

Dynamic density functional theory of fluids

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Abstract. We present a new time-dependent density functional approach for studying the relaxational dynamics of an assembly of interacting particles, subject to thermal noise. Starting from the Langevin stochastic equations of motion for the velocities of the particles, we are able by means of an approximate closure to derive a self-consistent deterministic equation for the temporal evolution of the average particle density. The closure is equivalent to assuming that the equal-time two-point correlation function out of equilibrium has the same properties as its equilibrium version. The changes over time of the density depend on the functional derivatives of the grand canonical free-energy functional $F[\rho]$ of the system. In order to assess the validity of our approach, we performed a comparison between the Langevin dynamics and the dynamic density functional method for a one-dimensional hard-rod system in three relevant cases and found remarkable agreement. In addition, we consider the case where one is forced to use an approximate form of $F[\rho]$.

The present theoretical understanding of the static behaviour of fluids owes much to density functional (DF) methods, which provide a rigorous tool for studying all of their equilibrium properties [1]. In fact, such an approach deals successfully both with diverse problems such as adsorption, wetting, confinement, and solid–liquid and gas–liquid phase transitions, and with the response to static perturbations. In principle, if one knew the exact form of the free-energy functional for a given system, one could calculate the bulk and surface properties, the non-uniform density profiles in the presence of static external fields, and all of the n -body correlations. On the other hand, if a system is subject to some external time-dependent field or if it has been brought away from an equilibrium state by removing some constraint, one cannot rely on such a rigorous framework because the usual approach based on standard statistical mechanical arguments is not applicable. Nevertheless, the growing attention which is being devoted to the off-equilibrium properties of fluids and the remarkable progress in the understanding of the nature of supercooled liquids render worthwhile the effort of finding a suitable extension to the dynamics of density functional methods.

Theories of phase transitions are usually formulated in terms of a suitable order parameter, and the dynamic density functional approach has been employed frequently in the past on a phenomenological basis. Our main intention is to obtain a direct microscopic link with the equilibrium DF formalism, making clear the assumptions behind the method and showing examples of its use for the dynamics of systems with strong correlations due to molecular packing effects.

Our derivation of a time-dependent density functional approach [2] is based on a generic microscopic model made up of N large colloidal particles whose dynamics is overdamped, i.e. we neglect inertial effects; each particle moves under the influence of the remaining $N - 1$ colloidal particles and experiences collisions with smaller particles (the bath) described by a random-noise term, leading to a Langevin dynamics:

$$\frac{d\mathbf{r}_i(t)}{dt} = -\Gamma \nabla_i \left[\sum_j V(\mathbf{r}_i - \mathbf{r}_j) + V_{ext}(\mathbf{r}_i) \right] + \boldsymbol{\eta}_i(t) \quad (1)$$

where the term $\boldsymbol{\eta}_i(t) = (\eta_i^x(t), \eta_i^y(t), \eta_i^z(t))$, representing the influence of the thermal bath, has zero average and variance $\langle \eta_i^\alpha(t) \eta_j^\beta(t') \rangle = 2D \delta_{ij} \delta^{\alpha\beta} \delta(t - t')$ where α, β run over x, y, z . The constants Γ and D are the mobility and the diffusion coefficient of the particles, respectively; the Einstein relation gives $\Gamma/D = \beta \equiv 1/T$. Hereafter, we assume $\Gamma = 1$ to fix the unit of time and have $D = T = \beta^{-1}$.

Instead of considering all of the trajectories generated from equation (1), we shall consider the evolution of the density of particles. It can be shown by standard manipulations [3,4] that the instantaneous global density operator

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

obeys the following stochastic equation:

$$\begin{aligned} \frac{\partial \hat{\rho}(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left[T \nabla \hat{\rho}(\mathbf{r}, t) + \hat{\rho}(\mathbf{r}, t) \nabla V_{ext}(\mathbf{r}) \right. \\ \left. + \hat{\rho}(\mathbf{r}, t) \int d\mathbf{r}' \hat{\rho}(\mathbf{r}', t) \nabla V(\mathbf{r} - \mathbf{r}') + \zeta(\mathbf{r}, t) \sqrt{\hat{\rho}(\mathbf{r}, t)} \right] \end{aligned} \quad (2)$$

where the vector noise ζ acting on the density has zero average and correlation

$$\langle \zeta^\mu(\mathbf{r}, t) \zeta^\nu(\mathbf{r}', t') \rangle = 2T \delta(t - t') \delta(\mathbf{r} - \mathbf{r}').$$

After performing an ensemble average over the noise in equation (2), one can replace $\hat{\rho}$ by its average ρ and the product by the instantaneous equal-time correlation function, while the last term disappears:

$$\begin{aligned} \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \cdot [T \nabla \rho(\mathbf{r}, t) + \rho(\mathbf{r}, t) \nabla V_{ext}(\mathbf{r})] \\ + \nabla \cdot \left[\int d\mathbf{r}' \langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', t) \rangle \nabla V(\mathbf{r} - \mathbf{r}') \right]. \end{aligned} \quad (3)$$

The resulting equation connects the single-particle distribution with the two-particle distribution, which in turn depends on the three-particle correlation function. We do not have information about the two-particle correlation unless we solve its governing equation, and this generates an infinite hierarchy.

In order to close the equations, we assume that the evolution of the system can be represented by an infinite sequence of equilibrium states obtained by applying at every instant a pinning field $u(\mathbf{r})$ which renders the average profile $\rho(\mathbf{r}, t)$ a minimum of the grand potential functional $\Omega[\rho]$ of the system. In other words, at any instant there is a profile $\rho_0(\mathbf{r}) \equiv \rho(\mathbf{r}, t)$ which is an equilibrium density profile of the system in the presence of the field $u(\mathbf{r})$. Rigorous theorems tell us that such a $u(\mathbf{r})$ always exists and is a unique functional of ρ . Actually we do not need to compute u explicitly.

Thus from the general properties of the equilibrium functionals we can eliminate the two-point correlation in favour of the direct correlation using the first equation of the BBGKY

hierarchy and the relation [5]

$$\begin{aligned} \beta \frac{1}{\rho_0(\mathbf{r})} \int d\mathbf{r}' \rho_0^{(2)}(\mathbf{r}, \mathbf{r}') \nabla V(\mathbf{r} - \mathbf{r}') &= - \int d\mathbf{r}' c^{(2)}(\mathbf{r}, \mathbf{r}') \nabla \rho_0(\mathbf{r}') \\ &= \nabla \frac{\delta}{\delta \rho_0(\mathbf{r})} [\beta \Delta F[\rho_0]] \end{aligned} \quad (4)$$

where $c^{(2)}(\mathbf{r}, \mathbf{r}')$ is the direct correlation function.

Thus we may rewrite the equation of evolution for the density as

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left[\rho(\mathbf{r}, t) \nabla \frac{\delta F[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} \right] \quad (5)$$

which has the form of a continuity equation, $\partial \rho / \partial t + \nabla \cdot \mathbf{j} = 0$, with the current of particles given by

$$\mathbf{j}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \nabla \left. \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r}, t)}. \quad (6)$$

Equations (5) and (6) have been proposed before on a phenomenological basis [6], while in our derivation we make direct contact with the initial Langevin dynamics, equation (1).

In summary, we have used the fact that at any instant we can find a fictitious external potential $u(\mathbf{r})$ which equilibrates the system, i.e. constrains its grand potential to be minimal. This minimum is characterized by the imposed density profile $\rho_0(\mathbf{r}) = \rho(\mathbf{r}, t)$ and by equilibrium correlations $\rho_0^{(2)}(\mathbf{r}, \mathbf{r}')$ consistent with it. The present approximation replaces the true off-equilibrium pair distribution function $\langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', t) \rangle$ by the equilibrium $\rho_0^{(2)}(\mathbf{r}, \mathbf{r}')$, and then uses the equilibrium density functional $\Delta F[\rho]$ to obtain the relevant information on this function, without its explicit evaluation.

The assumption that the two routes, BBGKY and equation (4), are equivalent implies that the fluctuation-dissipation theorem holds, while in general, out of equilibrium, it is violated. In fact the relation connecting $\rho_0^{(2)}(\mathbf{r}, \mathbf{r}')$ to $c^{(2)}(\mathbf{r}, \mathbf{r}')$ (the OZ equation) is an exact equilibrium property and is based on the idea that the correlation function is the matrix inverse of the second derivative of the functional F with respect to $\rho_0(\mathbf{r})$.

The main features of this approach are the following:

- (a) Since $F[\rho]$ is a functional solely of the density field, equation (5) is a closed non-linear equation for $\rho(\mathbf{r}, t)$.
- (b) The equation is deterministic and the variable $\rho(\mathbf{r}, t)$ has to be interpreted as the instantaneous density operator averaged over the realizations of the random noise $\eta_i(t)$. Such thermal noise generates the diffusion term and is associated with the ideal-gas entropy.
- (c) The only assumptions leading to equation (5) are that the system follows a relaxational dynamics, which may be described by the Brownian motion of the particles in a thermalized bath, and that the instantaneous two-particle correlations are approximated by those in an equilibrium system having the same density distribution and are calculated by means of the density functional $F[\rho]$.

In the long-time limit, the evolution of the system leads to its equilibrium density distribution, which corresponds to a uniform value of $\mu = \delta F / \delta \rho(\mathbf{r})$, i.e. the usual Euler-Lagrange equation in the equilibrium DF formalism. However, the trajectories that lead to the minima of F are not necessarily along the directions corresponding to the maximum slope. The continuity equation implies that the local conservation of particles is built in and imposes important constraints on the local changes of $\rho(\mathbf{r}, t)$.

The use of free-energy density functionals with many minima have led to the necessity for modifications. When the deterministic time evolution (5) gets trapped at a ‘metastable state’ it can never reach the true equilibrium state. In the literature, various authors [3, 9–11] have introduced an extra random-noise term in (5) in order to allow the system to jump over any ‘metastability barrier’ in a finite time. From our analysis it is clear that the use of the free-energy density functional makes sense only for the density $\rho(\mathbf{r}, t) = \langle \hat{\rho}(\mathbf{r}, t) \rangle$, averaged over the realizations of $\eta_i(t)$ in the Langevin dynamics, and this averaging gives the deterministic equation (5).

We validated the method in a one-dimensional case where the equilibrium DF is exactly known. Using equation (5) together with Percus’s [7] excess free-energy density functional for an assembly of hard rods of length σ , and defining

$$\eta(x) = \int_{x-\sigma/2}^{x+\sigma/2} dx' \rho(x')$$

we obtain the following equation for the time evolution of the density:

$$\begin{aligned} \frac{\partial \rho(x, t)}{\partial t} = & \frac{\partial^2 \rho(x, t)}{\partial x^2} + \frac{\partial}{\partial x} \left[\rho(x, t) \left(\frac{\rho(x + \sigma, t)}{1 - \eta(x + \sigma/2, t)} - \frac{\rho(x - \sigma, t)}{1 - \eta(x - \sigma/2, t)} \right) \right] \\ & + \frac{\partial}{\partial x} \left[\rho(x, t) \frac{dV_{ext}(x)}{dx} \right] \end{aligned} \quad (7)$$

where we have chosen the energy units such that $T = 1$.

The first term in (7) represents the diffusion equation for the ideal-gas case; the second term is the correction due to the hard-rod interaction. It is worthwhile to point out that

$$\rho(x)\rho(x + \sigma)/(1 - \eta(x + \sigma/2))$$

is just the two-point equilibrium correlation function $\rho_0^{(2)}(x, x')$ evaluated at contact, i.e. when $x' = x + \sigma$, so this term takes into account the collisions of the rod at x with the remaining particles on the right-hand side. Similarly the other term describes the interactions with the left-hand sector.

To check the accuracy of the method, we compared the direct simulation of the Langevin equation (1) with the results obtained by solving numerically the equation of evolution for the density (5) using the following tests [2]:

- *The free expansion from a dense state.* We considered a system of N hard rods initially nearly at contact and studied the evolution of the density profile. We observe that the system evolves from an initially highly packed state characterized by a peaked structure. As the time elapses the peaks become less pronounced and finally one observes a single bump. The agreement between the Langevin simulations and equation is good [2]. The main difference between the two simulations is given by the damping rate at which the oscillations disappear.
- *The collapse to a dense equilibrium state.* We have studied the evolution of a few particles collapsing in a parabolic potential well. Initially their centres of mass are apart. During an intermediate stage they diffuse nearly independently under the action of the field directed towards the bottom of the well; finally they start experiencing mutual repulsion. The results from the dynamic density functional and from the direct Langevin simulation with 2000 particles are in good agreement, although some differences can be seen in the initial stage and in the final profiles. These differences are due to the use of the grand canonical functional instead of the true canonical functional.

- *The relaxation through highly correlated states.* In this numerical experiment we have considered hard rods in a one-dimensional periodic potential. Initially the particles are located in alternate wells and then they start to diffuse. If the distance between consecutive wells is made smaller than the hard-rod diameter, the relaxation time becomes longer, in view of the fact that some configurations are unlikely. The time evolution of the density profiles showed different times, for both the DDF equation and the average of the Langevin simulations over 2000 realizations of the noise. In both cases the relaxation is slow, and it becomes much slower for increasing values of the potential barrier. The comparison of the result clearly shows that the DDF equation, with the exact Percus free energy, approaches the equilibrium state faster than the average of the Langevin simulation. This difference is related again to the use of different statistical ensembles: the canonical Langevin equation keeps N constant while the grand canonical $F[\rho]$ allows for fluctuations in the number of particles, keeping only the average fixed. The changes in N in the DDF open a new relaxation path and give a faster relaxation, even if the final equilibrium density profiles in the canonical and the grand canonical ensembles are very similar.

In the past, different prescriptions for the evolution of the density towards equilibrium have been proposed [8, 12]. The most popular is the one employed by several groups and is tantamount to performing a density expansion of the excess free-energy functional about some uniform reference state and retaining only the quadratic terms. In order to favour jumps over the metastability barriers, one adds small random perturbations to the values of the fields in the numerical integration. The resulting theory has been proposed in order to explain glassy behaviour in hard-sphere mixtures, but the origin of the noise remains somewhat obscure. Kawasaki [8] in a series of interesting papers suggested that an averaging procedure different from ours could lead to a stochastic equation for the density. Such an equation should be derived by considering a coarse graining of the density over length scales larger than the microscopic lengths of the problem. However, we believe that the coarse-graining procedure, although physically motivated, cannot be rendered explicit. Moreover, when we compared our method with the truncated density expansion we found that the latter showed, in the case of the periodic potential, a surprisingly fast relaxation towards the minima. Perhaps the effect of this approximation is to underestimate the packing effects.

To summarize, we have introduced a dynamic density functional approach to describe the Brownian motion of a system of colloidal particles which might be relevant in the field of phase separation and domain growth. The equilibrium DF is used to achieve the closure of the equations. Our study shows that the DF approach is consistent with the microscopic particle dynamics. The equations contain a density-dependent mobility but no noise term.

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