

# Derivation of dynamical density functional theory using the projection operator technique

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(Received 16 September 2009; accepted 2 November 2009; published online 22 December 2009)

Density functional theory is a particular case of a general theory of conjugate variables that serves as the basis of the projection operator technique. By using this technique we derive a general dynamical version of density functional theory which involves a generalized diffusion tensor. The diffusion tensor is given by a Green–Kubo expression. For Brownian dynamics of dilute colloidal suspensions, the standard dynamical density functional theory is recovered. © 2009 American Institute of Physics. [doi:10.1063/1.3266943]

## I. INTRODUCTION

Density functional theory (DFT) for classical many-body systems<sup>1–5</sup> is a versatile and powerful tool to predict one-particle density profiles of inhomogeneous liquids in equilibrium. The classical density functional approach allows to calculate bulk phase transitions like fluid–fluid phase separation and freezing<sup>6–8</sup> and is also applicable to interfacial structures between coexisting bulk phases or induced by external walls.<sup>9,10</sup>

More recently, dynamical extensions of DFT to nonequilibrium situations have been proposed.<sup>11–13</sup> In its simplest form, the dynamical DFT (DDFT) involves the continuity equation for the time-dependent one-particle density where the current density obeys generalized Fick’s law. In the latter, the current density is proportional to the gradient of a generalized chemical potential which is written as an equilibrium density functional derivative.<sup>1,14</sup> For a noninteracting system (ideal gas), the traditional diffusion equation is recovered, while DDFT makes nontrivial predictions for interacting systems.

Though conceptually simple and appealing, the theory needs a systematic derivation in order to discuss its limitations, the nature of the underlying approximations, and its possible extensions to more complex situations. Furthermore, the phenomenological prefactor in Fick’s law needs to be determined in terms of the molecular parameters. By now, in the context of Brownian particles, there have been two complementary derivations of DDFT. The first one was suggested by Marconi and co-workers<sup>11,15,16</sup> and starts from the Langevin equations describing trajectories of Brownian particles. The deterministic DDFT equation is derived by a noise average for the dynamical one-particle density. Note that the equation is different from earlier versions<sup>17,18</sup> which involve a stochastic noise term.<sup>19</sup> The second way of derivation was proposed by Archer and Evans<sup>12</sup> and starts from the

Smoluchowski equation<sup>20</sup> which is stochastically equivalent to the Langevin equations. Assuming that the two-body density correlations in nonequilibrium are the same as in equilibrium at the same one-body density, the DDFT theory was obtained. The approach reveals the underlying physical *adiabaticity* assumption, namely, that the two-body correlations relax much more quickly than the one-body density. The derivation by Archer and Evans has the further benefit that it can directly be used to generalize the dynamical equation to many-body interactions between the particles,<sup>12</sup> to hydrodynamic interactions between the particles,<sup>21,22</sup> to orientational degrees of freedom,<sup>23</sup> and to self-propelled particles.<sup>24</sup>

In this paper, we present a third derivation of DDFT which employs the technique of projection operators.<sup>25</sup> This approach is in particular appropriate if there are fast and slow observables. After discussing the general framework, a generalized DDFT equation is described which is based on the assumption that the density evolves in time much slower than the current correlation function (corresponding to the adiabaticity assumption). Our generalized DDFT equation involves a generalized diffusion tensor as a kernel which itself is a time integral of a current autocorrelation function. For Brownian dynamics of dilute colloidal suspensions, the standard DDFT as derived by Marconi and Tarazona<sup>11</sup> and Archer and Evans<sup>12</sup> is obtained as a special case of our general DDFT. Also the extension of the standard DDFT toward hydrodynamic interactions between colloids<sup>21,22</sup> fits within the framework of our general theory.

The implication of our derivation is twofold: first, it is obviously reassuring to recover the standard DDFT as a special case of a more general framework and to find consistency between complementary derivations using the Langevin and Smoluchowski picture. This provides a solid microscopic background for various applications which use the standard DDFT equations. Second, more importantly, our derivation opens the way to a more general class of dynamics which uses more general diffusion tensors. In the paper we therefore describe ways on how to deal with more general

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diffusion kernels for various circumstances. In particular, the projection operator technique is also the basic ground for deriving mode coupling theory<sup>26</sup> and therefore our derivation may be a starting point to establish a connection between mode coupling theory and DDFT. Though this connection was briefly touched by Archer<sup>27</sup> a full thorough link between these two powerful approaches to liquid dynamics is still missing.

This paper is laid out as follows. After recapitulating equilibrium DFT in Sec. II, we discuss the general framework of the time-dependent projection operator technique in Sec. III. Applying this technique to the case where the density itself is the relevant variable, we derive the generalized DDFT in Sec. IV. In Sec. V different approximations for the diffusion tensor are discussed and the standard DDFT equation as a special case is recovered. Final conclusions are presented in Sec. VI.

## II. EQUILIBRIUM DENSITY FUNCTIONAL THEORY

In this section, we present the DFT in a way slightly different from usual presentations<sup>1,2</sup> in order to show that DFT may be understood as a particular case of a more general thermodynamic theory of conjugate variables. Consider a set of phase functions  $A(z)$ , where  $z$  is the microscopic state of the system. Later we will particularize  $A(z)$  to the microscopic density operator,

$$\hat{n}_{\mathbf{r}}(z) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (1)$$

The idea is to introduce the relevant ensemble  $\bar{\rho}$  as

$$\bar{\rho}(z) = \frac{1}{Z[\lambda]} \rho^{\text{eq}}(z) \exp\{-\lambda \cdot A(z)\}, \quad (2)$$

where  $\rho^{\text{eq}}(z)$  is the equilibrium ensemble and  $\lambda$  is the set of variables conjugate to the relevant variables  $A(z)$ . The generalized partition function is given by

$$Z[\lambda] = \text{Tr}[\rho^{\text{eq}}(z) \exp\{-\lambda \cdot A(z)\}], \quad (3)$$

where the classical trace operation  $\text{Tr}[\dots]$  denotes an integration over  $z$  (and a sum over particle number in a grand canonical ensemble). The average  $a$  of the relevant variables with respect to the relevant ensemble is

$$a = \text{Tr}[A\bar{\rho}] = -\frac{\partial \ln Z}{\partial \lambda}[\lambda] \quad (4)$$

and is a function (or functional) of  $\lambda$ . For each  $\lambda$  we have an average  $a$  given by Eq. (4). If we take the derivative of Eq. (4) with respect to  $\lambda$  we arrive at

$$\frac{\partial a}{\partial \lambda} = -\langle \delta A \delta A \rangle, \quad (5)$$

where  $\delta A = A(z) - a$ . The covariance  $\langle \delta A \delta A \rangle$  is a definite positive matrix, and, therefore, the Jacobian of the change of variables from  $\lambda$  to  $a$  can be inverted to provide  $\lambda[a]$ . Therefore, there is a one to one connection between the pair of conjugate variables  $\lambda$  and  $a$ . This argument is valid for any pair  $a, \lambda$  of conjugate variables and it only depends on the

definition of the conjugate variables introduced in Eq. (2). It constitutes the basic content of the DFT when the relevant variable is the density defined in Eq. (1). Indeed, when the relevant variable  $A(z)$  is the density field in Eq. (1), the relevant ensemble in Eq. (2) becomes

$$\bar{\rho}(z) = \frac{1}{\Xi[\lambda]} \rho^{\text{eq}}(z) \exp\left\{-\beta \int d\mathbf{r} \lambda(\mathbf{r}) \hat{n}_{\mathbf{r}}(z)\right\}, \quad (6)$$

where we introduced the  $\lambda$ -dependent grand partition function as

$$\Xi[\lambda] = \sum_{N=0}^{\infty} \frac{\exp\{\beta\mu N\}}{N! h^{3N}} \int d\mathbf{r}_1 d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N \times \exp\left\{-\beta H_N - \beta \sum_{i=1}^N \lambda(\mathbf{r}_i)\right\}, \quad (7)$$

where  $H_N = K_N + U_N$  is the  $N$ -particle Hamiltonian, with kinetic energy  $K_N = \sum_i^N p_i^2/2m$  and potential of interaction  $U_N$  between the particles including any external field  $V_{\text{ext}}(\mathbf{r})$ ,  $\beta = (k_B T)^{-1}$ ,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant,  $T$  is the temperature, and  $\mu$  is the chemical potential. Here,  $\lambda(\mathbf{r})$  is the conjugate variable of the density field. By its very structure, this conjugate variable could be interpreted as an additional external field, but for other variables different from the density, the conjugate variable cannot be interpreted as an external potential. When  $\lambda=0$ , the relevant ensemble in Eq. (6) coincides with the equilibrium ensemble and the function  $\Xi[\lambda]$  becomes the actual grand partition function.

The  $\lambda$ -dependent grand potential  $\Omega[\lambda]$  is defined in terms of the grand partition function  $\Xi[\lambda]$  through

$$\Omega[\lambda] = -k_B T \ln \Xi[\lambda] \quad (8)$$

and it is itself a functional of the conjugate variable. The functional derivatives of the grand potential with respect to the conjugate field are related to the grand canonical averages of the density field (1). Equation (4) now takes the form

$$\frac{\delta \Omega[\lambda]}{\delta \lambda(\mathbf{r})} = \langle \hat{n}_{\mathbf{r}} \rangle^\lambda \equiv n(\mathbf{r}), \quad (9)$$

where  $\langle \dots \rangle^\lambda$  is the average with respect to the relevant ensemble (6). The second derivatives of the grand potential lead to

$$\frac{\delta^2 \Omega[\lambda]}{\delta \lambda(\mathbf{r}_1) \delta \lambda(\mathbf{r}_2)} = -\beta (\langle \hat{n}_{\mathbf{r}_1} \hat{n}_{\mathbf{r}_2} \rangle^\lambda - \langle \hat{n}_{\mathbf{r}_1} \rangle^\lambda \langle \hat{n}_{\mathbf{r}_2} \rangle^\lambda). \quad (10)$$

Higher derivatives of the grand potential with respect to the external potential lead to expressions involving higher particle distributions. These many particle distributions are all functionals of the external field. Equation (10) shows that, being proportional to a variance, the matrix of second derivatives is definite negative and, therefore, it has a well defined inverse. At the same time, the matrix of second derivatives is, from Eqs. (9) and (10),

$$\frac{\delta^2 \Omega[\lambda]}{\delta \lambda(\mathbf{r}_1) \delta \lambda(\mathbf{r}_2)} = \frac{\delta n(\mathbf{r}_1)}{\delta \lambda(\mathbf{r}_2)}, \quad (11)$$

and, therefore, this matrix can be interpreted as the Jacobian matrix in functional sense of a change of variables, from the external potential to the probability density. The fact that this Jacobian is negative definite implies that its functional determinant does not vanish and the functional  $n[\lambda]$  can be inverted to give  $\lambda[n]$ . In other words, there is a one to one relationship between the conjugate field and the one-particle distribution. This is the essence of the DFT. The corollary of this theorem is that all many particle equilibrium distribution functions, being themselves functionals of the conjugate field  $\lambda(\mathbf{r})$ , are actually functionals of the one-particle distribution. In this way, at equilibrium, the actual functional form of the one-particle distribution function determines the many-particle distribution functions.

In principle, we could use  $n(\mathbf{r})$  as the independent variable in the grand potential, instead of the conjugate field  $\lambda(\mathbf{r})$ . However, note in Eq. (9) that  $n$  is the functional derivative of  $\Omega[\lambda]$ . As we know from the usual treatment in thermodynamics,<sup>28</sup> such a change of variables implies a loss of information. The correct way to proceed is to introduce the Legendre transform  $\bar{\Omega}[n]$  of  $\Omega[\lambda]$ , which is defined by

$$\bar{\Omega}[n] = \Omega[\lambda[n]] - \int d\mathbf{r} n(\mathbf{r}) \lambda(\mathbf{r})[n]. \quad (12)$$

The functional  $\bar{\Omega}[n]$  contains exactly the same information as  $\Omega[\lambda]$ . The Legendre transform  $\bar{\Omega}[n]$  of the grand potential  $\Omega[\lambda]$  is called the *density functional*. By taking the functional derivative of  $\bar{\Omega}[n]$ , one obtains the usual connection between conjugate variables in the Legendre transform,

$$\frac{\delta \bar{\Omega}[n]}{\delta n(\mathbf{r})} = -\lambda(\mathbf{r}), \quad (13)$$

to be compared with Eq. (9). At equilibrium (in the presence of whatever actual external field present) we have that  $\lambda=0$ . As we will see in the next section,  $\lambda$  can be understood as the thermodynamic force driving the evolution of the density field toward equilibrium.

The construction of the density functional in Eq. (12) may be regarded as a purely mathematical transformation devoid of physical meaning. After all, all the information in  $\bar{\Omega}[n]$  is exactly the same as that in  $\Omega[\lambda]$ . But as it happens in some major advances in physics, just rewriting the same thing in different appearance helps in proposing approximation schemes that would otherwise be difficult to implement. In the case of the grand potential, it is easier to approximate the density functional  $\bar{\Omega}[n]$  than the grand potential  $\Omega[\lambda]$  as a functional of the conjugate field. This is usually done by modeling the interaction (or excess) part of the density functional.

### III. TIME-DEPENDENT PROJECTION OPERATOR TECHNIQUE

In general it is possible to derive the evolution equation for a given dynamic variable by using the technique of pro-

jection operators.<sup>25</sup> The projection operator method can be understood, at its most fundamental level as a way to approximate the actual time-dependent ensemble which is the solution of the Liouville equation with an approximate *relevant ensemble*. This relevant ensemble, in turn, is obtained by maximizing the entropy functional subject to macroscopic information. If the macroscopic information is given by the *probability distribution* of the macroscopic variables, the resulting projector is given by Zwanzig projector.<sup>29</sup> If this macroscopic information is just the *average* of certain phase functions one obtains Robertson projector.<sup>30</sup> In this latter case, the relevant ensemble which is obtained from the maximization of the entropy has the form given in Eq. (2).

When the variable selected to describe the system macroscopically is the density  $\hat{n}_r(z)$  one should use Robertson projector. Indeed, it makes no sense to speak about the probability that the phase function  $\hat{n}_r(z)$  takes certain values. The field  $\hat{n}_r(z)$  is a very “spiky” field where a delta function sits on top of every particle. Therefore, the Zwanzig projector is not applicable in this case and we have to resort to the Robertson time-dependent projection operator. We summarize in the rest of this section the time-dependent projection operator technique as presented in the classical textbook by Grabert.<sup>25</sup>

The aim is to derive equations of motion for the time-dependent average  $a_i(t)$  of a set of *relevant variables*  $A_i(z)$ . The time-dependent average is

$$a_i(t) = \text{Tr}[\rho_t(z) A_i(z)], \quad (14)$$

where  $z$  is the microscopic state of the system and  $\rho_t(z)$  is the nonequilibrium solution of the Liouville equation. As it is shown in Ref. 25, the Liouville equation can be rewritten in the following exact form:

$$\frac{\partial}{\partial t} a_i(t) = v_i(t) + \int_0^t dt' \sum_j K_{ij}(t, t') \lambda_j(t). \quad (15)$$

This exact equation is actually a closed equation for  $a_i(t)$ . The reversible term is given by

$$v_i(t) = \text{Tr}[\bar{\rho}_t L A_i], \quad (16)$$

where the Liouville operator is

$$iL = - \sum_i \left[ \frac{\partial H_N}{\partial \mathbf{r}_i} \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial H_N}{\partial \mathbf{p}_i} \frac{\partial}{\partial \mathbf{r}_i} \right], \quad (17)$$

and the relevant ensemble  $\bar{\rho}_t$  is of the form (2), with a time-dependent conjugate variable  $\lambda(t)$ . The conjugate variables  $\lambda$  are selected in such a way that the averages of the real and of the relevant ensemble coincide. Note that if only the reversible term  $v_i(t)$  would be present in Eq. (15), we would be approximating the actual ensemble that it is a solution of the Liouville equation with a relevant ensemble of the form (2), where the conjugate field  $\lambda(t)$  is now a function of time. The error in this approximation is, in fact, the memory term which describes irreversible behavior. The irreversible term in Eq. (15) involves the memory kernel

$$K_{ij}(t, t') = \text{Tr}[\bar{\rho}_{t'}(\mathcal{Q}_{t'} iLA_j)G_{t't}(\mathcal{Q}_t iLA_i)], \quad (18)$$

where the projection operator  $\mathcal{Q}_{t'}$  applied to an arbitrary function  $F(z)$  is

$$\begin{aligned} \mathcal{Q}_{t'}F(z) &= F(z) - \text{Tr}[\bar{\rho}_{t'}F] - \sum_i (A_i(z) \\ &\quad - a_i(t')) \frac{\partial}{\partial a_i(t')} \text{Tr}[\bar{\rho}(t')F]. \end{aligned} \quad (19)$$

Finally, the time ordered projected propagator  $G_{t't}$  is given by

$$\begin{aligned} G_{t't} &= 1 + \sum_{n=1}^{\infty} \int_{t'}^t dt_1 \cdots \int_{t'}^{t_{n-1}} dt_n iL\mathcal{Q}_{t_n} \cdots iL\mathcal{Q}_{t_1} \\ &= T_- \exp \left\{ \int_{t'}^t iL\mathcal{Q}_{t'} dt' \right\}. \end{aligned} \quad (20)$$

Equation (15) is a closed equation for  $a_i(t)$ . The relevant ensemble is a functional of  $a_i(t)$  through  $\lambda(t)$ . The kernel becomes a functional of  $a_i(t)$  through the relevant ensemble. Although Eq. (15) is a closed equation it is an integrodifferential equation which is difficult to treat in general. Nevertheless, the exact transport Eq. (15) can be approximated by a memoryless equation whenever a clear separation of time scales exists between the evolution of the averages and the decay of the memory kernel. Under this assumption and the neglect of terms of order  $\mathcal{O}(iLA^3)$ , assumed to be small due to the slowness of the relevant variables, one obtains the Markovian equation,<sup>25</sup>

$$\dot{a}_i(t) = v_i(t) + \sum_j D_{ij}(t)\lambda_j(t), \quad (21)$$

where the dissipative matrix is given by the Green–Kubo formula,

$$D_{ij}(t) = \int_0^\tau dt' \text{Tr}[\bar{\rho}_{t'}(\mathcal{Q}_{t'} iLA_j)\exp\{iLt'\}(\mathcal{Q}_t iLA_i)]. \quad (22)$$

Here,  $\tau$  is a time large compared to the decay time of the correlation integrand but short in front of the time scale of evolution of the relevant variables. The dissipative matrix depends in general on the relevant variables through the relevant ensemble.

#### IV. DYNAMIC DENSITY FUNCTIONAL THEORY

Now we specialize the above projection operator formalism to the case that the relevant variable is given by the density field, this is,  $A_i(z) \rightarrow \hat{n}_r(z)$ . The discrete index  $i$  becomes in this field description the continuum index  $\mathbf{r}$  and sums over  $i$  will become integrals over  $\mathbf{r}$ . We will denote by  $n(\mathbf{r}, t)$  the nonequilibrium average

$$n(\mathbf{r}, t) = \text{Tr}[\rho_t \hat{n}_r] = \text{Tr}[\bar{\rho}_t \hat{n}_r]. \quad (23)$$

By assuming that  $n(\mathbf{r}, t)$  is the only relevant variable in the system we are making the strong assumption that its time evolution is much slower than any other variable in the system. In particular, the momentum field is assumed to decay much faster than the density field.

The relevant ensemble  $\bar{\rho}_t(z)$  in Eq. (23) is of the form (6) with a time-dependent conjugate field  $\lambda(\mathbf{r}, t)$ ,

$$\bar{\rho}_t(z) = \frac{1}{\Xi[\lambda(t)]} \rho^{\text{eq}}(z) \exp \left\{ -\beta \int d\mathbf{r} \lambda(\mathbf{r}, t) \hat{n}_r(z) \right\}, \quad (24)$$

where  $\lambda(\mathbf{r}, t)$  is fixed by the constrain (4) [i.e., the second identity in Eq. (23)] which now becomes

$$n(\mathbf{r}, t) = \frac{\delta \Omega[\lambda]}{\delta \lambda(\mathbf{r}, t)}, \quad (25)$$

this is, Eq. (9) evaluated at the nonequilibrium average  $n(\mathbf{r}, t)$ .

The Liouville operator on the relevant variable,  $iLA_i$ , is now

$$iLA_i \rightarrow iL\hat{n}_r(z) = -\nabla \cdot \hat{\mathbf{J}}_r(z), \quad (26)$$

where the current of particles is defined as

$$\hat{\mathbf{J}}_r(z) = \sum_i \mathbf{v}_i \delta(\mathbf{r}_i - \mathbf{r}). \quad (27)$$

The term  $v_i(t)$  in Eq. (16) vanishes now, as it involves a Gaussian momentum integral of a velocity. For the same reason, the projected current simplifies to

$$\mathcal{Q}_t iLA_i \rightarrow \mathcal{Q}_t iL\hat{n}_r = \nabla \cdot \hat{\mathbf{J}}_r(z). \quad (28)$$

The dissipative matrix (22) now becomes

$$D_{ij} \rightarrow \nabla_r \nabla_{r'} \mathbf{D}(\mathbf{r}, \mathbf{r}', t), \quad (29)$$

where  $\nabla_r = \partial / \partial \mathbf{r}$  and the diffusion tensor is given by the Green–Kubo formula,

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = \int_0^\tau dt' \text{Tr}[\bar{\rho}_{t'} \hat{\mathbf{J}}_r \hat{\mathbf{J}}_{r'}(t')]. \quad (30)$$

Note that this nonlocal transport coefficient depends on time  $t$  only through the actual value of  $n(\mathbf{r}, t)$  on which it depends functionally (through the conjugate field  $\lambda$  appearing in the relevant ensemble  $\bar{\rho}_t$ ). In general, the calculation of  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$  is difficult because of the presence of the relevant ensemble. In order to deal with more tractable expressions, we may assume as a first approximation that we are *near equilibrium*, in such a way that  $\lambda(\mathbf{r}, t) \approx 0$  and we can substitute  $\bar{\rho}_t \approx \rho^{\text{eq}}$ , see Eq. (2). In this way, the kernel  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$  is just the time integral of the equilibrium current correlation tensor. In the absence of walls, we have translational and rotational invariance and  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D(\mathbf{r} - \mathbf{r}') \mathbf{1}$ . For situations far from equilibrium, we may always expand  $\exp\{-\lambda A\}$  in powers of  $\lambda$  and compute the corresponding corrections.

The final dynamic equation for the density field is given by

$$\partial_t n(\mathbf{r}, t) = \int d\mathbf{r}' \nabla_r \nabla_{r'} \mathbf{D}(\mathbf{r}, \mathbf{r}', t) \lambda(\mathbf{r}', t), \quad (31)$$

or, by virtue of Eq. (13) and an integration by parts, we have

$$\partial_t n(\mathbf{r}, t) = \nabla_{\mathbf{r}} \int d\mathbf{r}' \mathbf{D}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \frac{\delta \bar{\Omega}[n]}{\delta n(\mathbf{r}', t)}. \quad (32)$$

This closed dynamic equation for the evolution of the density field is the main result of this paper.

The operator  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$  being the integral of an autocorrelation is, by the Wiener–Kinchine theorem, positive definite. Therefore, if we compute the time derivative of  $\bar{\Omega}[n]$  we obtain

$$\begin{aligned} \partial_t \bar{\Omega}[n] = & - \int d\mathbf{r} \int d\mathbf{r}' \left[ \nabla_{\mathbf{r}} \frac{\delta \bar{\Omega}[n]}{\delta n(\mathbf{r})} \right] \mathbf{D}(\mathbf{r}, \mathbf{r}', t) \\ & \times \left[ \nabla_{\mathbf{r}'} \frac{\delta \bar{\Omega}[n]}{\delta n(\mathbf{r}')} \right] \leq 0. \end{aligned} \quad (33)$$

Therefore, the equilibrium state of Eq. (32) is the minimum of  $\bar{\Omega}[n]$ , which by virtue of Eq. (13) corresponds to  $\lambda(\mathbf{r}, t) = 0$ . Equation (33) is the H-theorem in this theory.

One important advantage of the projection operator derivation is that it provides a Green–Kubo formula for the diffusion tensor. Therefore, this diffusion tensor can be, in principle, computed from molecular dynamics simulations.<sup>31</sup> This should allow one to test the approximations used to obtain analytical expressions for the diffusion tensor. Note that the only assumption made so far is that the density evolves in a time scale much larger than the current correlation function. This needs to be checked explicitly *a posteriori* in actual simulations. A second main difference of the present derivation of the diffusion equation with respect to usual expressions linear in  $n(\mathbf{r}, t)$  is the fact that the thermodynamic force is given by the functional derivatives of the density functional, which in general is nonlinear and, with sufficiently good approximations for it, provides for the full structure of the system at microscopic scales.

## V. COLLOIDAL SYSTEMS

In the derivation of the dynamic Eq. (32) for  $\hat{n}_{\mathbf{r}}$  we assumed implicitly that the sum in definition (1) was over all the atoms labeled with index  $i$  in the system. However, the above derivation remains *exactly the same* when  $\hat{n}_{\mathbf{r}}$  is interpreted as the concentration field of a collection of colloidal particles. Of course, the different nature of the physical system (molecular fluid or colloidal suspension) will be reflected in the particular form for  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$  and  $\bar{\Omega}[n]$ . In what follows we show how the DDFT obtained with projection operators accommodate several recent proposals for DDFT in colloidal suspensions.

For a dilute colloidal suspension, the current correlation may be computed in an approximated way as follows. We assume that the positions evolve much slower than the velocities of the colloidal particles so we can approximate

$$\begin{aligned} \mathbf{D}(\mathbf{r}, \mathbf{r}') &= \int_0^\infty dt \text{Tr}[\bar{\rho}_t \hat{\mathbf{J}}_{\mathbf{r}} \hat{\mathbf{J}}_{\mathbf{r}'}(t')] \\ &= \int_0^\infty dt \sum_i \sum_j \text{Tr}[\bar{\rho}_t \mathbf{v}_i \mathbf{v}_j(t) \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j(t))] \\ &\approx \int_0^\infty dt \sum_i \sum_j \text{Tr}[\bar{\rho}_t \mathbf{v}_i \mathbf{v}_j(t) \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)]. \end{aligned} \quad (34)$$

In addition, we may assume that velocities and positions are statistically independent, and in the dilute limit, the correlations of velocities of different particles vanish. In this way,

$$\begin{aligned} \mathbf{D}(\mathbf{r}, \mathbf{r}') &\approx \int_0^\infty dt \sum_i \sum_j \text{Tr}[\bar{\rho}_t \mathbf{v}_i \mathbf{v}_j(t)] \text{Tr}[\bar{\rho}_t \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)] \\ &\approx \sum_i \sum_j \delta_{ij} D_0 \mathbf{1} \text{Tr}[\bar{\rho}_t \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j)] \\ &= D_0 \mathbf{1} n(\mathbf{r}, t) \delta(\mathbf{r}' - \mathbf{r}), \end{aligned} \quad (35)$$

where we introduced the diffusion coefficient  $D_0$  through the usual Green–Kubo expression

$$D_0 = \frac{1}{3} \int_0^\infty dt \text{Tr}[\bar{\rho}_t \mathbf{v}_i \cdot \mathbf{v}_i(t)]. \quad (36)$$

By inserting this form (35) into Eq. (32) we arrive at the equation proposed by Marconi and Tarazona,<sup>11</sup>

$$\partial_t n(\mathbf{r}, t) = \nabla_{\mathbf{r}} D_0 n(\mathbf{r}, t) \nabla_{\mathbf{r}} \frac{\delta \bar{\Omega}[n]}{\delta n(\mathbf{r}, t)}. \quad (37)$$

At finite colloidal density, hydrodynamic interactions mediated by the solvent flow play an important role for the dynamics.<sup>20</sup> Two different strategies have been employed to incorporate those in DDFT. We show now that both strategies fall within our general class of DDFT.<sup>31</sup>

The first and simplest strategy was proposed in Ref. 32. Here, on a phenomenological level, the diffusion coefficient  $D_0$  occurring in the standard DDFT in Eq. (37) was replaced by a density-dependent long-time self-diffusion  $D_s(\phi_c)$ , where  $\phi_c$  denotes the volume fraction of the colloids. For hard-sphere colloids, the function  $D_s(\phi_c)$  is known from equilibrium long-time dynamics, see, e.g., Ref. 33 for an empirical fitting formula. The following approximation for the diffusion tensor was used:

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D_s(\bar{\phi}_c(\mathbf{r})) \mathbf{1} n(\mathbf{r}, t) \delta(\mathbf{r}' - \mathbf{r}). \quad (38)$$

Here,  $\bar{\phi}_c(\mathbf{r})$  is a weighted packing fraction gained from the inhomogeneous packing fraction  $\phi_c(\mathbf{r})$  by convoluting the latter with the normalized volume function of a sphere.<sup>32</sup>

As a second strategy, the standard DDFT was generalized<sup>21,22</sup> to include hydrodynamic interactions between the particles explicitly using the approach of Archer and Evans.<sup>12</sup> The form proposed in Refs. 21 and 22 fits into the framework of our general Eq. (32) if the diffusion tensor  $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$  is approximated as

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D_0 k_B T \rho^{(2)}(\mathbf{r}, \mathbf{r}', t) \omega_{12}(\mathbf{r} - \mathbf{r}'). \quad (39)$$

Here,  $\rho^{(2)}(\mathbf{r}, \mathbf{r}', t)$  is the two-particle density in nonequilibrium and the distinct hydrodynamic tensor  $\omega_{12}(\mathbf{r} - \mathbf{r}')$  couples the velocity of a particle at position  $\mathbf{r}$  to the force exerted from another particle at position  $\mathbf{r}'$ . The latter can be further approximated by the Oseen or Rotne–Prager expression.<sup>34</sup>

## VI. CONCLUSIONS

In conclusion, we derived a dynamical density functional theory using the projection operator technique. Assuming that the one-particle is the only slow dynamical variable, a general dynamical deterministic equation was obtained which still involves a generalized diffusion tensor. The standard form of DDFT can be recovered as a special approximation for the diffusion tensor. We have seen that several recent proposals for DDFT for colloidal systems, including those with hydrodynamic interactions, arise as different models for the diffusion tensor. The standard result agrees with alternate derivations starting from the Langevin or Smoluchowski picture of Brownian particles. Our derivation relies on the adiabaticity assumption which in our case is expressed by the current correlations decaying in a much shorter time scale than the typical evolution of the density. This may not occur in general and one has to check explicitly whether the approximation is good enough by comparing these time-scales. When the adiabatic approximation fails, one needs to include the current as a relevant variable, and the resulting theory is a hydrodynamic functional theory (HDFT). The present projection operator framework based on the idea of conjugate variables can be directly used to find the corresponding HDFT that generalizes the Navier–Stokes equations in order to incorporate the microstructure of the fluid.<sup>35</sup> An alternative approach leading to the same HDFT equations is obtained starting from the kinetic level of description.<sup>36</sup> It is possible to show from HDFT that if the viscosity appearing in the generalized Navier–Stokes equations is large, implying fast decay of the momentum density, then one recovers the present DDFT, where the diffusion tensor is expressed then in terms of a generalized Stokes–Einstein relationship.<sup>35</sup>

The standard DDFT equations have been applied to a wealth of various situations including (i) time-dependent traps,<sup>37–39</sup> (ii) dynamical correlations,<sup>40</sup> (iii) tagged particle dynamics in confinement,<sup>41</sup> (iv) sedimentation dynamics,<sup>32</sup> (v) flow around particles,<sup>42,43</sup> (vi) dynamics of fluid phase separation,<sup>44</sup> (vii) crystal nucleation and growth,<sup>45</sup> and (viii) nonequilibrium phase transitions.<sup>46</sup> It would be interesting to extend the dynamical equations toward more complicated diffusion tensors and treat all these interesting applications (i)–(viii) again to check for corrections.

We finally mention that DDFT is the starting point for more coarse-grained dynamical descriptions such as phase-field<sup>47</sup> or phase-field crystal models,<sup>48</sup> which are an important tool to simulate various situations in material science. Recently it was shown how the phenomenological static<sup>49</sup> and dynamical<sup>50</sup> parameters of the phase-field crystal model can be microscopically determined by using DFT and

DDFT. An improvement of the DDFT equations leads directly to a more realistic parameter choice for phase-field simulations which will finally allow to match phase-field simulations<sup>51</sup> better to material properties.

## ACKNOWLEDGMENTS

We thank S. van Teeffelen and A. Härtel for helpful discussions. H.L. thanks the DFG for financial support within the priority Program No. SPP 1296. P.E. acknowledges the hospitality and support of the Freiburg Institute for Advanced Studies and BIFI. P.E. thanks MICINN for financial support under Project No. FIS2007-65869-C03-03.

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