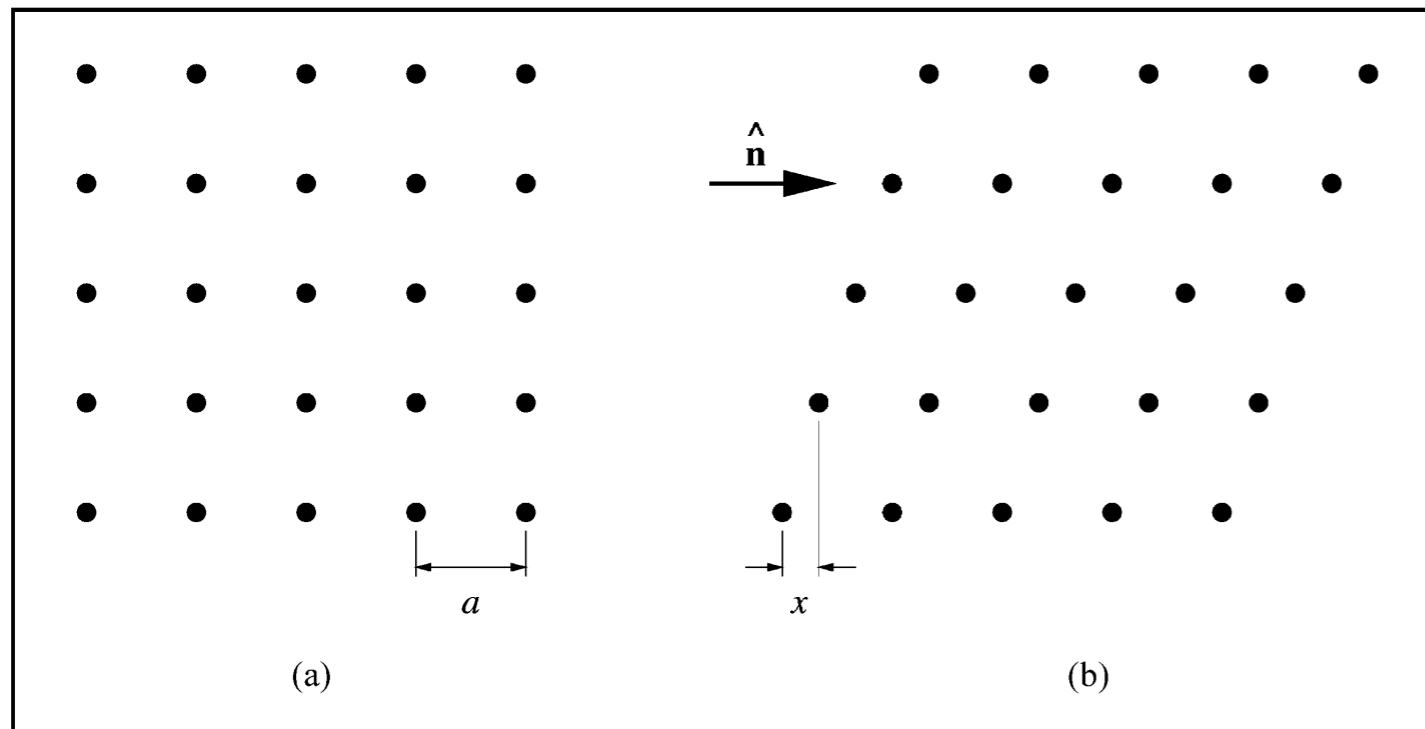
Soft matter is abundant in the everyday life and in numerous applications in chemical, pharmaceutical and food industry: mayonnaise, ink, blood etc.. Microemulsions and self-organized micelles of detergent in water belong to the same category, sometime called *association colloids*.

In these lectures I will focus on solutions of spherical mesoscopic particles in liquid solvent and I will review the progress done in understanding their structure and thermodynamics using the tools of statistical mechanics. The dispersed particles can be either **solid particles** (polystyrene, polymethylmethacrylate (PMMA), silica spheres) or “**fractal**” **objects** like polymers chains (linear or stars). The spherical shape of the mesoscopic objects imposes an important simplifying symmetry in the structure of the theory.

Why Soft?

Why Soft? It is a consequence of the mesoscopic size of the constituents.

Consider a perfect crystal of lattice constant a sheared in such a way to displace every lattice plane by an amount x . For small deformations, the energy $u(x)$ and the shear stress to deform the crystal by $a/4$ are



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

$$\sigma \left(\frac{a}{4} \right) = a \left(\frac{du(x)}{dx} \right)_{x=\frac{a}{4}} = \frac{G}{4}$$

G = generic elastic constant

To estimate G let us assume that the interactions $\phi(r)$ are pairwise additive and spherically symmetric and only nearest neighbours are relevant. In this case, for simple cubic lattice one obtains

$$c_{xxxx} = G = \frac{1}{v} a^2 \phi''(r = a) \quad v = a^3$$

Why Soft Matter?

a is set from the range of the interactions. To compare with typical atomic systems assume that we can use the same form for the interaction in both atomic and colloidal systems

$$\phi(r) = \varepsilon \tilde{\phi}(r/a; \{\mathbf{p}\}) , \quad \varepsilon = \text{energy scale, } \{\mathbf{p}\} = \text{set of parameters}$$

$$G = \frac{1}{v} \varepsilon \tilde{\phi}''(1, \{\mathbf{p}\}) .$$

Microscopic (atomic) systems $\varepsilon \approx (10^{-1} eV; 10 eV)$

Mesoscopic (colloidal) systems $\varepsilon \approx (k_B T; 100 k_B T) \approx (0.05 eV; 5 eV)$

$$\frac{G_{colloidal}}{G_{atomic}} \sim \frac{v_{atomic}}{v_{colloidal}} \approx 10^{-12} - 10^{-9}$$

Modeling Soft Matter

Soft systems with mesoscopic particles involve an enormous number of degrees of freedom.

Assume a system with large and small spheres with size ratio $R/r \sim 100$.

The volume ratio between large and small spheres is $\sim 10^6$.

At packing fraction of large spheres of ~ 0.5 , typical of a liquid of hard spheres, half of the available volume is occupied by large sphere and the remaining half is occupied by the small spheres. For a system of 100 large spheres in such condition we should consider $\sim 10^8$ small spheres. This rough estimate does not take into account the internal degrees of freedom of the mesoscopic and the solvent particles,

General strategy for modeling soft matter: coarse graining by elimination of solvent degrees of freedom.

Tools for coarse graining: Statistical Mechanics and Classical Density Functional Theory

Product of the coarse graining: effective interactions among the mesoparticles

Once the effective one component model is established, standard simulation methods can be exploited to describe the thermodynamics and the structure of the system.

Such strategy does not provide a model for studying dynamical properties of the system.

The effective one-component system

PHYSICAL REVIEW E

VOLUME 59, NUMBER 5

MAY 1999

Phase diagram of highly asymmetric binary hard-sphere mixtures

Marjolein Dijkstra, René van Roij, and Robert Evans

Consider a system of N_1 and N_2 classical particles of mass M and m in a volume V .
 $\{P, R\}$ and $\{p, r\}$ = momenta and coordinate of particles of specie 1 and 2 respectively
The Hamiltonian is

$$\mathcal{H} = K + H$$

$$K = K_1 + K_2 = \sum_{i=1}^{N_1} \frac{P_i^2}{2M} + \sum_{i=1}^{N_2} \frac{p_i^2}{2m}$$

$$H = H_{11} + H_{22} + H_{12} = \sum_{i < j}^{N_1} \phi_{11}(R_{ij}) + \sum_{i < j}^{N_2} \phi_{22}(r_{ij}) + \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \phi_{12}(|R_i - r_j|)$$

At fixed temperature T , the relevant thermodynamic potential in the variable (T, V, N_1, N_2) is the Helmholtz free energy $F_c(T, V, N_1, N_2)$

$$\exp[-\beta F_c] = \frac{1}{N_1! \Lambda_1^{3N_1}} \frac{1}{N_2! \Lambda_2^{3N_2}} \text{Tr}_1 \text{Tr}_2 \exp[-\beta H], \quad \beta = 1/k_B T$$

$$\Lambda_i = h / \sqrt{2 \pi m_i k_B T}$$

The effective one-component system

Legendre-transform to the semi-grand canonical ensemble of the system in contact with a bath of particles of species 2 at fixed chemical potential μ_2

$$F(N_1, \mu_2, V) = F_c(N_1, N_2, V) - \mu_2 N_2,$$

$$\exp[-\beta F] = \sum_{N_2=0}^{\infty} \exp[-\beta(F_c - \mu_2 N_2)] = \frac{1}{N_1! \Lambda_1^{3N_1}} \text{Tr}_1 \exp[-\beta(H_{11} + \Omega)] \quad (1)$$

$$\exp[-\beta \Omega] = \sum_{N_2=0}^{\infty} \frac{z_2^{N_2}}{N_2!} \text{Tr}_2 \exp[-\beta(H_{12} + H_{22})] \quad z_2 = \frac{\exp(\beta \mu_2)}{\Lambda_2^3}$$

$\Omega = \Omega(\{\mathbf{R}\}, N_1, z_2, V, T)$ is the grand-potential of a fluid species 2 in the external field of a fixed configuration of N_1 particles of species 1

From (1):

$$H^{\text{eff}} = H_{11} + \Omega.$$

How to compute Ω ?

The effective one-component system

- i) By diagrammatic expansion for models with short range (integrable) interactions
- ii) By Density Functional Theory for long range potentials
- iii) By approximated integral equations (liquid state theory)

Diagrammatic expansion (Dijkstra et al. PRE 59, 5744 (1999))

Define:
$$H_{12}^{(n)} = \sum_{i=1}^n \sum_{j=1}^{N_2} \phi_{12}(\vec{R}_i - \vec{r}_j)$$

$$\Xi_n(\vec{R}_1, \dots, \vec{R}_n, z_2, V) = \sum_{N_2=0}^{\infty} \frac{z_2^{N_2}}{N_2!} \int_V dr^{N_2} e^{-\beta H_{12}^{(n)}} e^{-\beta H_{22}}$$

It can be proved that
$$-\beta\Omega = -\sum_{n=0}^{N_1} \beta\Omega_n,$$

n=0

$$\Omega_0(z_2, V) = -k_B T \log [\Xi_0(z_2, V)] = -V p(z_2)$$

EOS of the solvent - independent on R

The effective one-component system

n=1

$$\Omega_1(\vec{R}, z_2, V) = -k_B T N_1 \log \left[\frac{\Xi_1(\vec{R}, z_2, V)}{\Xi_0(z_2, V)} \right] = N_1 \omega_1(z_2, R) = V \rho_1 \omega_1(z_2)$$

$$\omega_1(z_2, R) = -k_B T \log \left\langle e^{-\beta H_{12}^{(1)}} \right\rangle_{z_2}$$

contribution to the chemical potential of specie 1
from the solvent at fugacity z_2
independent on R for homogeneous solvents

n=2

$$\Omega_2 = -k_B T \sum_{i < j}^{N_1} \log \left[\frac{\Xi_2(R_{ij}, z_2, V) / \Xi_0}{(\Xi_1 / \Xi_0)^2} \right] = \sum_{i < j}^{N_1} \omega_2(R_{ij}, z_2)$$

$$\omega_2(R_{ij}, z_2) = -k_B T \log \frac{\left\langle \exp[-\beta H_{12}^{(2)}(R_{ij})] \right\rangle_{z_2}}{\left\langle \exp[-\beta H_{12}^{(1)}] \right\rangle_{z_2}^2}$$

Effective two-body interaction induced
by the solvent

The effective one-component system

n=3

$$\Omega_3 = -k_B T \sum_{i < j < k}^{N_1} \log \left[\frac{\Xi_3(R_i, R_j, R_k, z_2, V)}{\Xi_0} \frac{\Xi_1^3}{\Xi_2(R_{ij})\Xi_2(R_{ik})\Xi_2(R_{jk})} \right] = \sum_{i < j < k}^{N_1} \omega_3(R_i, R_j, R_k, z_2)$$

$$\omega_3(R_i, R_j, R_k, z_2) = -k_B T \log \frac{\langle \exp[-\beta H_{12}^{(3)}(R_i, R_j, R_k)] \rangle_{z_2} \langle \exp[-\beta H_{12}^{(1)}] \rangle_{z_2}^3}{\langle \exp[-\beta H_{12}^{(2)}(R_{ij})] \rangle_{z_2} \langle \exp[-\beta H_{12}^{(2)}(R_{ik})] \rangle_{z_2} \langle \exp[-\beta H_{12}^{(2)}(R_{jk})] \rangle_{z_2}}$$

effective three-body interaction

n>4

Formally:

$$\Omega_n(\{\mathbf{R}\}; N_1, z_2) = \sum_{i_1 < i_2 < \dots < i_n}^{N_1} \omega_n(\mathbf{R}_{i_1, \dots, i_n}; z_2),$$

$$H^{eff} = \underbrace{-Vp(z_2) + N_1\omega_1(z_2)}_{\text{volume term}} + \underbrace{\sum_{i < j}^{N_1} [\phi_{11}(R_{ij}) + \omega_2(R_{ij}, z_2)]}_{\text{two-body}} + \underbrace{\sum_{i < j < k}^{N_1} \omega_3(R_i, R_j, R_k, z_2) + \dots}_{\text{three-body}}$$

volume term

two-body

three-body

The effective one-component system

Remarks:

- General derivation valid for any two-component system with integrable pair interactions. The rate of convergence of the expansion depends on the form of the pair interactions ϕ_{12}, ϕ_{22}
- the effective interaction is state dependent: a change in temperature or in composition of the mixture can change the effective interaction which can therefore be externally controlled.
- the terms $\Omega_0 = -Vp(z_2); \quad \Omega_1 = V\rho_1\omega_1(z_2)$ that represent the zero and the first order terms in the effective hamiltonian do not depend on the instantaneous coordinates of the mesoparticles and therefore do not affect the structure of the effective system. Moreover they do not affect the thermodynamic behaviour because of their trivial dependence on density (at most linear) which do not affect any double tangent construction. This is in contrast with analogous terms appearing in system with long-ranged Coulomb interactions (not integrable) for which the Mayer expansion does not converge and for which the present derivation cannot be applied. In that case the volume term does affect the thermodynamics.
- $\omega_2(\mathbf{R}_{ij}; z_2)$ is the grand-potential difference between the solvent, of fugacity z_2 , containing two particles of species I at a finite separation R_{ij} and at infinite separation $R_{ij}=\infty$. In other word it is the work done to bring two particles from infinity to a distance R_{ij} within the solvent at fixed chemical potential

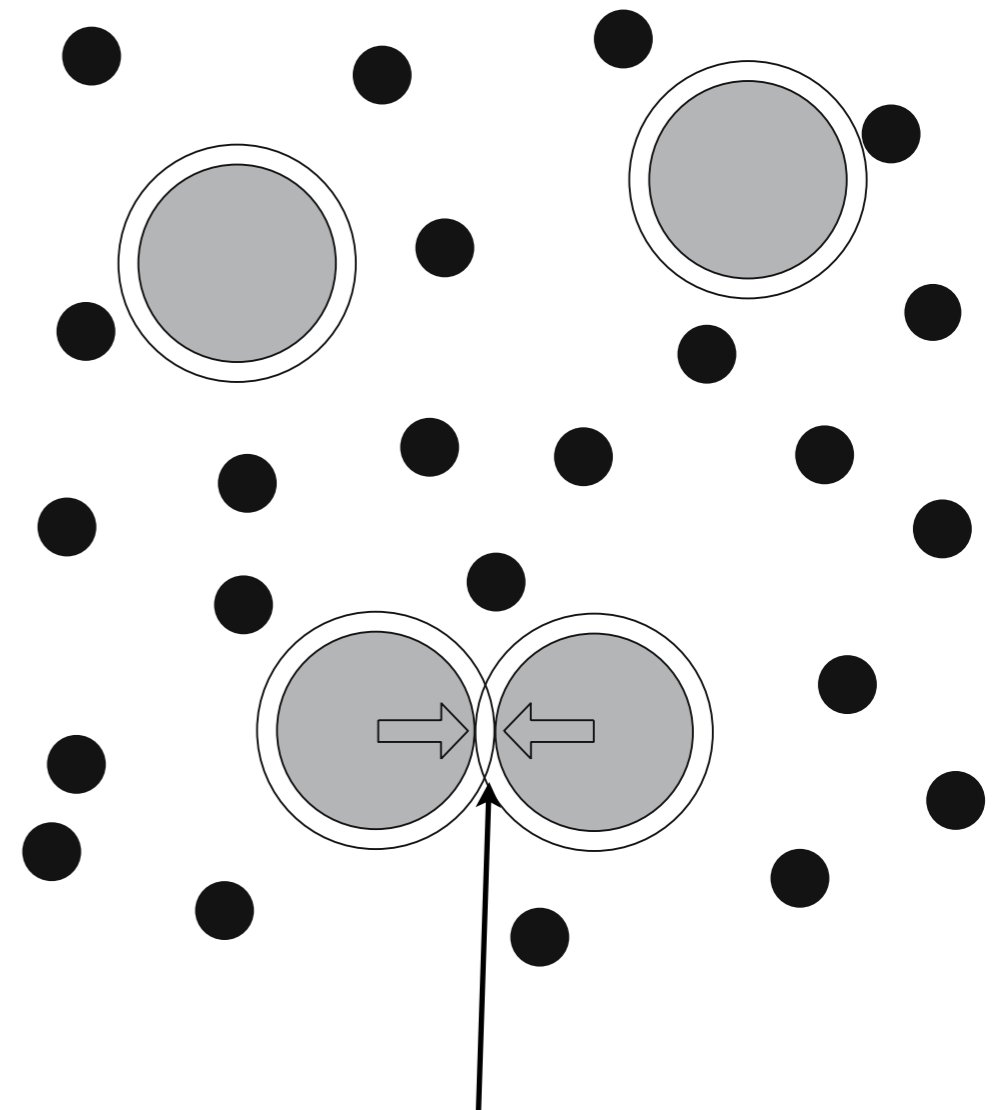
Phase diagram of highly asymmetric binary hard-sphere mixtures

Marjolein Dijkstra, René van Roij, and Robert Evans

Mixture of large size (σ_1) and small size (σ_2) hard spheres with size ratio $q=\sigma_2/\sigma_1$. For hard spheres very accurate expression for Ω_0 (Carnahan-Starling EOS) and Ω_1 (Henderson) are available.

The two body effective interactions is the **depletion interaction**, a solvent induced attraction between solute hard spheres. It is of entropic origin and arises from exclusion of the small particles between two large particles at separation less than the size of the small particles. The exclusion of small particles induces an osmotic pressure unbalance which results in an attraction between large spheres.

It is a mechanism for effective attraction through pure repulsions and may induce phase separation. To first order in the density of small spheres the depletion potential is represented by the **Asakura-Oosawa** model.



Ω is the volume of the overlapping depletion zone

Depletion interactions

Asakura-Oosawa model:

assumes the small spheres to be an ideal gas (neglects correlations)

$$\Pi = k_B T z_2$$

$$V_{\text{eff}}(r; \pi) = \begin{cases} \infty, & r < \sigma \\ V_{\text{AO}}(r; \pi), & \sigma < r < \sigma + \sigma' \\ 0, & r > \sigma + \sigma' \end{cases}$$

$$V_{\text{AO}}(r, \pi) = -\Pi \Omega(r, \sigma_1 + \sigma_2)$$

$$\Omega(r, x) = \frac{\pi x^3}{6} \left(1 - \frac{3r}{2x} + \frac{r^3}{2x^3} \right)$$

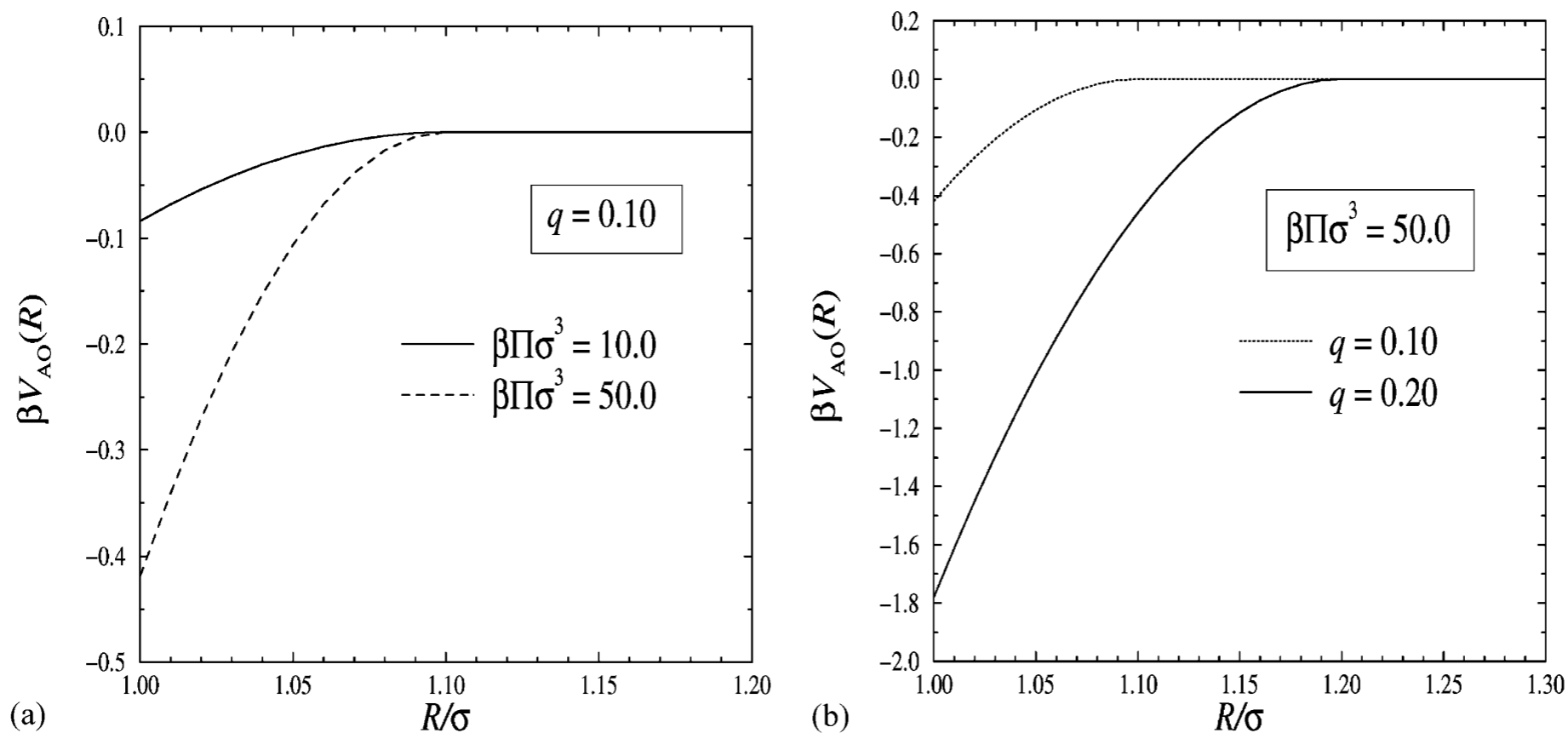


Fig. 28. The Asakura-Oosawa depletion potential [second and third lines in Eq. (4.8) above] for different parameter values: (a) $q = 0.10$ at $\beta \Pi \sigma^3 = 10.0$ and 50.0 ; (b) $\beta \Pi \sigma^3 = 50.0$ for $q = 0.10$ and 0.20 .

AO is valid for very small fugacity.

AO is a good model for colloids and ideal polymers mixtures (Dijkstra et al., J Phys. Cond. Mat. 11, 10079 (1999))

Depletion interactions

More refined model from DFT (Goetzelmann et al, PRE 57, 6785 (1998)) valid for higher solvent density (up to $\eta_2^r \sim 0.4$)

$$\beta\phi_{\text{dep}}(R_{ij}) = -\frac{1+q}{2q} [3x^2\eta_2^r + (9x+12x^2)(\eta_2^r)^2 + (36x+30x^2)(\eta_2^r)^3] \quad \text{for } -1 < x < 0, \quad x = R_{ij}/\sigma_2 - 1/q - 1$$

η_2^r is the packing fraction of a reservoir of small spheres at fugacity z_2 (via EOS)

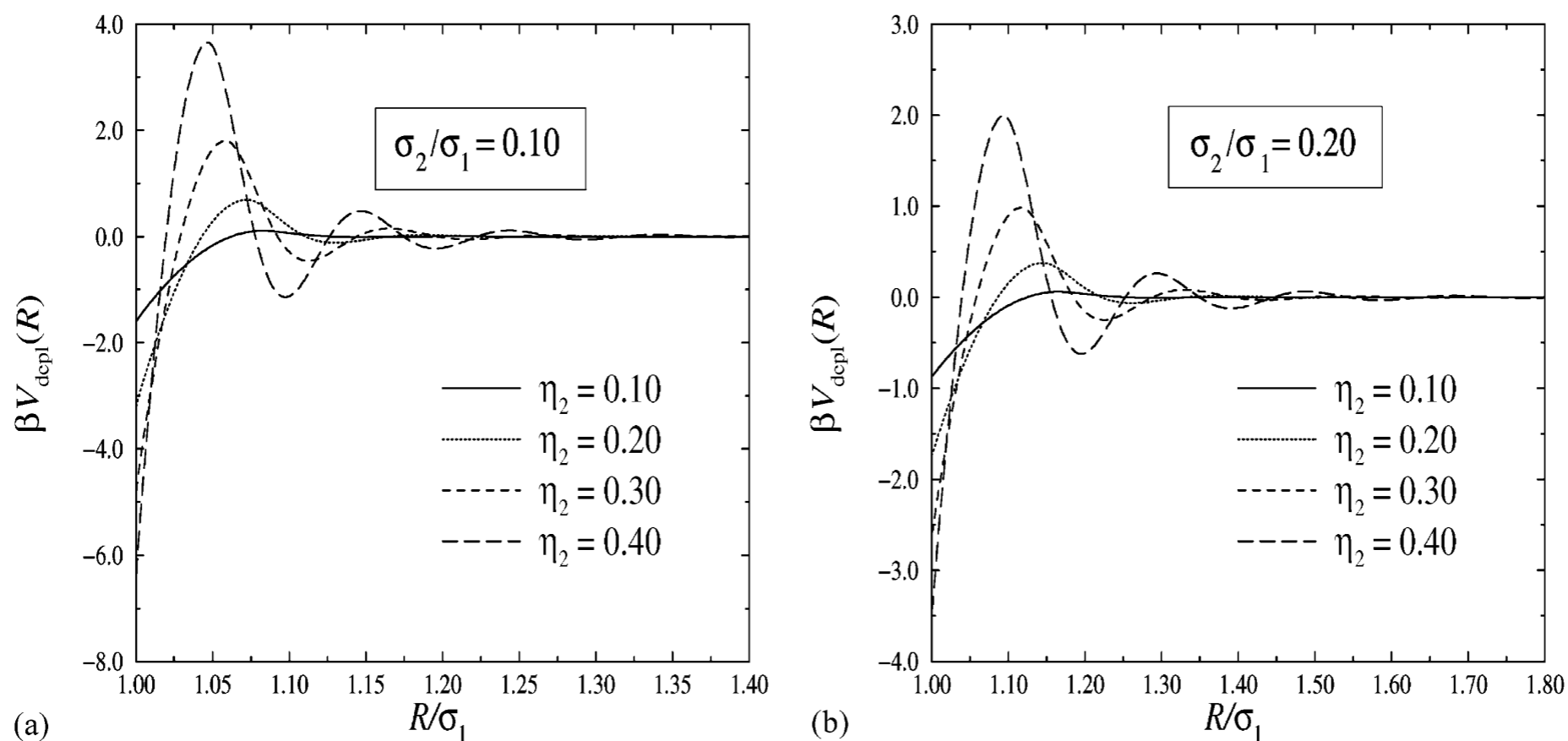
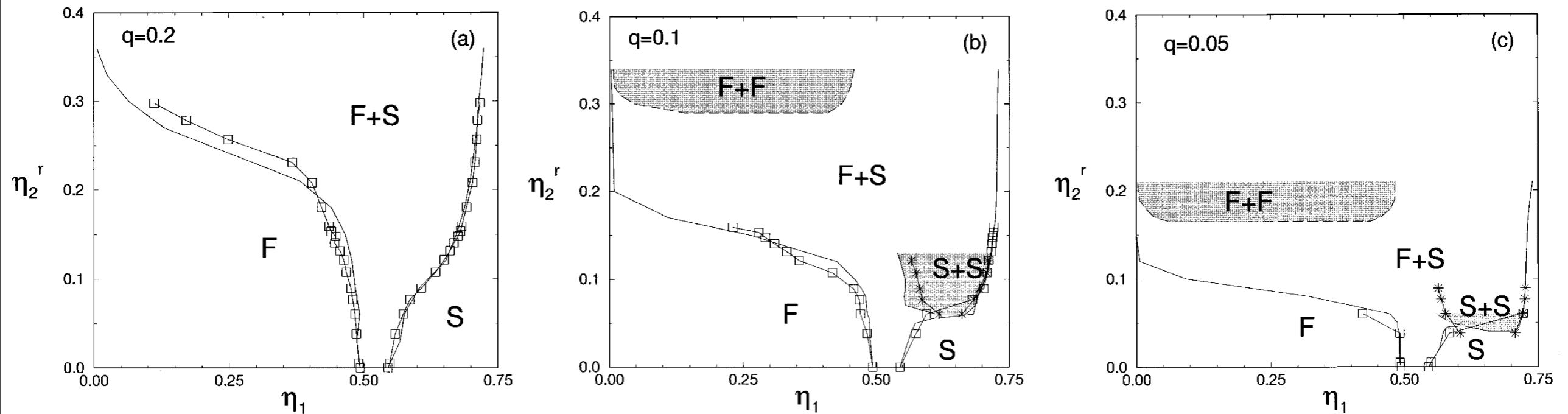


Fig. 29. The depletion potential $V_{\text{depl}}(R)$ between two large hard spheres at center-to-center distance R due to the presence of a sea of small ones, at different packing fractions η_2 of the small. (a) Size ratio $\sigma_2/\sigma_1 = 0.10$ and (b) size ratio $\sigma_2/\sigma_1 = 0.20$. Notice the effects of η_2 and of the size ratio on the range and strength of the depletion. The curves were produced using the analytical fit to the density-functional results given in Ref. [221].

Phase diagram of highly asymmetric binary hard-sphere mixtures

Marjolein Dijkstra, René van Roij, and Robert Evans



F=fluid phase; S=solid (fcc) phase; F+S=fluid-solid coexistences region; F+F= metastable fluid-fluid coexistence; S+S=metastable solid-solid coexistence.

Solid lines: results of the effective one component system

Data points: results from the fully microscopic binary mixture

Remarks:

- simulations of the full mixture to low enough packing fraction of specie 2
- comparison between the effective one component model and the mixture suggests that higher order interaction terms are irrelevant to the thermodynamics of the mixture

The effective one-component system

Density Functional Theory:

$$\exp[-\beta\Omega] = \sum_{N_2=0}^{\infty} \frac{z_2^{N_2}}{N_2!} \text{Tr}_2 \exp[-\beta(H_{12} + H_{22})]$$

$$z_2 = \frac{\exp(\beta\mu_2)}{\Lambda_2^3}$$

$\Omega = \Omega(\{\mathbf{R}\}, N_1, z_2, V, T)$ grand-potential of a fluid species 2 in the external field of a fixed configuration of N_1 particles of species 1

$$H^{\text{eff}} = H_{11} + \Omega.$$

Consider Ω a functional of the external field, i.e. the interaction of the solvent with the large particles: $\Omega = \Omega(T, V, z_2, [\Phi])$

$$\Phi(\vec{r}) = \sum_{i=1}^{N_1} \phi_{12}(\vec{r} - \vec{R}_i)$$

The partition function is also a functional:

$$\Xi(T, V, z_2, [\Phi]) = \sum_{N_2=0}^{\infty} \frac{z_2^{N_2}}{N_2! \Lambda_2^{3N_2}} \int_V dr^{N_2} e^{-\beta H_{22}^{(n)}} e^{-\beta \int_V dr \hat{\rho}(r) \Phi(r)}$$

$$\hat{\rho}(r) = \sum_{i=1}^{N_2} \delta(\vec{r} - \vec{r}_i)$$

density operator of specie 2

Using functional differentiation of Ω wrt $u(\mathbf{r}) = \mu_2 - \Phi(\mathbf{r})$ (“local” chemical potential) we get a hierarchy of correlation functions:

$$\frac{\delta\Omega}{\delta u(\mathbf{r})} = - \langle \hat{\rho}(\mathbf{r}) \rangle = -\rho(\mathbf{r})$$

$$\frac{\delta^2\Omega}{\delta u(\mathbf{r})\delta u(\mathbf{r}')} = -\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')} = -\beta [\langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle] = -\beta G^{(2)}(\mathbf{r}, \mathbf{r}')$$

.....

$$\langle \hat{\rho}(r) \rangle = \rho = \frac{N}{V}$$

Homogeneous and isotropic fluid:

$$G^{(2)}(r, r') = \rho^2 [g(r - r') - 1] + \rho\delta(r - r')$$

In DFT one focus on functional of the density ρ rather than on functional of the external field. The density itself is a functional of $u(\mathbf{r})$. $\rho(\mathbf{r})$ and $u(\mathbf{r})$ are conjugated fields and $\rho(\mathbf{r})$ can be consider as independent variable by operating a Legendre transform

$$F[\rho] = \Omega[\rho] + \int_V d\mathbf{r} \rho(\mathbf{r}) u(\mathbf{r})$$

Helmholtz free energy for inhomogeneous systems

$F[\rho]$ is a unique functional of the density without any reference to the external potential. It is an intrinsic property of the system (i.e. of the many body interactions).

At fixed “local” chemical potential $u(\mathbf{r})$, $\rho(\mathbf{r})$ plays the role of an “order” parameter and the equilibrium local density is that which minimize the generalization of Ω (Landau free energy functional)

$$\Omega_V[\tilde{\rho}] = F[\tilde{\rho}] - \int_V d\mathbf{r} \tilde{\rho}(\mathbf{r}) u(\mathbf{r})$$

The equilibrium density is obtained at the minimum

$$\left. \frac{\delta \Omega_V[\tilde{\rho}]}{\delta \rho(\tilde{r})} \right|_{\tilde{\rho}=\rho(r)} = 0 \quad \iff \quad \Omega_V[\rho] = \Omega[\Phi]$$

which corresponds to

$$\boxed{\frac{\delta F[\rho]}{\delta \rho(r)} + \Phi(r) = \mu_2} \quad (1) \quad \text{Euler-Lagrange}$$

Theorem 1: the intrinsic free energy functional $F[\rho]$ is a unique functional of the one particle density $\rho(r)$, i.e. for a given potential interaction H_{22} , $F[\rho]$ has the same functional form whatever the external potential $\Phi(r)$. This statement is equivalent to saying that there is only one external potential that can be associated with a given density profile $\rho(r)$, the equilibrium profile.

Theorem 2: the auxiliary functional $\Omega_V[\tilde{\rho}] = F[\tilde{\rho}] - \int_V d\mathbf{r} \tilde{\rho}(\mathbf{r}) u(\mathbf{r})$

reaches its minimum when the trial density profile $\tilde{\rho}(r)$ coincides with the equilibrium density profile (see R Evans, Adv. Phys. 28, 143 (1979) for the proofs)

Equation (1) allows, in principle, a determination of the equilibrium density for any given external potential. However, $F[\rho]$ being a property of an interacting many-body system, is in general a highly non trivial object which is unknown. For classical systems it factors in ideal and excess part

$$F[\rho] = F_{id}[\rho] + F_{ex}[\rho] \quad \text{and the ideal part is local} \quad F_{id}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\log(\Lambda^3 \rho(\mathbf{r})) - 1]$$

Ideal gas

$$F_{id}[\rho] = \int d\mathbf{r} f_{id}(\rho(\mathbf{r}))$$

$$F_{id}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\log(\Lambda^3 \rho(\mathbf{r})) - 1]$$

$$f_{id}(\rho(\mathbf{r})) = k_B T \rho [\log(\Lambda^3 \rho) - 1]$$

Using eq. (I) we obtain:

$$\frac{\delta F_{id}}{\delta \rho(r)} = k_B T \log[\Lambda^3 \rho(r)] = \mu - \Phi(r)$$

$$\rho(r) = \frac{e^{[\mu - \Phi(r)]/k_B T}}{\Lambda^3} = z e^{-\Phi(r)/k_B T} \quad \text{Barometric law}$$

Excess free energy

$F_{ex}[\rho]$ can be used to derive another hierarchy of the so called “direct correlation functions”

$$\begin{aligned}c^{(1)}(r) &= -\frac{\delta\beta F_{ex}[\rho]}{\delta\rho(r)} \\c^{(2)}(r_1, r_2) &= \frac{\delta c^{(1)}(r_1)}{\delta\rho(r_2)} = -\frac{\delta^2\beta F_{ex}[\rho]}{\delta\rho(r_1)\delta\rho(r_2)} = c^{(2)}(r_2, r_1) \\&\dots \\&\dots \\c^{(n)}(r_1, \dots, r_n) &= \frac{\delta c^{(n-1)}(r_1, \dots, r_{n-1})}{\delta\rho(r_n)}\end{aligned}$$

Using the definition of $c^{(1)}$ above and the ideal gas free energy in the Euler-Lagrange equation we obtain

$$\log(\Lambda^3 \rho(r)) - c^{(1)}(r) + \beta\Phi(r) = \beta\mu \quad \Longrightarrow \quad \boxed{\rho(r) = ze^{[-\beta\Phi(r) + c^{(1)}(r)]}} \quad (2)$$

$c^{(1)}$ represents the part of the density profile coming from the direct many-body interactions. It is the classical analogous of the effective one-body potential in the Kohn-Sham theory.

Eq. (2) is the link between single body correlations $\rho^{(1)}(r)$ and $c^{(1)}(r)$. An analogous link between two body correlations $h^{(2)}(r, r')$ and $c^{(2)}(r, r')$ is the Ornstein-Zernike relation

$$\boxed{h^{(2)}(r, r') = c^{(2)}(r, r') + \int_V dr'' c^{(2)}(r, r'') \rho(r'') h^{(2)}(r'', r')}$$

Excess free energy: weak inhomogeneity

Φ be a weak perturbation applied to the homogeneous reference system. To linear order in the field, the induced density profile is (Linear Response Theory)

$$\Delta\rho(r) = \rho(r) - \rho_0 = \int d^3r' \chi_0(r-r') \Phi(r') \quad \text{with}$$

$$\chi_0(r-r') = \left. \frac{\delta\rho(r)}{\delta\Phi(r')} \right|_{\Phi=0} = \left. \frac{\delta\rho(r)}{\delta u(r')} \right|_{u=\mu} = -\beta G^{(2)}(r-r') = -\beta\rho_0 \left[\rho_0 h^{(2)}(r-r') + \delta(r-r') \right]$$

In a periodic system

$$\Phi(r) = \frac{1}{V} \sum_k \phi_k e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Delta\hat{\rho}_k = -\beta\rho_0 S_0(k) \phi_k$$

$$S_0(k) = \frac{1}{N} \langle \hat{\rho}_k \hat{\rho}_{-k} \rangle = 1 + \rho_0 \hat{h}_k \quad \text{Structure factor}$$

$$\hat{\chi}_0(k) = \frac{\Delta\hat{\rho}_k}{\phi_k} = -\beta\rho_0 S_0(k) \quad \text{FDT (Yvon)}$$

From OZ for the homogeneous systems: $S_0(k) = \frac{1}{1 - \rho\hat{c}^{(2)}(k)} \xrightarrow{k \rightarrow 0} \frac{\chi_T}{\chi_T^{(0)}}$

which is the linear response of the local density to a variation of pressure

Excess free energy: weak inhomogeneity

The LRT is closely related to the quadratic approximation for the intrinsic free energy functional. For weakly inhomogeneous density perturbations ($|\Delta\rho|/\rho \ll 1$) we can expand the functional up to second order around the equilibrium uniform state (minimum)

$$F[\rho] \simeq F[\rho_0] + \int d^3r \int d^3r' \Delta\rho(r) A(r, r') \Delta\rho(r')$$

a) $F[\rho_0] = Vf(\rho_0)$ is the free energy of the uniform system

b) at equilibrium the linear term vanishes

c) the reference system is homogenous and isotropic: $A(r, r') = A(|r - r'|)$

$$F[\rho] \simeq Vf(\rho_0) + \frac{1}{2V} \sum_k \hat{A}_k \Delta\rho_k \Delta\rho_{-k} + O(\delta\rho^3)$$

Using this form in the variational principle one gets:

$$\hat{A}_k \Delta\rho_k = -\Phi_k \quad \Longrightarrow \quad \hat{A}_k = -\frac{1}{\hat{\chi}_0(k)} = \frac{k_B T}{\rho_0 S_0(k)}$$

To quadratic order in the density fluctuations

$$F[\rho_0 + \Delta\rho] \simeq Vf(\rho_0) + \frac{1}{2V\rho_0} \sum_k \frac{\Delta\rho_k \Delta\rho_{-k}}{S_0(k)} + O(\delta\rho^3)$$

Excess free energy: slow modulation limit

Long wavelength inhomogeneities: $|\Delta\rho|/\rho = l/\xi \ll l/\xi_0$ with ξ_0 the typical correlation length in the bulk. It is possible to define a local free energy density and assume local thermodynamic equilibrium:

Local Density Approximation (LDA):
$$F[\rho] = \int_V dr f(\rho(r))$$

At variance with electronic problems, it is an approximation for $F_{\text{ex}}[\rho]$ only.

Variational principle within LDA

$$f'(\rho(r)) = \frac{P(\rho(r)) + f(\rho(r))}{\rho(r)} = \mu - \Phi(r)$$

$$\nabla P(r) = -\rho(r)\nabla\Phi(r) \quad \text{mechanical equilibrium}$$

Gradient corrections: expansion of the intrinsic free energy functional in powers of the l/ξ

$$F[\rho] = \int_V dr [f_0(\rho(r)) + f_2(\rho(r))|\nabla\rho|^2]$$

Expanding to second order in $\Delta\rho$

$$\begin{aligned} F[\rho] &= \int_V dr \left\{ f_0(\rho_0) + \frac{1}{2} f_0''(\rho_0) [\Delta\rho]^2 + f_2(\rho_0) |\nabla\Delta\rho|^2 \right\} \\ &= V f_0(\rho_0) + \frac{1}{2V} \sum_k [f_0''(\rho_0) + f_2(\rho_0)k^2] \Delta\rho_k \Delta\rho_{-k} \end{aligned}$$

$$S_0(k) \sim \frac{S_0(0)}{1 + \xi^2 k^2} \quad k \rightarrow 0 \quad (\text{RPA})$$

$$\xi^2 = \rho_0 S_0(0) f_2(\rho_0)$$

Long range interactions: mean field theory

For long range interactions a local approximation (even with gradient corrections) is in general not adequate. To perform perturbation theory we can split the interaction potential $v(r)$ in two parts: a reference potential $v_0(r)$ and a “perturbation” $w(r)$

$$v_\lambda(r, r') = v_0(r, r') + \lambda w(r, r') \quad 0 \leq \lambda \leq 1$$

Considering F a functional of the pair interaction

$$2 \frac{\delta F[v]}{\delta v(r, r')} = \rho^{(2)}(r, r')$$

and integrating this expression one gets

$$\begin{aligned} F[\rho] &= F_0[\rho] + \frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' \rho_\lambda^{(2)}(r, r') w(r, r') = \\ &= F_0[\rho] + \frac{1}{2} \int d^3r d^3r' \rho(r) w(r, r') \rho(r') + F_{corr}[\rho] \end{aligned}$$

$$F_{corr}[\rho] = \frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' h_\lambda^{(2)}(r, r') \rho(r) w(r, r') \rho(r')$$

- Mean Field approximation (MFA): $F_{corr}[\rho]=0$
- Starting point for the Poisson-Boltzmann theory of electric double layers
- Taking the second functional derivative of $F[\rho]$ within MFA provides the RPA for $c^{(2)}$

$$c^{(2)}(r, r') = c_0^{(2)}(r, r') - \beta w(r, r')$$

Electric double layers

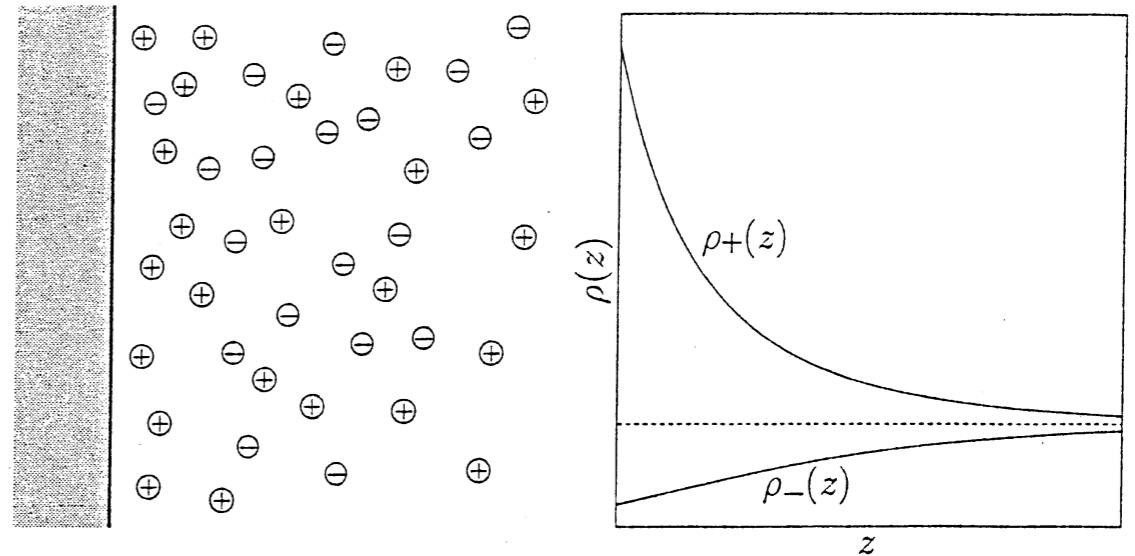
Charge surfaces or mesoparticles in water will assume a net free charge by releasing anions or cations (*counterions*) because of the highly dielectric permittivity of the solvent. There is a balance between electrostatic attraction between polyions and counterions and their thermal motion. Moreover in water dissolved electrolytes carrying positive and negative free charges (salt) are also present. The region in which the charge distribution of microions varies around the polyion is called *electric double layer*.

Primitive model of electrolytes: on the scale of the thickness of the double-layer, the discrete nature of the solvent can be ignored and water is replaced by a dielectric continuum with permittivity ϵ

Single charged plane

Impenetrable plane at $z=0$ with surface charge σ (<0) and monovalent counterions.

Compute the density profile within mean field approximation neglecting interactions between microions:



$$\begin{aligned}
 F[\rho_+(z), \rho_-(z)] &= F_{id}[\rho_+] + F_{id}[\rho_-] + F_{coul}[\rho_c(z)] \\
 &= \sum_{\alpha=\pm} k_B T \int_0^{\infty} dz \rho_{\alpha}(z) \{ \log [\Lambda_{\alpha}^3 \rho_{\alpha}(z)] - 1 \} + \frac{e^2}{2} \int_0^{\infty} dz [\rho_+(z) - \rho_-(z)] \Psi(z)
 \end{aligned}$$

$$\frac{d^2 \Psi(z)}{dz^2} = \frac{e^2}{\epsilon_0 \epsilon} [\rho_+(z) - \rho_-(z)] \quad \text{Poisson equation}$$

Electric double layers

applying the Variational principle

$$k_B T \log [\Lambda_\alpha^3 \rho_\alpha(z)] \pm e\Psi(z) = \mu_\alpha \quad \alpha = \pm$$

$$\rho_\pm(z) = \rho_0 e^{\mp e\beta\Psi(z)} \quad \text{Boltzmann eq.} \quad \rho_0 = \text{positive and negative charge density at infinity}$$

Substituting Boltzmann into Poisson we get *Poisson-Boltzmann* equation

$$\frac{d^2\Psi(z)}{dz^2} = \frac{2e\rho_0}{\epsilon_0\epsilon} \sinh[\beta e\Psi(z)]$$

$$\lim_{z \rightarrow \infty} \frac{d\Psi(z)}{dz} = 0 \quad \text{boundary conditions}$$

$$-\left. \frac{d\Psi(z)}{dz} \right|_{z=0} = \frac{\sigma}{\epsilon_0\epsilon} \quad \epsilon_{in} = \epsilon_{out}$$

Counterions number density: $\rho_N = \rho_+ + \rho_-$

From Boltzmann

$$\frac{d\rho_N(z)}{dz} = e\beta\Psi'(z)[\rho_+ - \rho_-] = \frac{\epsilon_0\epsilon}{2}\beta \frac{d}{dz} \left(\frac{d\Psi(z)}{dz} \right)^2 \quad \Longrightarrow \quad k_B T[\rho_N(z) - \rho] = \frac{\epsilon_0\epsilon}{2} E^2(z)$$

Mechanical equilibrium condition:
the variation of osmotic pressure with z must be balanced by the electrostatic pressure

Electric double layers

Enhancement of the microions concentration at contact is quadratic with σ . $\rho_N(0) - \rho = \frac{\sigma^2}{2\epsilon_0\epsilon}$

For large σ , PB breaks down predicting density corresponding to packing fraction larger than close-packing. Remedy by introducing a *Stern* layer of tightly bound counterions which partially screen the surface charge. PB theory now applies to the *diffusive* layer only.

The thickness of the Stern layer can be treated as a phenomenological parameter.

Solution of PB (analytical)

$$\Psi(z) = \frac{4k_B T}{e} \operatorname{arctanh}(g e^{-\kappa_D z})$$

$$g = \tanh\left(\frac{e\Psi(0)}{4k_B T}\right) \implies \rho_{\pm} = \rho_0 \left[\frac{1 \mp g e^{-\kappa_D z}}{1 \pm g e^{-\kappa_D z}} \right]^2$$

$$\kappa_D = \lambda_D^{-1} = \sqrt{\frac{e^2(\rho_+ + \rho_-)}{k_B T \epsilon_0 \epsilon}} \quad \text{inverse Debye screening length}$$

Linear Poisson-Boltzmann: if ($\beta e\Psi < 1$) PB can be linearized ($\sinh(x) \sim x$)

$$\Psi(z) = \Psi(0) e^{-\kappa_D z} = \frac{\sigma}{\epsilon_0 \epsilon \kappa_D} e^{-\kappa_D z}$$

$$\rho_{\pm} = \rho_0 \pm \kappa_D \frac{|\sigma|}{2\epsilon} e^{-\kappa_D z}$$

Electric double layers

Two charged planes:

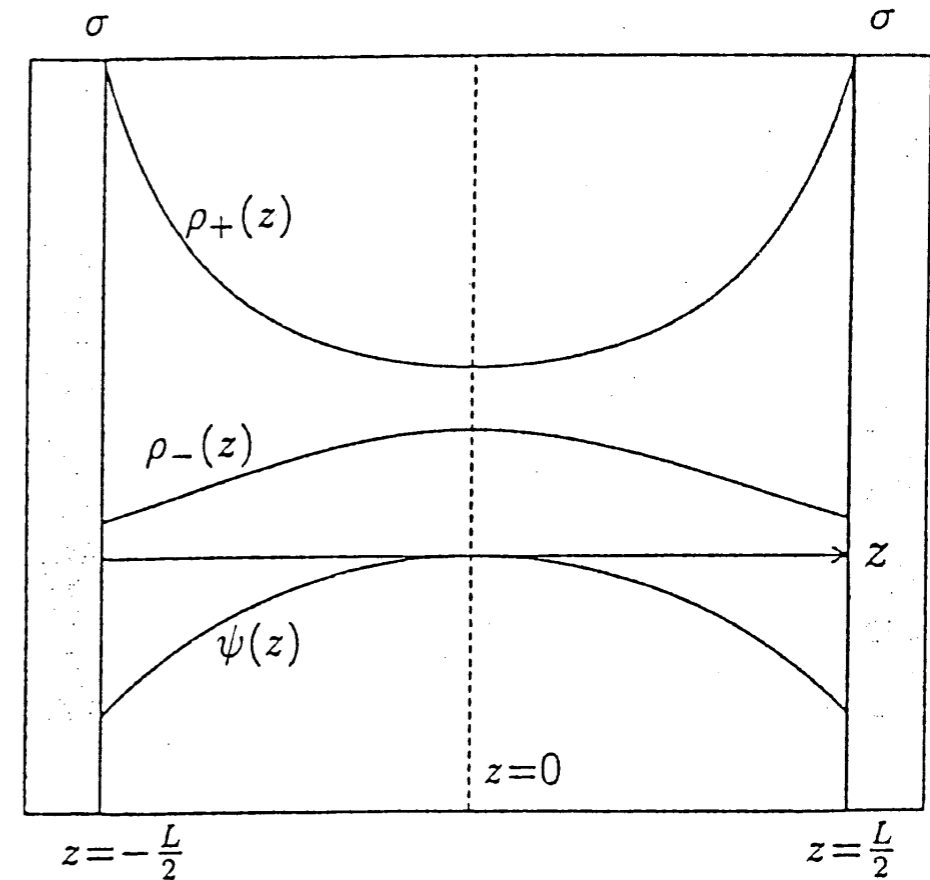
- The solvent confined between the two planes contains monovalent co and counterions in equilibrium with a solution in an infinite reservoir fixing the chemical potential of the non-interacting ions $\mu_\alpha = k_B T \log(\Lambda^3 \rho_\alpha)$.
- The midplane $z=0$ is a symmetry plane and $E(0)=0$.
- The electroneutrality condition is

$$e \int_{-L/2}^0 \rho_c(z) dz = e \int_0^{L/2} \rho_c(z) dz = -\sigma$$

$$-\left. \frac{d\psi(z)}{dz} \right|_{z=-L/2} = \frac{\sigma}{\epsilon_0 \epsilon}$$

boundary
conditions

$$\left. \frac{d\psi(z)}{dz} \right|_{z=0} = 0$$



The disjoining pressure, i.e. the force per unit area to keep the two repelling plane at distance L apart, is obtained from the mechanical equilibrium condition

$$P(L) = \pi(z) - \frac{\epsilon_0 \epsilon}{2} \left[\frac{d\psi(z)}{dz} \right]^2 = k_B T \rho_N(z) - \frac{\epsilon_0 \epsilon}{2} [E(z)]^2 = k_B T \rho_N(0)$$

$$\implies P(L) - P(\infty) = k_B T [\rho_N^L(0) - \rho] \quad \text{Disjoining Pressure}$$

Electric double layers

In this case PB is not analytically solvable. We can solve the linearized version obtaining

$$\psi(z) = \frac{\psi_o}{\sinh(\kappa_D L/2)} \cosh(\kappa_D z) \quad \text{with} \quad \psi_o = \sigma / (\epsilon_o \epsilon \kappa_D)$$

$$\Delta P(L) = \frac{\rho}{2} [\beta e \psi(0)]^2 = \frac{2\sigma^2}{\epsilon_o \epsilon} e^{-\kappa_D L} \quad \text{Exponential decay of the disjoining pressure}$$

Charged stabilized colloidal suspensions

PHYSICAL REVIEW E

VOLUME 59, NUMBER 2

FEBRUARY 1999

Phase diagram of charge-stabilized colloidal suspensions: van der Waals instability without attractive forces

René van Roij and Marjolein Dijkstra
Jean-Pierre Hansen

Highly charged mesoscopic spherical polyions plus microscopic coions and counterions dissolved in solvent (water).

N_p polyions of charge $-Ze$;

$N_c = ZN_p$ counterions of charge $+e$;

N_s fully dissociated pairs of monovalent salt ions of charge $+/-e$

Primitive model of water.

Short range hard-core repulsion between polyions and between microions and polyions.

Remarks:

a) dispersion interaction between polyions are absent: justified in the low salt-weak screening regime. At high salt concentration the coulomb repulsion competes with the dispersion attractive force ($1/R^6$).

b) hard sphere repulsion between microions is not necessary for the stability within the mean field treatment

c) the model hamiltonian admits a well defined thermodynamic limit because of the global charge neutrality

Charged stabilized colloidal suspensions

$$\text{DFT: } F[\rho_+, \rho_-] = F_{id}[\rho_+] + F_{id}[\rho_-] + F_{coul}[\rho_c] + F_{ext}[\rho_+, \rho_-] + F_{corr}[\rho_+, \rho_-]$$

$$F_{id} = \sum_{\alpha=\pm} k_B T \int_0^\infty dz \rho_\alpha(z) \{ \log [\Lambda_\alpha^3 \rho_\alpha(z)] - 1 \}$$

$$F_{coul} = \frac{e^2}{2\epsilon} \int d^3r d^3r' \frac{[\rho_+(r) - \rho_-(r)][\rho_+(r') - \rho_-(r')]}{|r - r'|}$$

$$F_{ext} = \sum_{\alpha=\pm} \int d^3r \rho_\alpha(r) U_\alpha(r)$$

$$F_{corr} = 0 \quad \text{Mean Field approx.}$$

$$U_\pm(\mathbf{r}) = \sum_{j=1}^{N_p} u_\pm(\mathbf{r} - \mathbf{R}_j)$$

Polyions-counterions interactions

$$u_\pm(\mathbf{r}) = \begin{cases} \mp \frac{Ze^2}{\epsilon} \frac{1}{r}, & r > R \\ \mp \frac{Ze^2}{\epsilon} \frac{1 \mp \gamma_\pm}{R}, & r < R. \end{cases} \quad \text{“pseudopotential” constant inside the polyion}$$

Charged stabilized colloidal suspensions

Expanding the functional to quadratic order in the fluctuations the final result for the effective two body interaction between polyions is

$$V_p^{\text{eff}}(\{\mathbf{R}_i\}) = \Phi_0 + \sum_{i < j}^{N_p} v_{\text{eff}}(R_{ij}),$$

$$v_{\text{eff}}(r) = \begin{cases} \infty, & r < 2R \\ \frac{Z_{>}^2 e^2}{\epsilon} \frac{\exp(-\kappa r)}{r}, & r > 2R, \end{cases}$$

Hard sphere repulsive Yukawa - DLVO potential

$$\Phi_0(V, T, n_p, n_s) = F_{\text{id}}(V, T, n_+) + F_{\text{id}}(V, T, n_-)$$

$$- \frac{Z^2 e^2 N_p \kappa R}{2 \epsilon R (1 + \kappa R)} + k_B T \frac{\eta \bar{\sigma}}{1 - \eta} V - \frac{1}{2} \frac{4 \pi e^2}{\epsilon \kappa^2} (Z n_p)^2 V$$

$$Z_{>} = Z \left(\frac{\exp(\kappa R)}{1 + \kappa R} \right). \quad \text{effective polyion charge}$$

$$\bar{\sigma} = \frac{2n_+ n_-}{n_+ + n_-} = \frac{2n_+ n_-}{n}$$

$$\eta = \frac{4 \pi R^3}{3} n_p \quad \text{polyions packing fraction}$$

$$\kappa^2 = 4 \pi l n \quad \text{Debye inverse screening}$$

$$l = \beta e^2 / \epsilon \quad \text{Bjerrum length}$$

the volume term dominates the phase diagram now

Charged stabilized colloidal suspensions

Repulsive Yukawa system:

single fluid phase at high T with a freezing line to a fcc phase for large κ and to a bcc phase for small κ
 fluid-fcc-bcc triple point at $\kappa n_p^{-1/3} \sim 4.9$

Charge stabilized colloids: at $T=300K$

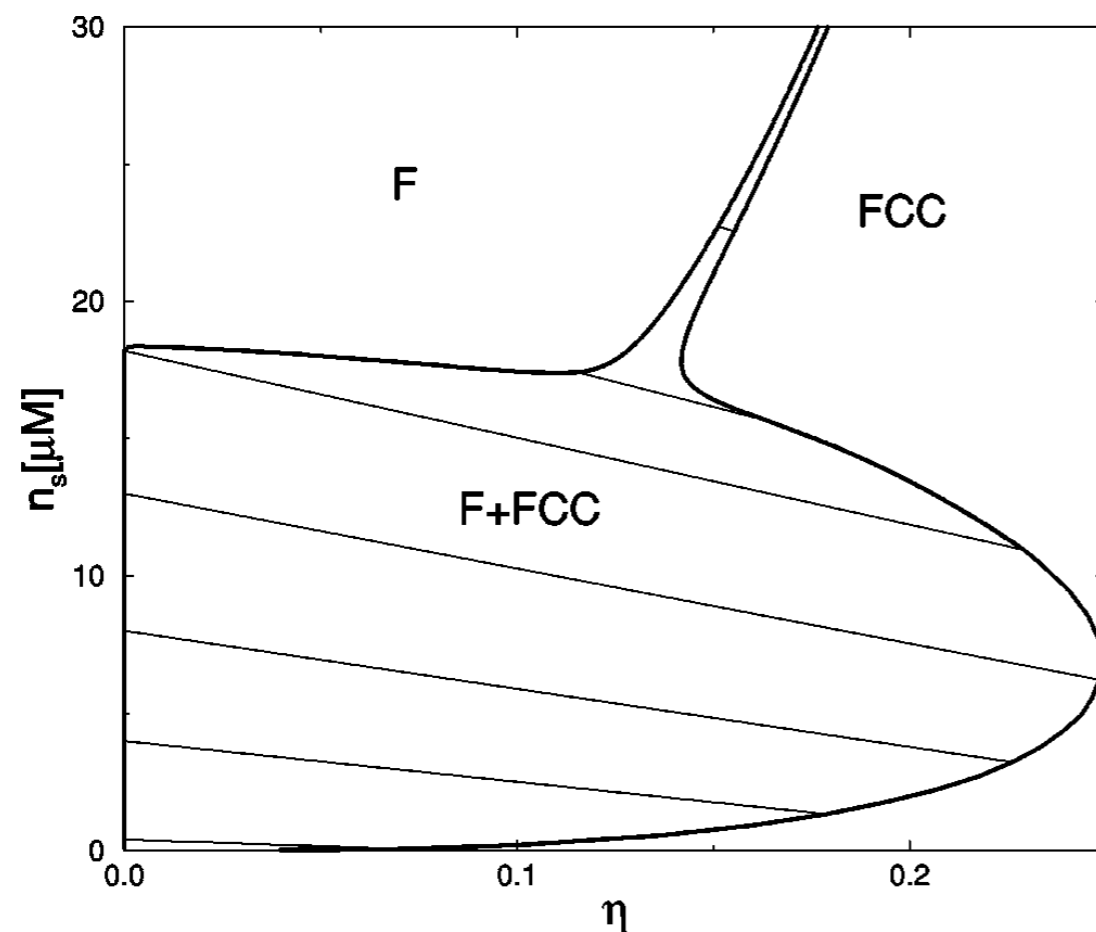


FIG. 3. Room-temperature phase diagram of aqueous colloidal suspension (charge $Z=7300$ and diameter $D=652$ nm) as a function of colloid packing fraction η and salt concentration n_s (μM). The narrow fluid (F) to fcc-solid transition at $n_s > 20 \mu\text{M}$ broadens and narrows again at lower salt concentrations. The (thinner) tie lines connect coexisting state points on the (thicker) phase boundaries.

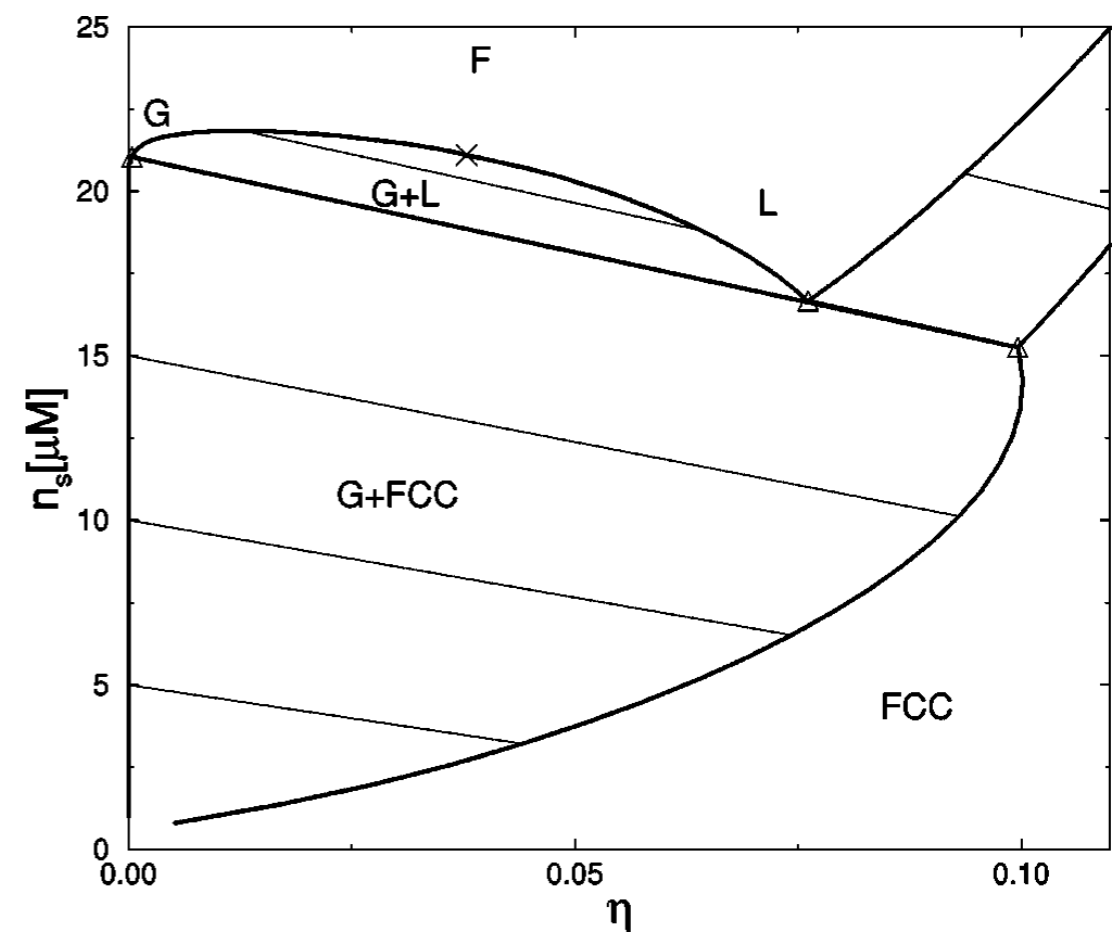


FIG. 5. As in Fig. 3, but with $Z=2086$ and $D=349$ nm. There is now stable coexistence of a gas (G) and liquid (L) phase between a critical point (\times) and triple points (Δ). Above the critical point the homogeneous fluid (F) phase is stable at low η and freezes into the fcc solid at higher η . Below the triple point, there is G -fcc coexistence.

Charged stabilized colloidal suspensions

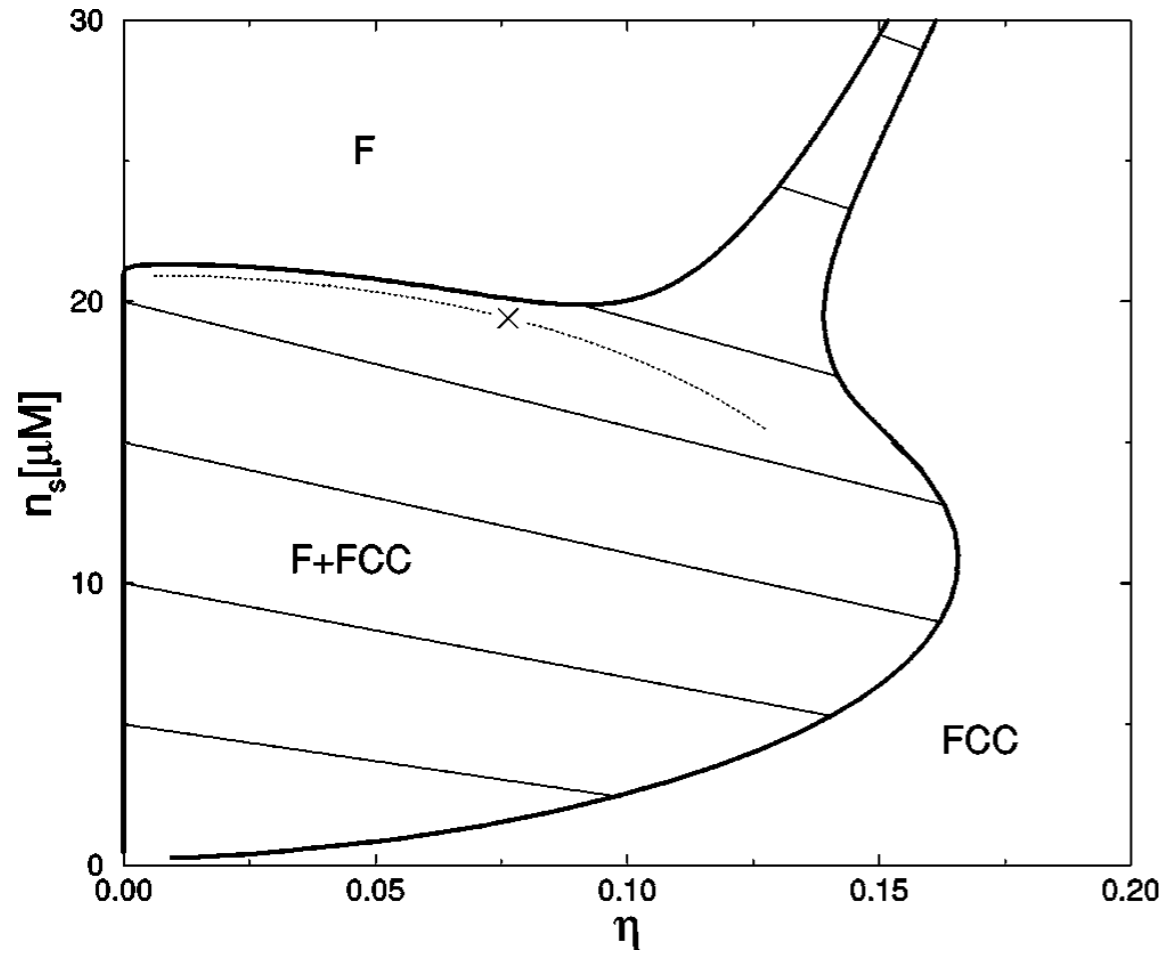


FIG. 4. As in Fig. 3, but with $Z=3650$ and $D=461$ nm. The dotted curve denotes a metastable gas-liquid binodal with the critical point indicated by \times .

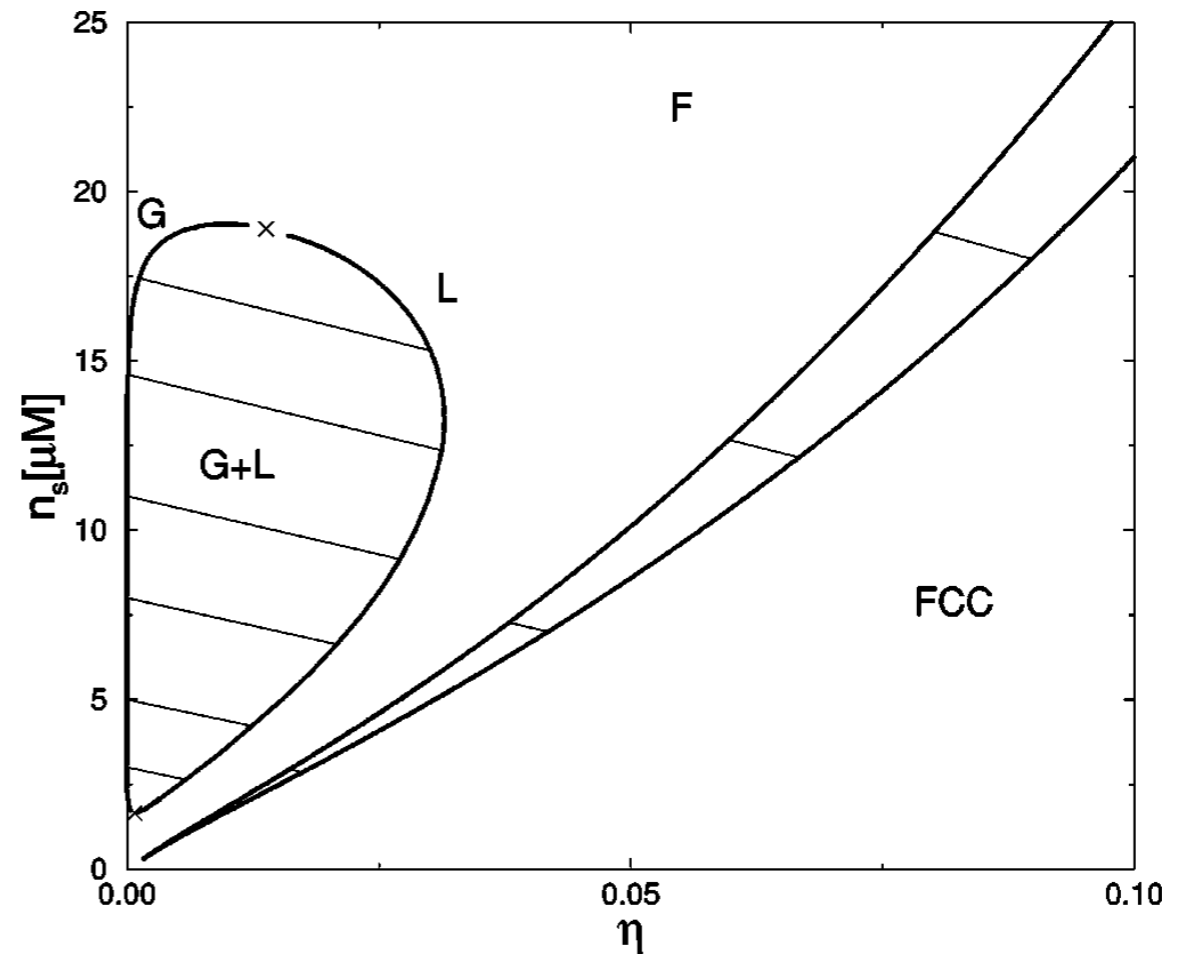


FIG. 6. As in Fig. 3, but with $Z=1217$ and $D=266$ nm. Here the van der Waals-like instability only persists at such low η that it is decoupled from the freezing transition. The G - L coexistence exhibits *two* critical points (\times) while the freezing transition does not show any broadening at low n_s .

Due to the volume term a fluid-fluid transition and a triple point (gas-fluid-solid) appear even in absence of direct attractions between the particles.

A fluid-gas or solid-gas coexistence is in qualitative agreement with experimental observations