# Density Functional Methods at Finite Temperature

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## Abstract

After a brief summary of Density Functional Theory (DFT) for both classical and quantum inhomogeneous systems, the theory is applied to the simulation of systems having widely different time and/or length scales. These include "ab-initio" Molecular Dynamics and Monte Carlo simulations of colloidal suspensions, polyelectrolytes and metallic systems.

## I. INHOMOGENEOUS SYSTEMS AND EFFECTIVE INTERACTIONS

Density Functional Theory (DFT) is the art of dealing with *inhomogeneous* many-particle systems of Condensed Matter Science, in which translational and/or rotational invariance is broken either spontaneously (as in crystals) or by an external field. The main objective of these notes is to show how DFT can be put to use in the simulations of highly asymmetric systems, made up of at least two species of particles with widely different masses and sizes. The resulting difference in time and length scales does not allow the "large" and "small" particles to be described on an equal footing within traditional Monte Carlo (MC) or Molecular Dynamics (MD) algorithms. It will often prove more efficient to adopt a discrete ("particle") representation of the large particles, referred to hereafter as species 1, which will always be assumed to obey classical Statistical Mechanics, while a continuum ("field") representation is used for the small particles (species 2), which may be either classical or partially degenerate. The basic field for the latter is the one-particle density (or density profile) $\rho(\mathbf{r})$.

Two examples of such asymmetric systems are polyelectrolytes, made up of mesoscopic polyions and microscopic counterions (both classical), and ion-electron systems, including semiconductors, metals and plasmas, where the ions can usually be treated as classical, while the electrons are almost invariably degenerate.

A formal reduction of the initial two-component system to an effective one-component system, involving only the degrees of freedom of the large particles, may be carried out as follows; it is worth stressing that this derivation does not depend in any crucial way on the asymmetry between the two two species. For the sake of simplicity, all particles will be assumed to have translational degrees of freedom only. Let $\{\mathbf{R}_i, \mathbf{P}_i\},\ 1 \leq i \leq N_1$ and $\{\mathbf{r}_j, \mathbf{p}_j\},\ 1 \leq j \leq N_2$ denote the sets of coordinates and momenta of the large and small particles respectively. The total Hamiltonian of the system may be split into three terms:

$$H = H_1(\{\mathbf{R}_i, \mathbf{P}_i\}) + H_2(\{\mathbf{r}_j, \mathbf{p}_j\}) + V_{12}(\{\mathbf{R}_i, \mathbf{r}_j\}). \tag{1}$$

The parts $H_\alpha$ ($\alpha = 1, 2$), made up of kinetic and potential energy contributions ($H_\alpha = K_\alpha + V_{\alpha\alpha}$), involve the coordinates and momenta of species $\alpha$ only, while $V_{12}$ is the potential energy of interaction between particles of different species. The canonical partition function of the total system is:

$$Q_{N_1,N_2} = \mathrm{Tr}\, e^{-\beta(H_1+H_2+V_{12})} \tag{2}$$

where $\beta = 1/k_BT$ is the inverse temperature ($k_B$ is the Boltzmann's constant), and the trace is a sum over a complete set of quantum states, which reduces to a phase-space integration for degrees of freedom which may be treated classically. Since this is the case for the large particles (species 1), the trace operator factorizes according to:

$$Q_{N_1,N_2} = \mathrm{Tr}_1 \left[ e^{-\beta H_1} \mathrm{Tr}_2 e^{-\beta(H_2+V_{12})} \right]. \tag{3}$$

The second trace, over the degrees of freedom (or quantum states) of species 2, is just the partition function $Q_{N_2}(\{\mathbf{R}_i\})$ of the *inhomogeneous* system of small particles in the "external" field of the large particles frozen at positions $\{\mathbf{R}_i\}$. The corresponding Helmholtz free energy $F_2(\{\mathbf{R}_i\}) = -k_B T \log(Q_{N_2}(\{\mathbf{R}_i\}))$ depends parametrically on the $\{\mathbf{R}_i\}$, and the total partition function now reduces to:

$$Q_{N_1,N_2} = \mathrm{Tr}_1 e^{-\beta[H_1+F_2(\{\mathbf{R}_i\})]} = \frac{1}{N_1!\Lambda^{3N_1}} \int d^{N_1}\mathbf{R} e^{-\beta V_{11}^{eff}(\{\mathbf{R}_i\})} \tag{4}$$

where the factor $\Lambda^{-3N_1}$ ($\Lambda$ denotes the de Broglie wavelength of a large particle) results from the trivial integration over the (classical) momenta of species 1, while the *effective* potential energy of interaction between particles of that species is the sum of the direct term $V_{11}$ and an induced contribution $F_2$:

$$V_{11}^{eff}(\{\mathbf{R}_i\}) = V_{11}(\{\mathbf{R}_i\}) + F_2(\{\mathbf{R}_i\}). \tag{5}$$

It is important to stress that, while $V_{11}$ may be essentially pair-wise additive (as is the case, e.g., for direct coulombic interactions), the induced contribution $F_2$ is state-dependent and generally many-body in nature.

The above reduction is formally exact, but an effective calculation scheme hinges on the formidable problem of obtaining accurate estimates of the free energy of species 2, for any configuration of species 1. In practice this is achieved within the density functional formalism, which relies in an essential way on a uniqueness theorem and a variational principle, to be explicitly formulated in the next section. In connection with the present reduction scheme, these theorems imply that the free energy $F_2$ is a *functional* of the density profile $\rho_2(\mathbf{r})$ of species 2. This functional reaches its minimum when its profile reaches its equilibrium value for any configuration $\{\mathbf{R}_i\}$ of large particles [which produces the external potential via $V_{12}$; cf. Eq.(1)].

The reduction process may hence be implemented, at least in principle, by standard minimization procedures, within MC or MD simulations.

In MC simulations, configurations of a system of large particles may be sampled from the Boltzmann distribution $P_{N_1}(\{\mathbf{R}_i\}) \sim e^{-\beta V_{11}^{eff}(\{\mathbf{R}_i\})}$ using the usual Metropolis algorithm, provided $F_2[\rho(\mathbf{r})]$ can be minimized efficiently, for each configuration $\{\mathbf{R}_i\}$, by a steepest descent or conjugate gradient method. An illustration of this procedure will be reported in section V.

An efficient MD implementation of the reduction process relies crucially on a clear separation of time scales [1], which requires $m_2/m_1 \ll 1$. Such a separation validates adiabatic dynamics, whereby the physical dynamics of the large (heavy) particles and the dynamic minimization of the free energy of the small (light) particles are carried out in parallel, using some standard finite time-step solver of coupled (classical) equations of motion (Car-Parrinello method [2]). Illustrations of this "ab-initio" MD methodology will be given in sections IV and VI. The effective force acting on particle $i$ $(1 \leq i \leq N_1)$ follows, at each step, from an implicit application of the Hellman-Feynman theorem, provided particles of species 2 constantly remain "sufficiently" close to their "Born-Oppenheimer" (BO) surface (i.e. the surface of lowest free-energy $F_2$). According to this theorem:

$$\mathbf{F}_i = -\nabla_i V_{11}^{eff}(\{\mathbf{R}_j\}) = -\nabla_i V_{11}(\{\mathbf{R}_j\}) - \langle \nabla_i V_{12}(\{\mathbf{R}_j\}, \{\mathbf{r}_l\}) \rangle_{\{\mathbf{R}_i\}}, \tag{6}$$

where the angular bracket denotes an equilibrium average over the degrees of freedom of species 2, for a fixed configuration $\{\mathbf{R}_i\}$ of species 1.

## II. DENSITY FUNCTIONAL THEORY: BASIC PRINCIPLES AND STANDARD APPROXIMATIONS

The reduction process of asymmetric systems, sketched in the previous section, may be effectively carried out, provided an efficient theoretical scheme is available for dealing with inhomogeneous systems characterized by spatially modulated density profiles $\rho(\mathbf{r})$. Familiar examples of systems with broken translational symmetry are the liquid-vapour interface, studied as far back as 1893 by van der Waals [3], an electrolyte solution in the vicinity of a planar electrode, a problem tackled in 1910 by Gouy [4], or a degenerate Fermi gas of valence electrons in the periodic field of an ionic lattice. The common theoretical framework to describe such inhomogeneous systems is DFT, pioneered by Percus [5] for classical fluids and by Hohenberg, Kohn and Sham [6,7] for the degenerate electron gas. Excellent reviews are available, both for classical [8] and quantum [9] DFT, and this section only provides a brief summary of of the basic principles involved, and of some approximation schemes which will be put to use in the perspective of computer simulations. The general formulation will be given for a system at equilibrium in an external field at finite temperature, and holds both for classical and quantum statistics.

The Hamiltonian of a system of $N$ identical particles subject to an external potential $\phi(\mathbf{r})$ reads:

$$H = K_N(\{\mathbf{p}_i\}) + V_N(\{\mathbf{r}_i\}) + \Phi_N(\{\mathbf{r}_i\}). \tag{7}$$

The contribution of the external field to the potential energy may be cast in the form:

$$\Phi_N = \sum_{i=1}^{N} \phi(\mathbf{r}_i) = \int_V d\mathbf{r}\tilde{\rho}(\mathbf{r})\phi(\mathbf{r}), \tag{8}$$

where $\tilde{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$ is the microscopic density operator.

Note that within the reduction scheme of a two-component system to an effective one-component system, the external potential acting on the "small" particles is provided by the "large" particles, i.e.:

$$\phi(\mathbf{r}) = \sum_{i=1}^{N_1} v_{12}(\mathbf{r} - \mathbf{R}_i) \tag{9}$$

where $v_{12}$ is the interaction between one particle of species 1 and the particles of species 2. The considerations of the present section are independent of such an identification. First consider the inhomogeneous system at fixed canonical potential $\mu$, volume $V$ and temperature $T$. The grand partition function involves a summation over all possible values of $N$:

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \mathrm{Tr}_N\, e^{-\beta(H_N - N\mu)} \tag{10}$$

where $\mathrm{Tr}_N$ refers to a classical or quantum-mechanical trace over all states with a fixed value of $N$ (canonical trace). The corresponding grand potential:

$$\Omega(\mu, V, T) = -k_B T \log[\Xi(\mu, V, T)] \tag{11}$$

is clearly a *functional* of the external potential $\phi(\mathbf{r})$ or, more conveniently, of the "intrinsic" local chemical potential $\Psi(\mathbf{r}) = \mu - \phi(\mathbf{r})$. Two successive functional differentiations of $\Omega$ with respect to $\Psi$ yield the one-particle density and the two-point linear-response function (or static susceptibility):

$$-\frac{\delta\Omega[\Psi]}{\delta\Psi(\mathbf{r})} = \frac{1}{\Xi}\sum_N \mathrm{Tr}_N\{e^{-\beta(H_N - N\mu)}\tilde{\rho}(\mathbf{r})\} = \langle\tilde{\rho}(\mathbf{r})\rangle \equiv \rho(\mathbf{r}) \tag{12}$$

$$-\frac{\delta^2\Omega[\Psi]}{\delta\Psi(\mathbf{r})\delta\Psi(\mathbf{r}')} = \frac{\delta\rho(\mathbf{r})}{\delta\Psi(\mathbf{r}')} = \chi(\mathbf{r}, \mathbf{r}'). \tag{13}$$

Eq. (12) defines the one-particle density (or density profile) as the equilibrium statistical average of the microscopic density, while Eq. (13) defines the susceptibility $\chi$. Its physical significance is easily understood by considering the effect of a small change in the external potential ($\phi(\mathbf{r}) \to \phi(\mathbf{r}) + \delta\phi(\mathbf{r})$) on the density profile ($\rho(\mathbf{r}) \to \rho(\mathbf{r}) + \delta\rho(\mathbf{r})$), at constant chemical potential $\mu$. A functional Taylor expansion, limited to linear order, then leads, according to Eq. (13), to the static linear response result:

$$\Delta\rho(\mathbf{r}) = \int d\mathbf{r}'\chi(\mathbf{r}, \mathbf{r}')\delta\Psi(\mathbf{r}') = -\int d\mathbf{r}'\chi(\mathbf{r}, \mathbf{r}')\delta\phi(\mathbf{r}') \tag{14}$$

For a homogeneous system ($\phi(\mathbf{r}) = 0$), transitional invariance implies that the density is uniform, i.e. $\rho(\mathbf{r}) = n = N/V$, and that the susceptibility depends only on the relative distance, i.e. $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r} - \mathbf{r}')$.

A standard perturbation calculation leads to the following expression for $\chi$ [10]:

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B T}\int_0^{\beta\hbar} \frac{d\lambda}{\beta\hbar}\,\langle\Delta\tilde{\rho}(\mathbf{r}, -i\lambda)\Delta\tilde{\rho}(\mathbf{r}')\rangle \tag{15}$$

where $\tilde{\rho}(\mathbf{r}, i\lambda)$ denotes the Heisenberg time-displaced density-fluctuation operator ($\delta\tilde{\rho} = \tilde{\rho} - \rho$) taken at the imaginary time $t = i\lambda$. In the classical ($\hbar \to 0$) limit, Eq. (15) reduces to:

$$k_B T \chi(\mathbf{r}, \mathbf{r}') = \langle \Delta\tilde{\rho}(\mathbf{r}) \Delta\tilde{\rho}(\mathbf{r}') \rangle \equiv \rho(\mathbf{r}) \left[ \delta(\mathbf{r} - \mathbf{r}') + \rho(\mathbf{r}') h^{(2)}(\mathbf{r}, \mathbf{r}') \right] \tag{16}$$

which defines the two-point correlation function $h^{(2)}(\mathbf{r}, \mathbf{r}')$ [11].

It turns out to be much more fruitful to consider the density profile $\rho(\mathbf{r})$, rather than $\Psi(\mathbf{r})$, to be the fundamental field variable. This is exemplified by the fact that a system may be spontaneously inhomogeneous at the microscopic level and thus be characterized by a spatially modulated $\rho(\mathbf{r})$, even in the absence of an external field $\phi(\mathbf{r}) \to 0$, as is the case for crystalline solids, where the local atomic density $\rho(\mathbf{r})$ is periodic rather than uniform. Switching from $\Psi$ to $\rho$ as independent variable ($V$ and $T$ being held constant) entails a corresponding change from the thermodynamic potential $\Omega[\Psi]$ to to the potential $\mathcal{F}[\rho]$. This is achieved by a generalized Legendre transformation:

$$\mathcal{F}[\rho] = \Omega[\Psi] + \int d\mathbf{r} \Psi(\mathbf{r}) \rho(\mathbf{r}) \tag{17}$$

where the new thermodynamic potential $\mathcal{F}[\rho]$ is the intrinsic free-energy which is a functional of $\rho(\mathbf{r})$. The total Helmholtz free energy $F$ is recovered by adding the contribution from the external field:

$$F = \mathcal{F}[\rho] + \int_V d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}) \tag{18}$$

Functional differentiation of (17) leads to:

$$\frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r})} = \Psi(\mathbf{r}) \tag{19}$$

while a further differentiation yields, according to (13):

$$\frac{\delta^2 \mathcal{F}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = \frac{\delta \Psi(\mathbf{r}')}{\delta \rho(\mathbf{r})} = \chi^{-1}(\mathbf{r}, \mathbf{r}') \tag{20}$$

where $\chi^{-1}$ denotes the functional inverse of the susceptibility $\chi(\mathbf{r}, \mathbf{r}')$, i.e.:

$$\int d\mathbf{r}'' \chi^{-1}(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{21}$$

It often proves convenient to split the functional into an "ideal" part, corresponding to a system of non-interacting particles (with the same density profile and temperature), and an "excess" part stemming from the interaction between particles:

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}[\rho]. \tag{22}$$

The inverse response function defined by Eq. (20) splits accordingly into two terms:

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = \chi_{id}^{-1}(\mathbf{r}, \mathbf{r}') - k_B T c^{(2)}(\mathbf{r}, \mathbf{r}') \tag{23}$$

where the second term, resulting from the second functional derivative of $\mathcal{F}_{ex}$, is referred to as the two-particle direct correlation function [11,12].

The functional $\mathcal{F}[\rho]$, which reduces to the ground-state energy of the inhomogeneous system at zero temperature, obeys two fundamental theorems, which were first stated and proved by Hohenberg and Kohn [6] for the ground state, and generalized to finite temperature by Mermin [13]. Both theorems follow easily from a lemma stating that there is a one-to-one correspondence between the fields $\rho(\mathbf{r})$ and $\phi(\mathbf{r})$.

**Theorem 1 (Hohenberg-Kohn)** *For any given system, characterized by the unperturbed Hamiltonian $H_N = K_N + V_N$, the intrinsic free-energy $\mathcal{F}$ is a unique functional of the equilibrium density $\rho(\mathbf{r})$. In other words, the functional form of $\mathcal{F}[\rho]$ is independent of the external potential $\phi(\mathbf{r})$.*

**Theorem 2 (Variational Principle)** *Let $\rho^*(\mathbf{r})$ be a properly normalized trial density profile. The functional*

$$\Omega_\phi[\rho^*] = \mathcal{F}[\rho^*] - \int d\mathbf{r} \rho^*(\mathbf{r}) \Psi(\mathbf{r}) \tag{24}$$

*reaches its minimum when $\rho^*(\mathbf{r})$ coincides with the equilibrium density $\rho(\mathbf{r})$, i.e.*

$$\left. \frac{\delta \Omega_\phi[\rho^*]}{\delta \rho^*(\mathbf{r})} \right|_{\rho^* = \rho} = 0 \tag{25}$$

*and, moreover, $\Omega_\phi[\rho]$ is equal to the equilibrium grand potential $\Omega$.*

In terms of the functional $\mathcal{F}[\rho]$, the variational principle reads:

$$\left. \frac{\delta \mathcal{F}[\rho^*]}{\delta \rho^*(\mathbf{r})} \right|_{\rho^* = \rho} = \Psi(\mathbf{r}) = \mu - \phi(\mathbf{r}). \tag{26}$$

These two theorems are instrumental in all practical applications of DFT.

Henceforth, up to section VI, restriction will be made to classical DFT ($\hbar = 0$ limit). For classical systems, the ideal part of the free-energy functional takes on the particularly simple form appropriate for a classical ideal gas, namely:

$$\mathcal{F}_{id}[\rho] = k_B T \int_V d\mathbf{r} \rho(\mathbf{r}) \{\log[\Lambda^3 \rho(\mathbf{r})] - 1\} \tag{27}$$

where $\Lambda$ is some irrelevant length scale, generally identified with the De Broglie thermal length.

No general expression exists for the non-trivial "excess" part $\mathcal{F}_{ex}$, for which *approximate* functionals have to be constructed, which are tailored for given physical conditions. In the following, four of the most commonly used approximations are briefly described. Each is suited for fairly well-defined physical situations, and has an analog in quantum-mechanical DFT.

### A. Linear response

Linear response theory applies when the external perturbation is of small amplitude compared to the interactions between particles. If the unperturbed system ($\phi = 0$) is homogeneous, the density profile induced by a weak perturbation $\phi(\mathbf{r})$ is given by Eq. (14),

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - n_0 = -\int d\mathbf{r}' \chi_0(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \tag{28}$$

where the index 0 refers to the homogeneous "reference" system. For a spatially periodic perturbation $\phi(\mathbf{r}) = \phi_{\mathbf{k}} e^{i\mathbf{kr}}$ the Fourier components of the density profile are easily expressed with the help of the convolution theorem. Using the result (16), valid for classical systems, as adapted to a homogeneous reference system, the final linear response expression reads [14]:

$$\Delta\rho_{\mathbf{k}} = -\hat{\chi}(\mathbf{k})\phi_{\mathbf{k}} = -\beta n_0 [n_0 \hat{h}^{(2)}(\mathbf{k}) + 1]\phi_{\mathbf{k}} = -\beta n_0 S_0(\mathbf{k}) \phi_{\mathbf{k}} \tag{29}$$

where $\hat{f}$ denotes the Fourier transform of $f$, and $S(\mathbf{k})$ is the static structure factor of the homogeneous reference system [11].

### B. Gradient expansion

If the inhomogeneity is slowly varying in space, on a characteristic scale $\xi$ much larger than the mean spacing between particles, the free-energy density $f[\rho]$ may be formally expanded in powers of $1/\xi$. For an isotropic fluid, rotational invariance then leads to the following gradient expansion [8]:

$$\mathcal{F}[\rho] = \int_V d\mathbf{r} f[\rho(\mathbf{r})] = \int_V d\mathbf{r}\{f_0(\rho(\mathbf{r})) + f_2(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2\} + O(\xi^{-4}). \tag{30}$$

Keeping only the zeroth order term amounts to making the *local density approximation* (LDA); $f_0(\rho(\mathbf{r}))$ is the free-energy per unit volume of a homogeneous fluid of density $n = \rho(\mathbf{r})$, a function (as opposed to a functional) of $\rho(\mathbf{r})$. Note that the ideal contribution (27) to $\mathcal{F}$ is precisely of the LDA form, so that an approximation is only made for $\mathcal{F}_{ex}$.

The quadratic gradient correction to the LDA involves the function $f_2(\rho(\mathbf{r}))$ which is expressible in terms of the direct correlation function [cf. Eq. (23)] of the homogeneous reference system [8]:

$$f_2(\rho(\mathbf{r})) = \frac{k_B T}{12}\int d\mathbf{r}'\mathbf{r}'^2 c_0^{(2)}(\rho(\mathbf{r}); |\mathbf{r}-\mathbf{r}'|). \tag{31}$$

The gradient expansion (30), limited to second order, is the basis of van der Waals' theory of the liquid-vapour interface [3,15] and of Cahn's theory of wetting [16]. Higher-order corrections involve higher moments of $c_0^{(2)}$ (as well as more-than-two-body direct correlation functions). Since $c_0^{(2)}$ is known to behave asymptotically (as $r \to \infty$) like the pair potential [11], the integrals defining higher-order coefficients $f_{2n}$ diverge for long-range interactions, so that the expansion is ill-defined, and should wisely be truncated at second order. In fact, for coulombic interactions, $c_0^{(2)}(r) \sim 1/r$ at large $r$, so that even $f_2$ does not exist. An entirely different approximation scheme is required to handle ionic systems.

### C. Mean-field approximation

For systems with long-range interactions, like ionic systems, *non-local* effects may be expected to become important, which cannot be properly coped with by a gradient expansion.

In the spirit of thermodynamic perturbation theory [11], it proves convenient to split the pair interaction potential between particles into a short-range part $v_0$, usually repulsive, and a long-range contribution $w$, the Coulomb potential in the case of ionic systems:

$$v(\mathbf{r},\mathbf{r}') = v_0(\mathbf{r},\mathbf{r}') + w(\mathbf{r},\mathbf{r}'). \tag{32}$$

If the long-range part $w$ is treated within the van der Waals mean-field approximation, the free-energy functional may be cast in the form [8,11]:

$$\mathcal{F}[\rho] = \mathcal{F}_0[\rho] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r})w(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') \tag{33}$$

where $\mathcal{F}_0[\rho]$ is the intrinsic free-energy functional of the reference system, i.e. a system of particles interacting via $v_0(\mathbf{r},\mathbf{r}')$ only. Since the latter is short-ranged, the gradient expansion may be appropriate to estimate $\mathcal{F}_0[\rho]$. If the LDA is adopted for the latter, the variational principle (26) leads to the following Euler-Lagrange equation for $\rho(\mathbf{r})$:

$$f_0'(\rho(\mathbf{r})) = \mu - \phi(\mathbf{r}) - \int d\mathbf{r} w(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') \tag{34}$$

where $f_0$ is the free-energy density of the homogeneous reference system, and the prime denotes a derivative with respect to the argument. Eq. (34) shows that the long-range interactions act like a self-consistent external (or Hartree) potential; it provides the basis for the study of electric double-layers (cf. Section IV).

### D. Functional Taylor expansion

If, contrary to the situation in section 2B, the inhomogeneity varies rapidly in space, while remaining of small amplitude, it is natural to seek an expansion of $\mathcal{F}_{ex}[\rho]$ around its value for a homogeneous reference system, of density $n$, in powers of the local "order parameter"

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - n. \tag{35}$$

Using the results (20) and (23), one easily arrives at:

$$\mathcal{F}_{ex}[\rho] = \mathcal{F}_{ex}(n) + \mu_{ex}(n) \int_V d\mathbf{r} \Delta\rho(\mathbf{r})$$
$$- \frac{k_B T}{2} \int d\mathbf{r} \int d\mathbf{r}' \Delta\rho(\mathbf{r}) c_0^{(2)}(n_0, \mathbf{r} - \mathbf{r}') \Delta\rho(\mathbf{r}') + O((\Delta\rho)^3). \quad (36)$$

The linear term vanishes whenever the mean density of the inhomogeneous system equals that of the reference system. The expansion (36) holds even for a vanishing external potential $\phi(\mathbf{r})$, i.e. in particular for systems with spontaneously broken translational invariance. It provides the basis of DFT of first-order phase transitions like freezing [17].

## III. A GENTLE APPLICATION OF DFT: SEDIMENTATION EQUILIBRIUM AND OSMOTIC EQUATION-OF-STATE

As a simple illustration of how DFT can be efficiently combined with computer simulation, consider a suspension of mesoscopic colloidal particles under the action of gravity, which supplies the external potential $\phi(z) = mgz$ where $m$ is the buoyant mass of the particles, $g$ is the gravitational acceleration and $z$ the vertical coordinate. Gravity breaks translational invariance in that direction and induces a density profile $\rho(z)$. The overall colloid concentration is characterized by the average number of particles per unit area at the bottom:

$$n_s = \int_0^h dz \rho(z) \quad (37)$$

where $h$ is the height of the sample. The details of the z-dependence of the density profile depend on the resolution of the observational apparatus.

At *high resolution* (finer than the particle diameter $\sigma$), $\rho(z)$ is found to exhibit strong oscillatory behaviour near the bottom wall (say $z = 0$), characteristic of *layering*, as shown by MC simulations [18]. At sufficiently high concentrations $n_s$, the lowest layers exhibit 2D crystalline order (triangular lattice in the x-y plane [19]). Sophisticated versions of DFT (the so-called "weighted density approximation" [20]) are required to reproduce such refinements [19].

At *much lower resolution* (i.e. on a scale significantly larger than $\sigma$), as is achieved in depolarized light scattering experiments [21], one is looking at a coarse-grained density profile:

$$\overline{\rho}(z) = \int_0^\infty dz' \rho(z') w(z - z') \tag{38}$$

where $w(z)$ is a suitably normalized resolution function, characteristic of the experimental set-up, or of the bin-width of computer-generated histograms. Sufficient coarse-graining (resolution of typically $2 - 3\ \sigma$) smoothes out the low-z oscillations in $\rho(z)$ and leads to a monotonically decreasing profile [18,21]. Such a smoothly varying $\overline{\rho}(z)$ may be calculated directly from DFT at the LDA level. The Euler-Lagrange equation associated with the variational principle (26) is particularly simple within the LDA, namely (dropping the index 0):

$$f'(\overline{\rho}(z)) \equiv \frac{\Pi(\overline{\rho}(z))}{\overline{\rho}(z)} + \frac{f(\overline{\rho}(z))}{\overline{\rho}(z)} = \mu - mgz \tag{39}$$

where $f(\overline{\rho})$ is the free-energy density of a homogeneous suspension of concentration $\overline{\rho}$, and $\Pi(\overline{\rho})$ is the corresponding osmotic pressure. Taking the gradient of both sides of Eq. (39) leads to the macroscopic osmotic equilibrium condition:

$$\frac{d\Pi(z)}{dz} = -mg\overline{\rho}(z). \tag{40}$$

Along an isotherm, $\Pi$ varies with altitude $z$ via its $\overline{\rho}$-dependence (this is the local thermodynamic equilibrium assumption implicit in LDA). Hence Eq. (40) can be re-cast into the following non-linear differential equation for $\overline{\rho}(z)$:

$$\frac{d\overline{\rho}(z)}{dz} = -\chi_T(\overline{\rho}(z))\frac{\overline{\rho}(z)}{\xi} \tag{41}$$

where $\xi = k_B T/mg$ is the gravitational length and $\chi_T = (\partial\beta\Pi/\partial\rho)^{-1}$ denotes the dimensionless osmotic compressibility. Since $\chi_T > 0$, the LDA can only lead to a monotonously decreasing $\overline{\rho}(z)$. For an ideal suspension of non-interacting particles, $\chi_T = 1$, and the density profile decays exponentially. At finite concentrations, excluded-volume effects between the colloidal particles lead to a much more slowly decaying $\overline{\rho}(z)$ at low altitudes [18,21,22].

An interesting application of sedimentation equilibrium is the *inverse problem*, which amounts to extracting the osmotic equation-of-state $\Pi(\rho)$ from experimental [21,23] or computer-generated [18] density profiles of concentrated suspensions.

Integration of the osmotic equilibrium condition (40) from $z$ to an altitude $h$ sufficiently high for the osmotic pressure to vanish yields:

$$\beta\Pi(z) = \frac{1}{\xi}\int_z^h dz'\overline{\rho}(z'). \tag{42}$$

At each altitude, $\overline{\rho}(z)$ and $\Pi(z)$ are thus known simultaneously, and hence, upon elimination of $z$, the whole osmotic equation-of-state $\Pi(\rho)$ is determined, for $\rho \leq \rho_0 = \overline{\rho}(z=0)$, by a single simulation or measurement [21]. The resulting $\Pi(\rho)$ should be independent of the intensity of the gravitational field, as characterized by the dimensionless ratio $\alpha = \sigma/\xi$; this independence provides a test for the validity of the procedure based on the LDA. The method has proved its efficiency by reproducing quite accurately the well-documented equation-of-state of a hard sphere liquid, by inversion of density profiles determined by MC simulations [18] and by depolarized light scattering measurements on a sterically stabilized colloidal suspension [21].

In a recent application, a system of infinitely thin disks, carrying a quadrupole moment $\overleftrightarrow{Q}$, was used as a model for a clay colloid suspension [24]. The quadrupole accounts for the electrostatic interactions between the double-layers formed by the charged clay platelets and their associated counterion charge distribution. If $\sigma$ denotes the disc diameter, the relevant dimensionless state variables are $n^* = N\sigma^3/V$ and $\beta^* = Q^2/(\varepsilon k_B T\sigma^5)$, where $Q$ is is the magnitude of the quadrupole moment and $\varepsilon$ the dielectric constant of the suspending fluid (water). The density profiles $\overline{\rho}(z)$ computed by MC simulations for several values of $\beta^*$ show a marked change in behavior around $\beta^* \simeq 0.1$ (cf. Fig. 1); inversion of these density profiles leads to the osmotic equations-of-state shown in Fig. 2; the dramatic change at $\beta^* = 0.1$ points to a first-order phase transition between a dilute sol-phase and a concentrated gel-phase [24]. The nearly-incompressible gel results from a competition between entropy, which favors stacking at high concentrations [25] (the loss of orientational entropy being outweighted by the gain in translational entropy), and the quadrupolar interactions favoring "edge-to-face" pair configurations, which leads to a characteristic "house-of-cards" structure.

## IV. A DENSITY FUNCTIONAL APPROACH TO POLYELECTROLYTES

Polyelectrolytes are made up of multiply charged, mesoscopic *polyions* and microscopic *counterions* of opposite sign. If salt is added, microscopic coions (carrying charges of the same sign as the polyions) are also present, but for the sake of simplicity this physically more realistic situation will not be considered here. These charged particles are in solution in a solvent (generally water), which will be assumed to act as an inert continuum of dielectric constant $\varepsilon$. Taking the counterions to be monovalent, and the polyions to carry $Z$ elementary charges, electrical neutrality requires that $N_1 Z = N_2$. Polyions may be linear objects (flexible charged polymer chains), rod-like (a good example is the tobacco mosaic virus), lamellar (charged clay platelets or membranes), or globular (spherical colloidal particles). The case of spherical polyions will be considered first.

Apart from overlap repulsion at short distances (which will be assumed to be of the hard sphere type in the following), the *bare* interactions between ions are purely coulombic; thus, for instance, returning to the notations of section I:

$$\begin{aligned} V_{11}(\{\mathbf{R}_I\}) &= \sum_I \sum_{J>I} v_{11}(|\mathbf{R}_I - \mathbf{R}_J|) \\ v_{11}(\mathbf{R}) &= \infty \qquad\qquad R < \sigma \\ &= \frac{Z^2 e^2}{\varepsilon R} \qquad R > \sigma. \end{aligned} \tag{43}$$

Counterions may be regarded as point charges, attracted by the oppositely charged polyions, which they cannot penetrate, so that an *electric double layer* builds up at the surface of of the polyions; this double layer is characterized by a counterion density profile $\rho(\mathbf{r})$ which takes on large values whenever $|\mathbf{r} - \mathbf{R}_I|$ is close to $\sigma$.

From the analysis of section I it follows that, after integration over the counterion coordinates, the total *effective* potential energy of interaction of the macroions is the sum of a direct term, $V_{11}$, which is pairwise additive, and an indirect (or induced) term, a complicated function of the polyion configuration, which is intrinsically many-body in nature:

$$V_{11}^{eff}(\{\mathbf{R}_I\}) = V_{11}(\{\mathbf{R}_I\}) + F_2[\rho(\mathbf{r}), \{\mathbf{R}_I\}] \tag{44}$$

where $F_2$ is the free-energy of the inhomogeneous fluid of counterions, which is a functional of $\rho(\mathbf{r})$ and depends parametrically on the polyion coordinates. It is convenient to split the non-trivial excess part into a mean-field Coulomb (also called Hartree) term (cf. section IIc) and a correction due to correlations. Dropping the index 2:

$$F[\rho(\mathbf{r}), \{\mathbf{R}_I\}] = \mathcal{F}_{id} + \mathcal{F}_{coul} + \mathcal{F}_{corr} + \mathcal{F}_{ext} \tag{45}$$

where $\mathcal{F}_{id}$ is given by Eq. (27),

$$\mathcal{F}_{coul} = \frac{e^2}{2\varepsilon} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{46}$$

$$\mathcal{F}_{ext} = \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r}, \{\mathbf{R}_I\}) = \sum_{I=1}^{N_1} \int d\mathbf{r} \rho(\mathbf{r}) v_{12}(|\mathbf{r} - \mathbf{R}_I|). \tag{47}$$

The (normally small) correlation part can be approximated by the LDA ansatz:

$$\mathcal{F}_{corr} = \int_V d\mathbf{r} f_{OCP}^{ex}(\rho(\mathbf{r})) \tag{48}$$

where $f_{OCP}^{ex}$ is the excess free-energy density of a homogeneous system of point charges in a uniform background of opposite charge. Such a system is referred to as a "one-component plasma" (OCP), where $f_{OCP}^{ex}$ is well documented [26].

For any macroion configuration $\{\mathbf{R}_I\}$, $\rho(\mathbf{r})$ is determined by the variational principle (26). The resulting minimal free-energy is then substituted into Eq. (44) to determine the effective many-body potential between polyions.

An analytic solution of the variational problem can be obtained [27], provided two approximations are made: a) $\mathcal{F}_{corr}$ is neglected [which is akin to Poisson-Boltzmann (PB) theory in electrochemistry]; b) $\mathcal{F}_{id}$ is expanded to second order in $\rho(\mathbf{r}) - n$, where $n = N_2/V$ is the mean counterion density. With these approximations the free-energy reduces to a quadratic functional of $\rho(\mathbf{r})$ and the resulting $V_{11}^{eff}$ turns out to be pairwise additive; the effective polyion pair potential is of the "DLVO" form [28]:

$$v_{11}^{eff}(\mathbf{r}) = \frac{Z_{eff}^2}{\varepsilon r} e^{-k_D r}; \qquad r > \sigma \tag{49}$$

where $Z_{eff} = Z e^{k_D \sigma/2}/(1 + k_D \sigma/2)$, and $k_D$ is the inverse of the Debye screening length associated with the counterions.

If the full functional (45 – 48) is used instead, minimization must be carried out numerically. In principle this could be achieved, for each polyion configuration, by steepest descent or conjugate gradient methods. The resulting effective interaction between polyions could then be used in a regular Metropolis MC algorithm to obtain macroion configuration space averages. This procedure will be used in section V for linear polyelectrolytes. Alternatively, the effective forces between polyions could be calculated from the classical version of the Hellman-Feynman theorem (6), which results in:

$$\mathbf{F}_I = -\nabla_I V_{11}(\{\mathbf{R}_J\}) - \int_V d\mathbf{r} \rho(\mathbf{r}) \nabla_I v_{12}(\mathbf{r} - \mathbf{R}_I). \tag{50}$$

These forces could then be used to evolve polyion positions in an MD or Brownian dynamics simulation. More efficiently, along the lines pioneered by Car and Parrinello for ion-electron systems [2], successive minimization and polyion updating steps are replaced by a single dynamical evolution, which involves physical motions of the polyions and fictitious dynamics of the counterion density, arranged such that the latter readjusts adiabatically to the much slower motion of the polyions. In practice, the time-dependent density profile $\rho(\mathbf{r}, t)$ is parameterized by a plane-wave expansion

$$\rho(\mathbf{r}, t) = \sum_{\mathbf{k}} \rho_{\mathbf{k}}(t) e^{i\mathbf{k}\mathbf{r}} \tag{51}$$

where the Fourier components $\rho_{\mathbf{k}}(t)$ are considered to be dynamical variables. A fictitious mass $m_{\mathbf{k}}$ is associated with the corresponding "velocities" $\dot{\rho}_{\mathbf{k}}(t)$ and the following generalized Lagrangian is introduced:

$$\mathcal{L} = \frac{1}{2} M \sum_{I=1}^{N_1} \dot{\mathbf{R}}_I^2 + \frac{1}{2} \sum_{\mathbf{k}} m_{\mathbf{k}} \dot{\rho}_{\mathbf{k}}^2 - V_{11}(\{\mathbf{R}_I\}) - F[\rho, \{\mathbf{R}_I\}] \tag{52}$$

The resulting equations of motion couple the physical time evolution of the $\{\mathbf{R}_I\}$, and the fictitious dynamics of the $\rho_{\mathbf{k}}$:

$$M\ddot{\mathbf{R}}_I = -\nabla_I V_{11}(\{\mathbf{R}_I\}) - \nabla_I F[\rho, \{\mathbf{R}_I\}] \tag{53}$$

$$m_{\mathbf{k}}\ddot{\rho}_{\mathbf{k}} = -\frac{\delta F[\rho, \{\mathbf{R}_I\}]}{\delta \rho_{\mathbf{k}}} + \alpha \int_V d\mathbf{r}[\rho(\mathbf{r}) - n] \tag{54}$$

where the last term implements the constraint that the number of counterions is conserved: $\rho_{\mathbf{k}=\mathbf{0}} = n$. To achieve adiabaticity, the "masses" $m_{\mathbf{k}}$ must be chosen sufficiently small (compared to $M$, in some suitable units) to ensure a clear-cut separation of time scales and thus to prevent equipartition between the degrees of freedom associated with the polyions and the counterion density. With these precautions, the counterion density remains close to the optimum density (which minimizes the free-energy functional $F$ for each polyion configuration), all along the dynamical evolution of the system.

A technical difficulty arises from the discontinuous variation of the density profile $\rho(\mathbf{r})$ near the surfaces of the the polyions, which are impenetrable to the counterions. This would make it necessary to include a large number, in principle infinite, of Fourier components in the representation (51). Fortunately, this difficulty may be overcome via the introduction of a continuous polyion-counterion pseudopotential, reminiscent of the pseudopotentials used in quantum ion-electron systems [27].

Results obtained by such "ab-initio" simulations for various properties of concentrated suspensions of moderately charged colloidal particles ($Z \geq 100$) differ significantly from the data obtained from standard MD or Brownian Dynamics simulations based on the DLVO effective pair potential, Eq. (49). In view of the high computational cost of the "ab-initio" simulations, it has been suggested to fit the many-body "ab-initio" forces by forces derived from the pairwise additive DLVO potential for a representative set of polyion configurations [29]. In this scheme the effective valence $Z_{eff}$ of the polyions and the inverse screening length $k_D$ are considered as free parameters to be determined by a least-squares fitting procedure.

The "ab-initio" method for polyelectrolytes with spherical polyions has been successfully extended to the case of rod-like polyions [30], and is at present being generalized to treat lamellar clay-colloid suspensions [24].

## V. "AB-INITIO" MONTE CARLO SAMPLING

Linear polyelectrolytes, consisting of charged polymer chains and counterions, pose methodological problems quite different from those encountered in the simulation of globular polyelectrolytes. In order to explore the phase space of a polymer chain efficiently, large conformational changes must be mapped out in a simulation. Such changes can only be generated by allowing "non-physical" displacements of the individual monomers, and hence MC sampling of configuration space is generally more efficient for polymers than "deterministic" MD.

Again, for the sake of simplicity, only the case of a single polyelectrolyte chain, together with an adequate number of counterions, will be considered hereafter. The following model will be adopted: the chain consists of $\nu$ identical segments of length $l$, carrying a charge $Ze$. A segment is generally made up of several monomers. The center of a segment and its orientation will be denoted by $\mathbf{R}_i$ and the unit vector $\mathbf{u}_i$, $(1 \leq i \leq \nu)$, respectively. The segments are assumed to be freely-jointed, but intrinsic rigidity is introduced via a harmonic coupling between the orientations of two successive segments. This rigidity is enhanced by the Coulomb repulsion between segments, as epitomized by the delicate concept of electrostatic persistence length [31]. The total potential energy of a chain thus reads:

$$V_{11} = \frac{k}{2} \sum_{i=1}^{\nu-1} \theta_i^2 + \sum_i \sum_{j>i} \frac{Z^2 e^2}{\varepsilon |\mathbf{R}_i - \mathbf{R}_j|} \tag{55}$$

where $\cos(\theta_i) = \mathbf{u}_i \cdot \mathbf{u}_{i+1}$. The dielectric constant $\epsilon$ will be set to 1.

The counterions are once more described in terms of the density profile $\rho(\mathbf{r})$, and a free-energy functional in the form of Eqs. (45 – 48). However, in contrast to the case of the colloidal particles considered in section IV, the size $l$ of the individual segments is comparable to that of the microscopic counterions, so that excluded volume effects are not expected to play an important role; in particular $l$ is generally significantly smaller than the Debye screening length $\lambda_D = k_D^{-1}$, which determines the scale of the counterion charge distribution around a segment. Under these conditions it is reasonable to replace the bare Coulomb attraction between a segment and a counterion by the following smooth "pseudopotential":

$$v_{12}(\mathbf{r}) = -\frac{Ze^2}{\varepsilon r}\mathrm{erf}(r/r_c) \tag{56}$$

with $r_c \simeq l$; this functional form will subsequently prove very favorable for a cut-off of the plane-wave representation (51) at a low wavenumber. Segments are prevented from overlapping by the bare Coulomb repulsion in Eq. (55). An MC simulation of the polyelectrolyte then proceeds via Metropolis sampling of the Boltzmann distribution:

$$P \sim \exp\{-\beta V_{11}(\{\mathbf{R}_i\}) - \beta F_2[\rho, \{\mathbf{R}_i\}]\} = P_{harm}(\{\mathbf{u}_i\})P_{coul}(\{\mathbf{R}_i\}) \tag{57}$$

where the harmonic factor corresponds to the intrinsic rigidity term in the potential energy (55).

Each MC trial move comprises a) a conformational change of the polymer, and b) a subsequent minimization of the counterion free-energy $F_2$, which amounts to readjusting $\rho(\mathbf{r})$ to the new polymer configuration.

a) The "reptation" algorithm [32] provides a simple and reasonably efficient way of displacing the polymer segments. A trial move consists in detaching one segment from one of the ends (chosen at random and designated as "tail") of the chain and reattaching it to the opposite end (the "head"), with an orientation sampled from $P_{harm}$. The polymer chain thus "slithers" like a snake. In approaches based on a discrete description of counterions, care must be taken when defining an attempted MC move, as any move leading to an overlap between monomers and counterions will be rejected, leading to a slow sampling of phase-space. On the contrary, in a DFT approach like the present one this problem does not exist, since the short-range repulsion is implicit in $v_{12}$, and therefore even complex trial moves of the polymer, which may lead to very efficient algorithms, can be easily used.

b) The simplest algorithm to minimize $F_2[\rho]$ is steepest descent. The density profile is parameterized as in Eq. (51), a fictitious time variable $s$ is introduced, and the coupled equations for "overdamped dynamics" of the form

$$m_{\mathbf{k}} \frac{d}{ds} \rho_{\mathbf{k}} = -\frac{\delta F_2[\rho]}{\delta \rho_{\mathbf{k}}} \tag{58}$$

are solved by a finite "time-step" algorithm. The $\rho_{\mathbf{k}}$ become stationary when the free-energy minimum is reached. The choice of the coefficients $m_{\mathbf{k}}$ is crucial since they determine the convergence rate of the procedure without affecting the location of the free-energy minimum. To see why, consider what happens close to that minimum. There the free-energy is a quadratic function of the deviations $\delta\rho_{\mathbf{k}}$ of the Fourier coefficients from their equilibrium values:

$$\begin{aligned} F_2[\rho] &= F_2^{(0)} + \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \left. \frac{\delta^2 F_2}{\delta \rho_{\mathbf{k}} \delta \rho_{\mathbf{k}'}} \right|_{\rho_{eq}} \delta\rho_{\mathbf{k}} \delta\rho_{\mathbf{k}'} + O(\delta\rho_{\mathbf{k}}^3) \\ &= F_2^{(0)} + \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \hat{\chi}^{-1}(\mathbf{k}, \mathbf{k}') \; \delta\rho_{\mathbf{k}} \delta\rho_{\mathbf{k}'} + O(\delta\rho_{\mathbf{k}}^3) \end{aligned} \tag{59}$$

according to the Fourier-space version of Eq. (20). Assume that the counterion density in the equilibrium state is nearly uniform; as a consequence of translational invariance, $\hat{\chi}^{-1}$ is then diagonal, $\hat{\chi}^{-1}(\mathbf{k}, \mathbf{k}') \simeq \hat{\chi}^{-1}(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}'}$. The quadratic free-energy expansion is then substituted into the steepest descent equations (58):

$$m_{\mathbf{k}} \frac{d}{ds} \rho_{\mathbf{k}} = -\frac{\delta}{\delta \rho_{\mathbf{k}}} \{ F_2^{(0)} + \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \hat{\chi}^{-1}(\mathbf{k}, \mathbf{k}') \delta\rho_{\mathbf{k}} \delta\rho_{\mathbf{k}'} \} = -\sum_{\mathbf{k}'} \hat{\chi}^{-1}(\mathbf{k}, \mathbf{k}') \delta\rho_{\mathbf{k}'} \simeq -\hat{\chi}^{-1}(\mathbf{k}) \delta\rho_{\mathbf{k}}. \tag{60}$$

The resulting linear equation is trivially solved in the form

$$\delta\rho_{\mathbf{k}} \sim e^{-\gamma(\mathbf{k})s} \tag{61}$$

where the "friction" coefficient is

$$\gamma(\mathbf{k}) = \frac{\hat{\chi}^{-1}(\mathbf{k})}{m_{\mathbf{k}}}. \tag{62}$$

The rate of convergence is clearly dictated by the smallest $\gamma(\mathbf{k})$, while the stability of the numerical integration is governed by the largest $\gamma(\mathbf{k})$. The optimal situation would be to have all $\gamma(\mathbf{k})$ equal. This may be achieved by choosing

$$m_{\mathbf{k}} \propto \hat{\chi}^{-1}(\mathbf{k}). \tag{63}$$

In order to obtain a rough estimate of $\hat{\chi}^{-1}$, one can start from the general expression for a diagonal $\chi$

$$\hat{\chi}^{-1}(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}'} = \left[\hat{\chi}_{id}^{-1}(\mathbf{k}) + \frac{4\pi e^2}{\varepsilon \mathbf{k}^2} - \hat{c}^{(2)}(\mathbf{k})\right]\delta_{\mathbf{k},\mathbf{k}'} \tag{64}$$

where the susceptibility has been split into its ideal, mean-field (or Hartree) and correlation contributions. In classical Statistical Mechanics $\hat{\chi}_{id}^{-1}$ reduces to the constant $k_BT/n$. For low counterion concentration the correlation term $\hat{c}^{(2)}(\mathbf{k})$ may be neglected (PB theory), so that

$$\hat{\chi}^{-1}(\mathbf{k},\mathbf{k}') \simeq \left[k_BT/n + \frac{4\pi e^2}{\varepsilon \mathbf{k}^2}\right]\delta_{\mathbf{k},\mathbf{k}'}. \tag{65}$$

and a sensible choice for the $m_{\mathbf{k}}$ becomes

$$m_{\mathbf{k}} \propto \frac{k_BT}{n} + \frac{4\pi e^2}{\varepsilon \mathbf{k}^2}. \tag{66}$$

This amounts to the "preconditioning" proposed by Pearson *et al.* [33] to achieve optimal convergence of the steepest descent minimization, and optimal adiabaticity in the dynamical runs. They noted that, since steepest descent is most efficient if the parabolic potential well (59) is as nearly as possible axially symmetric, the choice (63) for the $m_{\mathbf{k}}$ optimizes the efficiency of the algorithm by transforming an initially "long and narrow valley" into a "circular" one.

Preliminary MC runs have been made on a thirty-segment chain in the PB approximation, using both the full free energy functional (45), neglecting $\mathcal{F}_{corr}$ and the linearized version alluded to in Section IV. The effective charge of the monomers is $Z = 1$, and the counterion density is such that the Debye length $\lambda_D = 1/k_D = 6l$. The simulations were performed in a simple cubic cell. This of course introduces a spurious periodicity and thus unphysical interactions between the charges inside the box and their periodic images. To minimize this effect, a cell edge $L = 46l$ was used; with this value of $L$, even in the worst possible case (a fully stretched chain parallel to one of the box edges) the distance between a monomer and any one of the periodic images is about $3\lambda_D$, which gives a spurious interaction energy of less than 0.01 $k_BT$. The results obtained with the use a pseudopotential of the form (56), $r_c = l$, were indistinguishable from those obtained using the bare coulombic potential.

The results show that excellent convergence to a relative accuracy $\Delta F_2/k_BT \sim 10^{-3}$ is achieved in about 10 steps for each chain configuration. It is worth noting that in simulations using a linearized energy functional [which is equivalent to using an interaction of the DLVO form, Eq. (49)], the steepest-descent procedure fully converges after a single step, showing the preconditioning at its best. At each attempted MC move, the trial density used to start the energy minimization is the converged density at the previous polymer configuration. However this is probably not the best startup, since a large charge imbalance is created by the reptation algorithm when a "tail-to-head" move is attempted [34]. The new head in fact is by necessity placed in a region of nearly uniform density, while leaving behind a peak in the counterion density. More suitable choices for the starting density are possible and should make the simulation appreciably faster.

The simulation runs were 10000 MC steps (i.e., attempted head-to-tail moves) long. All the calculations were carried out on a desktop workstation. The acceptance ratio was 65% for the linear-screening run and 76% for the full PB simulation, rather higher than the "optimal" 50% ratio. This suggests that the reptation trial moves produce changes in the polymer configuration that are unnecessarily small. More complex MC algorithms, involving the simultaneous displacement of many segments, should lead to more efficient sampling of phase space.

The physical problems which can be addressed in these simulations are Manning "condensation" of counterions [35], which takes place when the ionic strength is high enough to cause a massive accumulation of counterions on the polyelectrolyte, and the electrostatic persistence length [31]. The latter has attracted much attention recently since the theory predicts the existence of two different regimes, one in which the persistence length is proportional to $1/k_D$ and another where it is proportional to $1/k_D^2$. The parameters chosen for the present simulation correspond roughly to those appropriate to the transition regime, a case where non-linear effects on screening begin to be important. This can be seen by the computed persistence lengths in the two cases of linear screening and of PB. Fig. 3 shows the average correlation function between the orientations of the monomers for the zero-charge case (an exponential with persistence length of 1) and for the two runs. The difference between charged and ideal cases is considerable, showing the expected charge-induced stiffening of the chain. Longer chain lengths are required to obtain significant results and are presently being investigated [34].

Refinement of the physical model are straightforward and are currently being implemented. In particular, the important case of non-dialized solutions (i.e. systems with added salt), which have never been addressed numerically, is simply dealt with by adding a second density field which represents the coionic density. It is also easily possible to go beyond PB theory by adding a correlation term to the energy functional, for example within the LDA.

## VI. THE QUANTUM REGIME: ORBITAL-FREE DENSITY FUNCTIONALS

The basic theorems and most of the approximation schemes introduced in the previous sections apply to classical and quantum systems alike. When the "light" particles are valence electrons while the "heavy" particles are ions, the mass ratio $m_2/m_1 < 10^{-3}$, so that the BO approximation is, under most circumstances, quite adequate.

However, under room-temperature conditions, the electrons are almost invariably degenerate. Indeed, if $T_F$ denotes the Fermi temperature of the valence electron gas of average density $n$, it is customary to define the degeneracy parameter $\theta = T/T_F = 2(9/4\pi)^{2/3} r_s^2 T^*$ where $r_s = (3/4\pi n)^{1/3}$ and $T^* = k_B T$ expressed in atomic (Hartree) units: $e = \hbar = m_{el} = 1$, which will be adopted throughout in this section. In metals, $\theta < 10^{-2}$, so that the valence electrons may be considered as fully degenerate, and the free energy $F$ reduces for all practical purposes to the ground state energy $E$, which, according to the Hohenberg-Kohn theorem, is a unique functional of the local electron density $\rho(\mathbf{r})$, which reaches its minimum when $\rho$ coincides with the equilibrium density. One is thus left with the problem of determining the ground state energy functional of an inhomogeneous electron gas in its ground state, subjected to the instantaneous "external field" of the (classical) ions.

This functional can be decomposed, in analogy with (45), into a kinetic, Hartree, exchange-correlation and external part:

$$E[\rho, \{\mathbf{R}_I\}] = K + E_{hartree} + E_{xc} + E_{ext} \tag{67}$$

$$E_{hartree}[\rho] = \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{68}$$

$$E_{ext}[\rho] = \sum_{I=1}^{N_1} \int d\mathbf{r}\rho(\mathbf{r}) v_{12}(\mathbf{r} - \mathbf{R}_I) \tag{69}$$

The ion-electron interaction potential $v_{12}$ is often modeled using a pseudopotential, which eliminates core electrons from the calculation.

The main problem, which does not arise in classical DFT, is to write down an accurate kinetic energy functional $K$. Neglecting spin variables for simplicity, if $\psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ denotes the many-body ground state wavefunction, $K$ is given exactly by:

$$\begin{aligned} K &= -\frac{1}{2} \sum_{I=1}^{N} \int d\mathbf{r}^N \psi^*(\mathbf{r}_1, \cdots, \mathbf{r}_N) \frac{\partial^2 \psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)}{\partial \mathbf{r}_I^2} \\ &= -\frac{N}{2} \int d^N \mathbf{r} \psi^*(\mathbf{r}_1, \cdots, \mathbf{r}_N) \frac{\partial^2 \psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)}{\partial \mathbf{r}_1^2} \\ &= -\frac{N}{2} \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \frac{\partial^2 \psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)}{\partial \mathbf{r}^2} \\ &= -\frac{1}{2} \int d\mathbf{r} \left. \frac{\partial^2 \rho^{(1)}(\mathbf{r}, \mathbf{r}')}{\partial \mathbf{r}^2} \right|_{\mathbf{r}' = \mathbf{r}} \end{aligned} \tag{70}$$

where $\rho^{(1)}(\mathbf{r}, \mathbf{r}') = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ is the density-matrix in real space. The usual density is the diagonal part of $\rho^{(1)}$:

$$\rho(\mathbf{r}) = \int d^N \mathbf{r} \tilde{\rho}(\mathbf{r}) |\psi|^2 = \rho^{(1)}(\mathbf{r}, \mathbf{r}). \tag{71}$$

The usual DFT representations of $K$ are of one of the following types:

a) Write $K$ as the kinetic energy of a system of non-interacting electrons moving in a self-consistent, effective potential. That is, $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ where the $\phi$'s are single particle wavefunctions of electrons moving in the mean-field generated by the others (Kohn-Sham orbitals [7]). In this case $K$ assumes the familiar form $K =$

$\frac{1}{2}\sum_i \int d\mathbf{r}\phi_i^* \nabla^2 \phi_i$. This approach is extensively discussed in the lectures of R. Car and W. Kohn included in this volume.

b) Use approximations of $K$ which do not use orbitals but directly $\rho$ as the basic variable. This is closer in spirit to the Hohenberg-Kohn approach but, on the other hand, it is not clear a priori whether good approximations for $K$ can be found.

The simplest approach of type (b) is to use the LDA approximation for $K[\rho]$: this leads to the Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) theories. Gradient-corrected functionals [9] can also be used to improve upon them. Another straightforward road for improvement is is to use the linear response theory, as in Eq. (28) (Hohenberg-Kohn functional [6]). These approaches, together with the more recent "hybrid" schemes, are briefly discussed in the following.

### A. Thomas-Fermi Molecular Dynamics

The kinetic energy per particle of a uniform electron gas of density $n$ is

$$E_K^0 = c_k n^{2/3} \sim 1/r_s^2, \qquad c_k = \frac{3}{10}(3\pi^2)^{2/3}. \tag{72}$$

If one assumes that the kinetic energy of an inhomogeneous electron gas is a function of the local density only, the result is the well-known TF kinetic energy:

$$K_0 = c_k \int d\mathbf{r}[\rho(\mathbf{r})]^{5/3}. \tag{73}$$

This can be inserted in the energy functional (69) and $\rho$ can be used as variable in a Car-Parrinello scheme, in complete analogy with the dynamical treatment of polyelectrolytes in Section IV.

The obvious way of proceeding is to write $\rho$ on a discrete grid in real space and to use the values of $\rho$ at the grid points as the additional degrees of freedom. This leads to the following Lagrangian:

$$\mathcal{L} = \frac{1}{2}M\sum_{I=1}^{N_1}\dot{\mathbf{R}}_I^2 + \frac{1}{2}m\int d\mathbf{r}\dot{\rho}^2(\mathbf{r}) - E[\rho,\{\mathbf{R}_I\}] - \sum_J\sum_{I<J}\frac{Z^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \mu\left\{\int d\mathbf{r}\rho(\mathbf{r}) - N_2\right\}. \tag{74}$$

The last term ensures the conservation of the number of the electrons via the Lagrange multiplier $\mu$, the chemical potential of the electrons. As discussed in Sec. IV, the "fake" mass $m$ must be small enough to ensure adiabatic separation between ionic and (fake) electronic degrees of freedom. The coupled equations of motion derived from Eq. (74) are

$$M\ddot{\mathbf{R}}_I = Z^2\sum_{I=1}^{N_1}\mathbf{R}_{IJ}/R_{IJ}^3 - \frac{\partial E[\rho,\{\mathbf{R}_I\}]}{\mathbf{R}_I} \tag{75}$$

$$m\ddot{\rho}(\mathbf{r}) = -\frac{\delta E[\rho,\{\mathbf{R}_I\}]}{\delta\rho} + \mu = -\frac{5}{3}c_k\rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r}) - \int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu. \tag{76}$$

This real-space approach has been successfully applied to the study of dense hydrogen plasmas [36]. However it has the drawback that no effective preconditioning procedure is known and as a consequence the efficiency of the algorithm is sensibly reduced. Thus a plane-wave expansion of $\rho$ [Eq. (51)], using fast Fourier transform techniques to switch back and forth from real to reciprocal space, seems preferable.

Other, more basic problems lie with the functional itself. TF is known to have several unphysical features: for instance, it leads to divergence of the density at the atomic nucleus and, perhaps even worse, cannot give chemical binding. An effortless improvement is to include the LDA exchange functional [7]:

$$E_{xc} = c_x\int d\mathbf{r}[\rho(\mathbf{r})]^{4/3} \tag{77}$$

which leads to the TFD theory. Unfortunately this only make matters worse: the non-binding theorem still holds and the quantitative (dis-)agreement with both experiments and other, more accurate theoretical results worsens.

### B. Gradient correction to TF

The leading gradient correction to $K_0$ turns out to have the same form for both the cases of rapidly and slowly varying density:

$$K_2[\rho] = K_0 + \frac{c_2}{8}\int d\mathbf{r}\frac{(\nabla\rho(\mathbf{r}))^2}{\rho(\mathbf{r})} \tag{78}$$

where $c_2 = c_g = 1/9$ if $\rho$ is slowly varying (second-order gradient expansion) and $c_2 = c_w = 1$ if $\rho$ is rapidly varying (Thomas-Fermi-von Weizsäcker functional). In both cases the curses of the divergence at the atomic nucleus and of the absence of chemical binding are nullified.

Still, this functional has the problem of not being able to yield the correct linear-response behaviour. It is instructive to examine this point in detail. Let us consider a system of non-interacting electrons subject to a weak external potential $\phi$. Using the above gradient-corrected functional,

$$E[\rho] = c_k\int d\mathbf{r}\rho^{5/3}(\mathbf{r}) + \frac{c_2}{8}\int d\mathbf{r}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} + \int d\mathbf{r}\phi(\mathbf{r})\rho(\mathbf{r}) \tag{79}$$

The minimum condition reads

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \frac{5}{3}c_k\rho^{2/3}(\mathbf{r}) - \frac{c_2}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} - \frac{c_2}{4}\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})} + \phi(\mathbf{r}) = \mu \tag{80}$$

where the presence of $\mu$, the chemical potential, ensures the conservation of the number of electrons. Writing now $\rho(\mathbf{r}) = n + \delta\rho(\mathbf{r})$, where $\delta\rho(\mathbf{r}) = O(\phi)$, and expanding $\frac{\delta E}{\delta\rho}$ to first order in $\delta\rho$ and $\phi$, one obtains upon Fourier transformation :

$$\delta\rho_{\mathbf{k}} = \chi_2(\mathbf{k})\phi_{\mathbf{k}}; \qquad \chi_2(\mathbf{k}) = -\frac{k_F}{\pi^2}\frac{1}{1+3c_2q^2} \tag{81}$$

where $q = k/2k_F$ and $k_F = (9\pi/4)^{1/3}/r_s$ is the Fermi wavevector (in a.u.). On the other hand the exact linear response function for non-interacting electrons is the Lindhard function [37] and it is easy to check that the gradient corrected kinetic energy gives the correct answer in the limit of large $q$ (if $c_2 = c_w = 1$, von Weizsäcker), or in the limit of small $q$ (if $c_2 = c_g = 1/9$, gradient expansion).

### C. The Hohenberg-Kohn functional

The correct linear response behaviour can, on the other hand, be directly built in the functional as suggested by Hohenberg and Kohn [6]. In this case one may write

$$K_L[\rho] = K_0(n) + \frac{1}{2}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\frac{\delta^2 K}{\delta\rho_{\mathbf{k}}\delta\rho_{\mathbf{k}'}}\bigg|_n \delta\rho_{\mathbf{k}}\delta\rho_{\mathbf{k}'} = K_0(n) + \frac{1}{2}\sum_{\mathbf{k}}\chi_{id}^{-1}(\mathbf{k})\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}} \qquad (82)$$

where again $\chi_{id}$ is the Lindhard function. For weak density modulations this functional is superior to TF, since the latter implies a constant $\chi_{id} = k_F^2/\pi^2$. The Hohenberg-Kohn functional has been used to derive effective ion-ion potentials [38] for simple metals. In this approach, a weak ion-electron pseudopotential is constructed and the corresponding response of a uniform electron gas at the appropriate $n$ is calculated in the linear response approximation (which is equivalent to using Eq. (82) plus possibly a linearized exchange-correlation potential). The resulting energy $E_2$ is then used to calculate the effective potential $V_{11}^{eff}$ via Eq. (5). If the assumption of weak pseudopotentials holds, it is easy to show that $V_{11}^{eff}$ is pairwise additive, as in the classical case of polyelectrolytes [cf. Eq. (49)]. A disadvantage of the Hohenberg-Kohn functional is that it can lead to unphysical negative values of $\rho(\mathbf{r})$, even in conjunction with weak pseudopotentials like those for Na [33].

### D. Hybrid functionals

Given that the approaches described in the last two paragraphs run into complementary difficulties, it is quite natural to ask whether it is possible to combine the above functionals into a new one which is free from these problems [33,39,40]. In general, one may write a family of functionals of the form:

$$K_\alpha = K_w + \frac{1}{2}\sum_{\mathbf{k}}\rho_{\mathbf{k}}^{\alpha *}[\chi_{id}^{-1} - \chi_2^{-1}]\rho_{\mathbf{k}}^{\alpha}. \qquad (83)$$

By $K_w$ it is meant the functional (78) with $c_2 = c_w$, and $\chi_2$ is the linear response function derived from it [Eq. (81)], while $\chi_{id}$ is the Lindhard function. $\rho_{\mathbf{k}}^{\alpha}$ is the Fourier transform of $\rho^\alpha(\mathbf{r})$, and the exponent $\alpha$ is a free parameter which has been set to 1 [40], 1/2 [33], and 5/6 [39].

By construction, $K_\alpha$ is exact in the linear regime and is superior to Hohenberg and Kohn's in that it includes non-linearity via the TF-von Weizsäcker term. This term gives, for instance, the correct asymptotic behavior in the case of rapidly varying density even for large density variations.

These functionals give good results for alkali metals [33,41] and plasmas [42]. Extensions and improvements are under way [43].

### E. Kohn-Sham vs. orbital-free functionals

To conclude this section, it seems appropriate to summarize the comparative advantages and disadvantages of the Kohn-Sham and orbital-free approaches.

The Kohn-Sham functional certainly gives a more accurate representation of the kinetic energy, in particular for semiconductors and insulators. (One should be careful not to consider it as "exact", though: it is simply the best possible $K$ in a single-particle, mean-field approach). Another advantage of an orbital-based scheme is that the density is, by construction, positive ($\rho = \sum_i |\phi_i|^2$).

On the other hand orbital-free schemes offer great practical advantages:

- The basic variable being $\rho$, the number of degrees of freedom is $O(N_2)$ times smaller, with savings both in computer time and memory.

- There is no need for Brillouin zone sampling. The use of an insufficient number of sampling points is a major source of error in orbital-based calculations, occasionally making them *less* accurate than orbital-free ones [41].

- No orthonormality has to be imposed (the charge conservation constraint is trivial). Orthonormalization causes the computer time required by orbital-based schemes to scale as $N_2^3$; orbital-free methods are instead intrinsically $O(N_2)$.

- Very good preconditioning (along lines similar to those illustrated in section V) is possible, giving excellent adiabaticity in the MD runs even for metallic systems, where Kohn-Sham-based Car-Parrinello methods often run into difficulties [1].

- Inclusion of finite-$T$ effects is more straightforward. All one has to do is to modify the functional as follows [44]. First, change the Thomas-Fermi-von Weizsäcker part:

$$K_w = \sqrt{2}/\pi^2 (k_B T)^{5/2} [-\frac{2}{3} I_{3/2}(\eta) + \eta I_{1/2}(\eta)] \\ + \frac{c_w}{8} \int d\mathbf{r} \left[ -\frac{3\sqrt{2}\pi^2}{8(k_B T)^{3/2}} \frac{d}{d\eta} (1/I_{-1/2}(\eta)) \right] (\nabla \rho(\mathbf{r}))^2 \tag{84}$$

where $I_\nu(\eta) = \int_0^\infty dx \frac{x^\nu}{e^{x-\eta}+1}$ and $\eta$, the reduced chemical potential, is defined via $\rho = \sqrt{2}/\pi^2 (k_B T)^{3/2} I_{1/2}(\eta)$. Secondly, replace the linear response function in Eq. (83) with its finite-temperature counterpart:

$$\chi_{id}(k; T) = -\frac{k_F^2}{\pi^2 k} \int_0^\infty dy \frac{y}{e^{(1/2k_F^2 y^2 - \mu)/k_B T} + 1} \ln \left| \frac{k + 2k_F y}{k - 2k_F y} \right| \tag{85}$$

On balance, orbital-free functionals appear to be better adapted to the simulation of metals and plasmas, especially if dynamical properties, requiring long trajectories in phase space, are to be investigated.

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## FIGURES

FIG. 1. Density profiles for the model clay system described in the text, for several values of the dimensionless parameter $\beta^* = Q^2/(\varepsilon k_B T \sigma^5)$.

FIG. 2. Osmotic equation of state for clay, extracted from the profiles of Fig. 1. The stars are results obtained from direct NVT MC simulations.

FIG. 3. Averaged monomer-monomer correlation function. Dashed line: PB simulation. Dotted line: simulation using the linearized functional. Full line: theoretical result in the absence of charges.