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Extended dynamical density functional theory for colloidal mixtures with temperature gradients

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In the past decade, classical dynamical density functional theory (DDFT) has been developed and widely applied to the Brownian dynamics of interacting colloidal particles. One of the possible derivation routes of DDFT from the microscopic dynamics is via the Mori-Zwanzig-Forster projection operator technique with slowly varying variables such as the one-particle density. Here, we use the projection operator approach to extend DDFT into various directions: first, we generalize DDFT toward mixtures of *n* different species of spherical colloidal particles. We show that there are in general nontrivial cross-coupling terms between the concentration fields and specify them explicitly for colloidal mixtures with pairwise hydrodynamic interactions. Second, we treat the internal energy density as an additional slow variable and derive formal expressions for an extended DDFT containing also the internal energy density. The latter approach can in principle be applied to colloidal dynamics in a nonzero temperature gradient. For the case without hydrodynamic interactions the diffusion tensor is diagonal, while thermodiffusion – the dissipative cross-coupling term between internal energy density and concentration – is nonzero in this limit. With finite hydrodynamic interactions also cross-diffusion coefficients assume a finite value. We demonstrate that our results for the extended DDFT contain the transport coefficients in the hydrodynamic limit (long wavelengths, low frequencies) as a special case. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4769101]

I. INTRODUCTION

While classical density functional theory has become a quite popular tool to calculate static properties of inhomogeneous fluids,[1–5] its generalization to dynamical, i.e., time-dependent, properties is much less advanced.[6] Most progress has been achieved for completely overdamped Brownian particles, which are realized as colloidal suspensions.[7,8] In a seminal paper of the year 1999, Marconi and Tarazona[9,10] have derived a dynamical density functional theory (DDFT) from the Langevin equations describing the motion of the individual particles. The resulting DDFT equation corresponds to the field-theoretical model B for a single scalar order parameter, where the current is proportional to the functional density derivative of the generalized equilibrium Helmholtz free-energy functional (generalized Fick's law). In 2004, Archer and Evans[11] have used the stochastically equivalent Smoluchowski picture to rederive this DDFT equation. In 2009, Español and Löwen[12] have employed the Mori-Zwanzig-Forster projection operator technique (MZFT)[13–19] as a third derivation route by using the one-particle density as the only slow variable of the system.

Subsequently, DDFT has been generalized toward binary mixtures[20–23] and anisotropic particles[24–26] as well as to the dynamics of freezing[27,28] and wetting.[29] Moreover, solvent-mediated hydrodynamic interactions between colloids, which are typically neglected in the modeling although they are important for actual colloidal samples, have been included into DDFT for the one-component case.[30–32] More recent generalizations concern particle self-diffusion in complex environments,[33,34] externally imposed flow fields,[35,36] colloidal sedimentation,[37] and "active" self-propelled particles.[26,38]

In this paper, we follow the route via the MZFT in order to derive an extended DDFT (EDDFT), which goes beyond former DDFT in two respects. At first, we consider a multicomponent mixture of *n* different species of spherical, i.e., isotropic, colloidal particles. Hitherto, calculations for binary mixtures[20–23] assumed a diagonal mobility matrix. Here, we show that there are in general nontrivial cross-coupling terms between the concentration fields. We specify these non-diagonal terms explicitly for colloidal mixtures with pairwise hydrodynamic interactions. Therefore, we establish the basic dynamical equations to apply DDFT to the dynamics of multicomponent colloidal systems including their hydrodynamic interactions. This constitutes a classic colloid problem, which has been explored intensely over several decades by using mode-coupling-like techniques,[39–42] computer simulations,[43,44] and experiments.[45,46] Second, we treat the internal energy density as an additional slow variable and derive formal expressions for an EDDFT containing also the internal energy density. This applies to situations, where a nonzero temperature gradient is imposed leading to thermodiffusion, which is also known as the Ludwig-Soret effect.[47–52] The derived equations also incorporate the reciprocal effect, which is the so-called Dufour effect,[53] where a concentration gradient causes energy transport.

The MZFT is also the standard derivation route for mode-coupling theory (MCT) describing the dynamics of liquids.

MCT has been applied both to molecular[54] and colloidal liquids[55–59] and is by now a pivotal theory for the glass transition. Here, we are using the same theoretical framework of the MZFT to derive an EDDFT. Furthermore, we are using this common basis to compare EDDFT and MCT. A possible connection between DDFT and MCT has already been pointed out by Archer.[60,61]

There is also a close connection of the MZFT with several versions of the classical MCT close to phase transitions,[62–65] which have been pioneered by Kawasaki. For example, for the isotropic-nematic phase transition in liquid crystal side-chain polymers a projection operator technique of MZFT-type[66,67] has been used to construct a MCT,[68,69] which was able to explain the experimental results obtained by two groups[70–72] as being due to a dynamic nonlinear coupling between order-parameter variations and the strain tensor.

The use of MZFT to hydrodynamic condensed systems started with the work by Forster for nematic liquid crystals[15,73] and has been applied in the following to a number of complex fluids with spontaneously broken continuous symmetries,[17] in particular to the superfluid phases of ^{3}He[74,75] and, more recently, to uniaxial magnetic gels.[76] These applications were based on a generalization of the use of correlation functions in the hydrodynamic regime with applications to simple fluids[77] and superfluid ^{4}He.[78] Thus, for all extensions of DDFT to more variables the hydrodynamic regime of long wavelengths and low frequencies emerges for all condensed systems as a natural limit to check the results obtained. Conversely, the EDDFT can be used to investigate how far the range of hydrodynamic considerations can be extended to larger values of frequencies and wave vectors.

The paper is organized as follows: in Sec. II, we summarize in detail the technical aspects of the projection operator technique we use in a coherent fashion. In Sec. III, we present the results of the application of the MZFT to colloidal mixtures in detail including the internal energy density as a variable. Finally, we summarize our results and present a perspective for future generalizations of the present work in Sec. IV.

II. MORI-ZWANZIG-FORSTER TECHNIQUE

The MZFT[13–15] is described in detail in several textbooks.[16–19] Further below, we comprehensively summarize the essential ideas that are relevant for this paper and adjust the notation to the problem at hand.

A. General formalism

For the purpose of this paper, it is most appropriate, but in general not necessary, to consider a grand-canonical ensemble of systems of N particles. The total ensemble $\hat{\Gamma}_t$ with Hamiltonian $\hat{H}(\hat{\Gamma}_t)$[79] involves as canonical variables the $6N$ coordinates $q_i(t)$ and momenta $p_i(t)$ of the N particles. It can be described by the total probability density $\hat{\rho}(t) \equiv \hat{\rho}(\hat{\Gamma}_t)$, which is given by the solution of the *Liouville-von Neumann equation*[80]

$$\dot{\hat{\rho}} = -\hat{\mathcal{L}}\hat{\rho} = -\frac{\mathrm{i}}{\hbar}[\hat{H},\hat{\rho}], \qquad \hat{\rho}(t) = e^{-\hat{\mathcal{L}}t}\hat{\rho}(0) \tag{1}$$

with the Liouvillian $\hat{\mathcal{L}}(\hat{\Gamma}_t)$, the imaginary unit i, the reduced Planck constant $\hbar = h/(2\pi)$, and the commutator $[X, Y] = XY - YX$ of X and Y. Alternatively, it is also possible to describe the same system in terms of only a few *relevant* variables $\hat{a}_i(t) \equiv \hat{a}_i(\vec{r}, t) \equiv \hat{a}_i(\hat{\Gamma}_t; \vec{r})$[81] with $i = 1, \dots, n$, which we assume to be real-valued in the following. The corresponding relevant ensemble Γ_t is associated with the relevant probability density $\rho(t) \equiv \rho(\hat{\Gamma}_t)$. Using the relevant probability density $\rho(t)$ and the grand-canonical trace Tr, which is given for classical systems by

$$\mathrm{Tr} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!h^{3N}} \int_{\hat{\Gamma}_t}\!\mathrm{d}\hat{\Gamma}_t \tag{2}$$

with the inverse thermal energy $\beta = 1/(k_{\mathrm{B}}T)$, Boltzmann constant k_{B}, absolute temperature T, chemical potential μ, and ensemble differential $\mathrm{d}\hat{\Gamma}_t = \mathrm{d}q_1\mathrm{d}p_1 \cdots \mathrm{d}q_{3N}\mathrm{d}p_{3N}$, the time-dependent ensemble average

$$\langle X(0)\rangle_t = \mathrm{Tr}(\rho(t)X(0)) = \mathrm{Tr}(\rho(0)X(t)) \tag{3}$$

of an arbitrary variable $X(t)$ can be defined. The averaged relevant variables $a_i(t) \equiv a_i(\vec{r}, t)$[82] are given by

$$a_i(t) = \langle \hat{a}_i(0)\rangle_t = \mathrm{Tr}(\rho(t)\hat{a}_i(0)) = \mathrm{Tr}(\hat{\rho}(t)\hat{a}_i(0)). \tag{4}$$

For a given thermodynamic functional like the generalized Helmholtz free-energy functional $\mathcal{F}$, their thermodynamic conjugates $a_i^\natural(t) \equiv a_i^\natural(\vec{r}, t)$ can be obtained by functional differentiation:[83]

$$a_i^\natural = \frac{\delta\mathcal{F}}{\delta a_i}. \tag{5}$$

A possible representation for the generalized Helmholtz free-energy functional is

$$\mathcal{F} = \mathrm{Tr}(\rho\hat{H}) + \frac{1}{\beta}\mathrm{Tr}(\rho\ln(\rho)). \tag{6}$$

The generalized Helmholtz free-energy functional $\mathcal{F}[\vec{a}]$[84] depends functionally on the averaged relevant variables $a_i(t)$ and is related to the grand-canonical functional $\Omega[\vec{a}^\natural]$, that depends functionally on the thermodynamic conjugates $a_i^\natural(t)$, by the Legendre transformation

$$\Omega[\vec{a}^\natural] = \mathcal{F}[\vec{a}] - a_i^\natural a_i. \tag{7}$$

A map from the total ensemble $\hat{\Gamma}_t$ onto the relevant ensemble Γ_t is constituted by a suitable projection operator $\hat{\mathcal{P}}_t = 1 - \hat{\mathcal{Q}}_t$. This projection operator can be written as[16]

$$\hat{\mathcal{P}}_t X = \mathrm{Tr}(\rho(t)X) + (\hat{a}_i - a_i(t))\,\mathrm{Tr}\bigg(\frac{\partial\rho(t)}{\partial a_i(t)}X\bigg). \tag{8}$$

It projects onto a space that is spanned by the linearly independent[85] variables $\hat{a}_i(t)$ and the unity id.

The MZFT consists in the application of this operator in order to obtain transport equations for the relevant variables $\hat{a}_i(t)$, that are equivalent to the *Liouville-von Neumann equations*

$$\dot{\hat{a}}_i = \hat{\mathcal{L}}\hat{a}_i = \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{a}_i], \qquad \hat{a}_i(t) = e^{\hat{\mathcal{L}}t}\hat{a}_i(0), \tag{9}$$

by projecting out all irrelevant variables. These transport equations are given, for example, in Ref. 16 in its general form.

The dynamics of the reduced relevant variables $\Delta\hat{a}_i(t) = \hat{a}_i(t) - a_i(t)$ is given by the (exact) *generalized Langevin equations*[16,17]

$$\Delta\dot{\hat{a}}_i(t) = \Omega_{ij}(t)\Delta\hat{a}_j(t) + \int_0^t \mathrm{d}t'\, K_{ij}(t,t')\Delta\hat{a}_j(t') + \hat{F}_i(t) \tag{10}$$

with the frequency matrix

$$\Omega_{ij}(t) = \frac{\partial}{\partial a_j(t)}\,\mathrm{Tr}(\rho(t)\dot{\hat{a}}_i), \tag{11}$$

the memory matrix

$$K_{ij}(t,t') = \mathrm{Tr}\biggl(\frac{\partial\rho(t')}{\partial a_j(t')}\,\hat{\mathcal{L}}\,\hat{\mathcal{Q}}_{t'}\hat{\mathcal{G}}(t',t)\dot{\hat{a}}_i\biggr) - \dot{a}_k(t')\,\mathrm{Tr}\biggl(\frac{\partial^2\rho(t')}{\partial a_j(t')\partial a_k(t')}\hat{\mathcal{G}}(t',t)\dot{\hat{a}}_i\biggr), \tag{12}$$

and the noise

$$\hat{F}_i(t) = \hat{\mathcal{Q}}_0\hat{\mathcal{G}}(0,t)\dot{\hat{a}}_i. \tag{13}$$

Here, $\hat{\mathcal{G}}(t',t)$ is the time-ordered exponential operator

$$\hat{\mathcal{G}}(t',t) = \mathcal{T}_-\exp\biggl(\int_{t'}^{t}\mathrm{d}t''\,\hat{\mathcal{L}}\,\hat{\mathcal{Q}}_{t''}\biggr), \tag{14}$$

where the time-ordering operator $\mathcal{T}_-$ orders operators from left to right as time increases.

Furthermore, the dynamics of the averaged relevant variables $a_i(t)$ is described by the *averaged Langevin equations*[16]

$$\dot{a}_i(t) = \mathrm{Tr}(\rho(t)\dot{\hat{a}}_i) + \int_0^t \mathrm{d}t'\,\mathrm{Tr}(\rho(t')\hat{\mathcal{L}}\,\hat{\mathcal{Q}}_{t'}\hat{\mathcal{G}}(t',t)\dot{\hat{a}}_i) + F_i(t) \tag{15}$$

with the averaged noise $F_i(t) = \mathrm{Tr}(\rho(0)\hat{F}_i(t))$.

The frequency matrix $\Omega_{ij}(t)$ takes the instantaneous reversible contributions to the dynamics of the relevant variables into account. In linearized form, it is an equal-time commutator of field operators. Whenever the chosen relevant variables $\hat{a}_i(t)$ have the same time-reversal behavior, the frequency matrix vanishes. The memory matrix $K_{ij}(t, t')$, on the other hand, comprises the non-instantaneous reversible contributions and all dissipative contributions to the dynamics of the relevant variables. The important finding that the memory matrix can also include (non-instantaneous) reversible contributions was first shown by Forster.[15,17,73]

B. Special generalized probability density

The transport equations for the relevant variables and their correlation functions are given in this section for the specific case of the generalized grand canonical probability density

$$\rho(t) = \frac{1}{\Xi(t)}\,e^{-\beta\hat{H}_{\mathrm{eff}}(t)} \tag{16}$$

with the grand-canonical partition sum $\Xi(t)$ and the effective Hamiltonian

$$\hat{H}_{\mathrm{eff}}(t) = \hat{H} - a_i^{\natural}(t)\hat{a}_i. \tag{17}$$

For this particular choice, the projection operator (8) is specified as the Robertson projector (see Refs. 12, 16, and 86)[87]

$$\hat{\mathcal{P}}_t X = \mathrm{Tr}(\rho(t)X) + (\hat{a}_i - a_i(t))\,\chi_{ij}^{-1}(t)\,\mathrm{Tr}\left(\frac{\partial\rho(t)}{\partial a_j^{\natural}(t)}X\right) \tag{18}$$

with the symmetric non-equilibrium susceptibility matrix

$$\chi_{ij}(t) = \frac{\delta a_i(t)}{\delta a_j^{\natural}(t)} = \beta\,\mathrm{Tr}(\rho(t)(\hat{a}_i - a_i(t))\hat{\mathfrak{C}}_t(\hat{a}_j - a_j(t))), \tag{19}$$

the derivative[88]

$$\frac{\partial\rho(t)}{\partial a_i^{\natural}(t)} = \beta\,\hat{\mathfrak{C}}_t(\hat{a}_i - a_i(t))\rho(t), \tag{20}$$

and the operator

$$\hat{\mathfrak{C}}_t X = \int_0^1 \mathrm{d}\lambda\, e^{-\lambda\beta\hat{H}_{\mathrm{eff}}(t)}X e^{\lambda\beta\hat{H}_{\mathrm{eff}}(t)}. \tag{21}$$

This operator can be omitted for a classical system: $\hat{\mathfrak{C}}_t X = X$.

1. Non-equilibrium dynamics

The particular choice (16) of $\rho(t)$ leads to the *exact transport equations*[16]

$$\dot{a}_i(t) = -B_{ij}(t)a_j^{\natural}(t) - \int_0^t \mathrm{d}t'\,R_{ij}(t,t')a_j^{\natural}(t') \tag{22}$$

with the antisymmetric drift matrix

$$B_{ij}(t) = \frac{\mathrm{i}}{\hbar}\,\mathrm{Tr}(\rho(t)[\hat{a}_i,\hat{a}_j]) = -B_{ji}(t) \tag{23}$$

and the retardation matrix

$$R_{ij}(t,t') = \beta\,\mathrm{Tr}(\rho(t')(\hat{\mathcal{Q}}_{t'}\hat{\mathcal{G}}(t',t)\dot{\hat{a}}_i)(\hat{\mathfrak{C}}_{t'}\dot{\hat{a}}_j)). \tag{24}$$

Notice that these transport equations are applicable also far from thermodynamic equilibrium.

2. Equilibrium correlations

In thermodynamic equilibrium, the transport equations for equilibrium time correlation functions (so-called *Kubo functions*[17])

$$C_{ij}(t) = \bigl\langle \Delta\hat{a}_i^{\mathrm{eq}}(t)\big|\Delta\hat{a}_j^{\mathrm{eq}}(0)\bigr\rangle_{\mathrm{eq}} \tag{25}$$

with the equilibrium fluctuations $\Delta\hat{a}_i^{\mathrm{eq}}(t) = \hat{a}_i(t) - a_i^{\mathrm{eq}}$ have no noise term. Here, the letters "eq" denote equilibrium quantities and Mori's scalar product is given by

$$\langle X|Y\rangle_{\mathrm{eq}} = \mathrm{Tr}(\rho^{\mathrm{eq}}X\,\hat{\mathfrak{C}}^{\mathrm{eq}}Y) \tag{26}$$

with the equilibrium probability density

$$\rho^{\mathrm{eq}} = \frac{1}{\Xi^{\mathrm{eq}}}\,e^{-\beta\hat{H}} \tag{27}$$

and the operator

$$\hat{\mathfrak{C}}^{\mathrm{eq}}X = \int_0^1 \mathrm{d}\lambda\, e^{-\lambda\beta\hat{H}}X\,e^{\lambda\beta\hat{H}}. \tag{28}$$

On the basis of Mori's scalar product (26), the equilibrium average $\langle X\rangle_{\mathrm{eq}} = \langle X\,|\,\mathrm{id}\rangle_{\mathrm{eq}} = \mathrm{Tr}(\rho^{\mathrm{eq}}X)$ is defined. In the following, we present transport equations for the time correlation functions $C_{ij}(t)$. These transport equations are at first given in position-time space $(\vec{r}, t)$ and later analyzed in the context of linear response theory in Fourier-Laplace space $(\vec{k}, z)$.

a. Position-time space: In the linear regime near equilibrium, the dynamics of the time correlation functions $C_{ij}(t)$ can be derived from Eq. (22) by linearization. The resulting transport equations are given by[16,17]

$$\dot{C}_{ij}(t) = \Omega^{\mathrm{eq}}_{ik}\, C_{kj}(t) + \int_0^t \mathrm{d}t'\, K^{\mathrm{eq}}_{ik}(t-t')C_{kj}(t') \tag{29}$$

with the equilibrium frequency matrix

$$\Omega^{\mathrm{eq}}_{ij} = -B^{\mathrm{eq}}_{ik}\, \chi^{\mathrm{eq}-1}_{kj} \tag{30}$$

and the equilibrium memory matrix

$$K^{\mathrm{eq}}_{ij}(t) = -R^{\mathrm{eq}}_{ik}(t)\, \chi^{\mathrm{eq}-1}_{kj}. \tag{31}$$

These equilibrium matrices depend on the equilibrium drift matrix[89]

$$B^{\mathrm{eq}}_{ij} = \frac{\mathrm{i}}{\hbar}\langle[\hat{a}_i, \hat{a}_j]\rangle_{\mathrm{eq}} = -\beta\big\langle\Delta\dot{\hat{a}}^{\mathrm{eq}}_i\big|\Delta\hat{a}^{\mathrm{eq}}_j\big\rangle_{\mathrm{eq}}, \tag{32}$$

on the equilibrium retardation matrix[90]

$$R^{\mathrm{eq}}_{ij}(t) = \beta\big\langle\hat{\mathcal{Q}}^{\mathrm{eq}}\hat{\mathcal{G}}^{\mathrm{eq}}(t)\dot{\hat{a}}_i\big|\dot{\hat{a}}_j\big\rangle_{\mathrm{eq}}, \tag{33}$$

and on the static equilibrium susceptibility matrix

$$\chi^{\mathrm{eq}}_{ij} = \beta\big\langle\Delta\hat{a}^{\mathrm{eq}}_i\big|\Delta\hat{a}^{\mathrm{eq}}_j\big\rangle_{\mathrm{eq}}. \tag{34}$$

Here, the equilibrium projector $\hat{\mathcal{P}}^{\mathrm{eq}} = 1 - \hat{\mathcal{Q}}^{\mathrm{eq}}$ is given by

$$\hat{\mathcal{P}}^{\mathrm{eq}}X = \langle X\rangle_{\mathrm{eq}} + \beta\,\Delta\hat{a}^{\mathrm{eq}}_i\, \chi^{\mathrm{eq}-1}_{ij}\big\langle\Delta\hat{a}^{\mathrm{eq}}_j\big|X\big\rangle_{\mathrm{eq}} \tag{35}$$

and the equilibrium exponential operator is

$$\hat{\mathcal{G}}^{\mathrm{eq}}(t) = e^{\hat{\mathcal{L}}\hat{\mathcal{Q}}^{\mathrm{eq}}t}. \tag{36}$$

Notice that the linearized transport equation (29) can be used to determine the equilibrium frequency matrix $\Omega^{\mathrm{eq}}_{ij}$ and the equilibrium memory matrix $K^{\mathrm{eq}}_{ij}(t)$ exactly. It is thus possible to calculate these matrices by the evaluation of equilibrium correlation functions obtained from experiments or microscopic simulations.

b. Fourier-Laplace space: In Fourier-Laplace space (see the Appendix) the dynamical equation (29) obtain the simpler form[17]

$$\big(z\delta_{ik} - \Omega^{\mathrm{eq}}_{ik} - \widetilde{K}^{\mathrm{eq}}_{ik}(z)\big)\widetilde{C}_{kj}(z) = C_{ij}(0) = \frac{\chi^{\mathrm{eq}}_{ij}}{\beta} \tag{37}$$

with the obvious solution

$$\widetilde{C}_{ij}(z) = \beta^{-1}(z\mathbf{1} - \Omega^{\mathrm{eq}} - \widetilde{K}^{\mathrm{eq}}(z))^{-1}_{ik}\,\chi^{\mathrm{eq}}_{kj}. \tag{38}$$

Notice that $\widetilde{C}_{ij}(z)$, $C_{ij}(0)$, $\Omega^{\mathrm{eq}}_{ij}$, $\widetilde{K}^{\mathrm{eq}}_{ij}(z)$, and χ^{eq}_{ij} are given in Fourier space, although their wave-vector dependence is not denoted explicitly here. Furthermore, $X(t)$ denotes a time-dependent quantity, $\widetilde{X}(\omega)$ its Fourier transform, and $\widetilde{X}(z)$ its Laplace transform in this paragraph.

The Fourier transformed equilibrium frequency matrix $\Omega^{\mathrm{eq}}_{ij}$ and the Fourier-Laplace transformed equilibrium memory matrix $\widetilde{K}^{\mathrm{eq}}_{ij}(z)$ in Eqs. (37) and (38) are given by

$$\Omega^{\mathrm{eq}}_{ij} = -B^{\mathrm{eq}}_{ik}\,\chi^{\mathrm{eq}-1}_{kj}, \qquad \widetilde{K}^{\mathrm{eq}}_{ij}(z) = -\widetilde{R}^{\mathrm{eq}}_{ik}(z)\,\chi^{\mathrm{eq}-1}_{kj} \tag{39}$$

with the Fourier transformed equilibrium drift matrix

$$B^{\mathrm{eq}}_{ij} = \frac{\mathrm{i}}{\pi}\int_{\mathbb{R}}\mathrm{d}\omega\,\widetilde{\chi}''_{ij}(\omega), \tag{40}$$

the Fourier-Laplace transformed equilibrium retardation matrix[91]

$$\widetilde{R}^{\mathrm{eq}}_{ij}(z) = \beta\big\langle\Delta\dot{\hat{a}}^{\mathrm{eq}}_i\big|\hat{\mathcal{Q}}^{\mathrm{eq}}\big(z + \hat{\mathcal{L}}^{\mathrm{eq}}_{\hat{\mathcal{Q}}}\big)^{-1}\hat{\mathcal{Q}}^{\mathrm{eq}}\big|\Delta\dot{\hat{a}}^{\mathrm{eq}}_j\big\rangle_{\mathrm{eq}} \tag{41}$$

with the equilibrium self-adjoined reduced Liouvillian $\hat{\mathcal{L}}^{\mathrm{eq}}_{\hat{\mathcal{Q}}} = \hat{\mathcal{Q}}^{\mathrm{eq}}\hat{\mathcal{L}}\hat{\mathcal{Q}}^{\mathrm{eq}}$,[92] and the Fourier transformed static equilibrium susceptibility matrix

$$\chi^{\mathrm{eq}}_{ij} = \lim_{\epsilon\to 0^+}\widetilde{\chi}_{ij}(z)\big|_{z=\epsilon} = \frac{1}{\pi}\int_{\mathbb{R}}\mathrm{d}\omega\,\frac{\widetilde{\chi}''_{ij}(\omega)}{\omega}. \tag{42}$$

Here, the dynamic susceptibility matrix

$$\widetilde{\chi}_{ij}(z) = \frac{1}{\pi}\int_{\mathbb{R}}\mathrm{d}\omega\,\frac{\widetilde{\chi}''_{ij}(\omega)}{\omega - \mathrm{i}z} \tag{43}$$

and the absorptive response function

$$\chi''_{ij}(t-t') = \frac{1}{2\hbar}\langle[\hat{a}_i(t), \hat{a}_j(t')]\rangle_{\mathrm{eq}} \tag{44}$$

have been introduced. As usual in the context of linear response theory, the absorptive response function appears as a contribution in the complex response function

$$\widetilde{\chi}_{ij}(\omega) = \widetilde{\chi}'_{ij}(\omega) + \mathrm{i}\,\widetilde{\chi}''_{ij}(\omega) \tag{45}$$

with the reactive part $\widetilde{\chi}'_{ij}(\omega)$ and the absorptive part $\widetilde{\chi}''_{ij}(\omega)$, whose non-diagonal elements are not necessarily real-valued. The reactive response function $\widetilde{\chi}'_{ij}(\omega)$ and the absorptive response function $\widetilde{\chi}''_{ij}(\omega)$ are dependent and related to each other by the Kramers-Kronig (dispersion) relations

$$\begin{aligned}\widetilde{\chi}'_{ij}(\omega) &= \frac{1}{\pi}\,\mathrm{P}\!\int_{\mathbb{R}}\mathrm{d}\omega'\,\frac{\widetilde{\chi}''_{ij}(\omega')}{\omega' - \omega},\\ \widetilde{\chi}''_{ij}(\omega) &= -\frac{1}{\pi}\,\mathrm{P}\!\int_{\mathbb{R}}\mathrm{d}\omega'\,\frac{\widetilde{\chi}'_{ij}(\omega')}{\omega' - \omega}.\end{aligned} \tag{46}$$

Also the time correlation functions $C_{ij}(t)$ can be expressed in terms of the absorptive response function:

$$\dot{C}_{ij}(t) = \frac{2}{\mathrm{i}\beta}\,\chi''_{ij}(t). \tag{47}$$

Hence, their Laplace transforms $\widetilde{C}_{ij}(z)$ are given by

$$\widetilde{C}_{ij}(z) = \frac{1}{\mathrm{i}\pi\beta}\int_{\mathbb{R}}\mathrm{d}\omega\,\frac{\widetilde{\chi}''_{ij}(\omega)}{\omega(\omega - \mathrm{i}z)}. \tag{48}$$

C. Slow variables

If the relevant variables vary sufficiently slowly with time so that there is a clear separation of time scales between the slowly relaxing relevant variables and the fast relaxing irrelevant variables, the transport equations (22) and (29) can be simplified by neglecting contributions of order $\mathcal{O}(\dot{\hat{a}}_i^3)$. Using the expansion[19]

$$e^{\hat{\mathcal{Q}}_t\hat{\mathcal{L}}t} = e^{\hat{\mathcal{L}}t} + \mathcal{O}(\dot{\hat{a}}_i), \tag{49}$$

the retardation matrix (24) can be approximated by[16]

$$R_{ij}(t,t') = \beta\,\mathrm{Tr}(\rho(t)(e^{\hat{\mathcal{L}}(t-t')}\hat{\mathcal{Q}}_t\dot{\hat{a}}_i)(\hat{\mathfrak{E}}_t\dot{\hat{a}}_j)) + \mathcal{O}\big(\dot{\hat{a}}_k^3\big). \tag{50}$$

1. Non-equilibrium dynamics

The approximation (50) results in the simplified *transport equations for slow variables*[16]

$$\dot{a}_i(t) = -B_{ij}(t)a_j^\natural(t) - \beta D_{ij}(t)a_j^\natural(t). \tag{51}$$

This Markovian approximation is also applicable far from thermodynamic equilibrium, but it is not appropriate, if effects related to "long time tails" (like the glass transition[92]) are investigated.[16] The transport coefficients are given by the drift matrix $B_{ij}(t)$ and the mobility matrix $D_{ij}(t)$. The mobility matrix is given by the Green-Kubo-type expression

$$D_{ij}(t) = \int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}(\rho(t)(e^{\hat{\mathcal{L}}t'}\hat{\mathcal{Q}}_t\dot{\hat{a}}_i)(\hat{\mathfrak{E}}_t\dot{\hat{a}}_j)). \tag{52}$$

In the classical limit, this expression simplifies to[12,19]

$$D_{ij}(t) = \int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}\left(\rho(t)(\hat{\mathcal{Q}}_t\dot{\hat{a}}_j)e^{\hat{\mathcal{L}}t'}(\hat{\mathcal{Q}}_t\dot{\hat{a}}_i)\right), \tag{53}$$

where a redundant $\hat{\mathcal{Q}}_t$ has been inserted in front of $\dot{\hat{a}}_j$ in order to symmetrize the expression. Further redundant operators $\hat{\mathcal{Q}}_t$ could be inserted in the exponential function in Eq. (53) by replacing the Liouvillian $\hat{\mathcal{L}}$ by the self-adjoint reduced Liouvillian $\hat{\mathcal{L}}_t^{\hat{\mathcal{Q}}} = \hat{\mathcal{Q}}_t\hat{\mathcal{L}}\hat{\mathcal{Q}}_t$. Notice that the transport equation (51) in combination with the approximation (53) is exact up to the third order in $\dot{\hat{a}}_i$.

2. Equilibrium correlations

With the same approximation, the transport equation (29) for the equilibrium time correlation functions $C_{ij}(t)$ becomes

$$\dot{C}_{ij}(t) = \Omega_{ik}^{\mathrm{eq}}\,C_{kj}(t) + \Gamma_{ik}^{\mathrm{eq}}\,C_{kj}(t). \tag{54}$$

Here, we introduced the transport matrix

$$\Gamma_{ij}^{\mathrm{eq}} = -\beta D_{ik}^{\mathrm{eq}}\,\chi_{kj}^{\mathrm{eq}-1} \tag{55}$$

with the mobility matrix

$$D_{ij}^{\mathrm{eq}} = \int_0^\infty\!\mathrm{d}t'\,\big\langle\Delta\dot{\hat{a}}_i^{\mathrm{eq}}\big|\hat{\mathcal{Q}}^{\mathrm{eq}}e^{\hat{\mathcal{L}}t'}\hat{\mathcal{Q}}^{\mathrm{eq}}\big|\Delta\dot{\hat{a}}_j^{\mathrm{eq}}\big\rangle_{\mathrm{eq}}. \tag{56}$$

D. Conserved quantities

An important example for slowly relaxing variables is local densities of conserved quantities. The transport equations of such conserved quantities $\hat{a}_i(\vec{r},t)$ can be written as conservation laws

$$\dot{\hat{a}}_i + \vec{\nabla}_{\vec{r}}\cdot\hat{\vec{J}}^{(i)} = 0 \tag{57}$$

with local currents $\hat{\vec{J}}^{(i)}(\vec{r},t)$ corresponding to $\hat{a}_i(\vec{r},t)$. Analogous conservation laws hold for the averaged variables $a_i(\vec{r},t)$ with the averaged local currents $\vec{J}^{(i)}(\vec{r},t) = \mathrm{Tr}(\rho(t)\hat{\vec{J}}^{(i)}(\vec{r},0))$: $\dot{a}_i + \vec{\nabla}_{\vec{r}}\cdot\vec{J}^{(i)} = 0$.

1. Non-equilibrium dynamics

Since only classical systems with slow variables are considered in the following, dynamical equations for the time-evolution of the averaged relevant variables $a_i(\vec{r},t)$ can be derived from Eqs. (15), (51), (53), and (57). These are the general classical *extended DDFT equations*

$$\begin{aligned}\dot{a}_i(\vec{r},t) = {}& -\vec{\nabla}_{\vec{r}}\cdot\mathrm{Tr}(\rho(t)\hat{\vec{J}}^{(i)}(\vec{r},0))\\ &+\sum_{j=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\;\beta D^{(ij)}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}a_j^\natural(\vec{r}\,',t)\end{aligned} \tag{58}$$

with the diffusion tensor

$$D_{kl}^{(ij)}(\vec{r},\vec{r}\,',t) = \int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}(\rho(t)(\hat{\mathcal{Q}}_t\hat{J}_l^{(j)}(\vec{r}\,',0))e^{\hat{\mathcal{L}}t'}(\hat{\mathcal{Q}}_t\hat{J}_k^{(i)}(\vec{r},0))). \tag{59}$$

If the variables $\hat{a}_i(t)$ are real and have definite time-reversal signatures, one can show that $D_{kl}^{(ij)}(\vec{r},\vec{r}\,',t)$ is symmetric:[17] $D_{kl}^{(ij)}(\vec{r},\vec{r}\,',t) = D_{lk}^{(ji)}(\vec{r},\vec{r}\,',t)$. This statement is known as *Onsager's principle*.[93]

The EDDFT equation (58) can be interpreted as generalized drift-diffusion equations, where the first term on the right-hand-side of Eq. (58) is associated with drift and the second term is associated with diffusion. Notice that the drift term, which is not present in traditional DDFT,[9–12,26] is closely related to the current $\hat{\vec{J}}^{(i)}(\vec{r},t)$, while the diffusion term is related to the time autocorrelation of $\hat{\vec{J}}^{(i)}(\vec{r},t)$.

2. Equilibrium correlations

The assumption of conserved quantities can also be used to rearrange the transport equation (54) for the equilibrium time correlation functions $C_{ij}(\vec{r},\vec{r}\,',t)$ into

$$\dot{C}_{ij}(\vec{r},\vec{r}\,',t) = \sum_{k=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\;L_{\mathrm{eq}}^{(ik)}(\vec{r},\vec{r}\,'')C_{kj}(\vec{r}\,'',\vec{r}\,',t) \tag{60}$$

with the total transport matrix

$$L_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,') = \Omega_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,') + \Gamma_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,'). \tag{61}$$

This matrix includes the contributions

$$\Omega_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,') = -\sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\;B_{\mathrm{eq}}^{(ik)}(\vec{r},\vec{r}\,'')\,\chi_{kj}^{\mathrm{eq}-1}(\vec{r}\,'',\vec{r}\,') \tag{62}$$

and

$$\Gamma^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \sum_{k=1}^{n} \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(ik)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{kj}(\vec{r}\,'',\vec{r}\,') \tag{63}$$

with the equilibrium drift tensor

$$B^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \beta\big\langle \hat{\vec{J}}^{(i)}(\vec{r},0)\big|\Delta\hat{a}^{\mathrm{eq}}_{j}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}} \tag{64}$$

and the equilibrium diffusion tensor

$$D^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \int_0^\infty\!\mathrm{d}t'\,\langle \hat{\vec{J}}^{(i)}(\vec{r},0)|\hat{\mathcal{Q}}^{\mathrm{eq}}e^{\hat{\mathcal{L}}t'}\hat{\mathcal{Q}}^{\mathrm{eq}}|\hat{\vec{J}}^{(j)}(\vec{r}\,',0)\rangle_{\mathrm{eq}}. \tag{65}$$

III. COLLOIDAL MIXTURES

So far, our considerations hold for arbitrary many-particle systems that are described by the Liouville-von Neumann equation (1). We now focus on colloidal systems, where N_{c} big and slow (colloidal) particles are suspended in a solvent consisting of $N_0 \gg N_{\mathrm{c}}$ much smaller and faster (atomic or molecular) particles so that there is a clear separation of time scales between the slow overdamped Brownian dynamics of the colloidal particles and the fast underdamped Newtonian dynamics of the solvent particles. This separation of time scales allows us to concentrate only on the colloidal particles, while the particles of the solvent do not have to be treated explicitly. In particular, we consider a mixture of $N_{\mathrm{c}} = \sum_{i=1}^{n} N_i$ isotropic colloidal particles of n different species in the following, where N_i is the total number of particles of species $i \in \{1, \dots, n\}$.[94] These colloidal particles are assumed to be suspended in a molecular solvent consisting of N_0 small isotropic particles of the same type.

The MZFT is now used to derive an EDDFT equation for mixtures of colloidal particles. When $\vec{r}^{(i)}_k(t)$ denotes the position, $\vec{p}^{(i)}_k(t)$ the momentum, and m_i the mass of the kth particle of species i, where $i = 0$ corresponds to the molecules of the molecular solvent and $i > 0$ corresponds to the colloidal particles, the Hamiltonian of the system is given by

$$\hat{H}(\hat{\Gamma}_t,t) = \sum_{i=0}^{n}\sum_{k=1}^{N_i}\hat{H}^{(i)}_k(\hat{\Gamma}_t,t) \tag{66}$$

with

$$\hat{H}^{(i)}_k(\hat{\Gamma}_t,t) = \frac{\vec{p}^{\,(i)2}_k}{2m_i} + U^{(i)}_1\big(\vec{r}^{(i)}_k,t\big) + \frac{1}{2}\sum_{j=0}^{n}\sum_{l=1}^{N_j}(1-\delta_{kl}\delta_{ij})U^{(ij)}_2\big(\vec{r}^{(i)}_k - \vec{r}^{(j)}_l\big). \tag{67}$$

$U^{(i)}_1(\vec{r}^{(i)}_k,t)$ is the external potential acting on the particles of species i, $U^{(ij)}_2(\vec{r}^{(i)}_k - \vec{r}^{(j)}_l)$ is the pair-interaction potential for two particles of species i and j, respectively, and $\hat{\Gamma}_t$ is the total ensemble introduced in the beginning of Sec. II. To assure that the MZFT as described in Sec. II is applicable, the external potential is assumed to vary sufficiently slowly with time (see Ref. 79). The Liouvillian $\hat{\mathcal{L}}(\hat{\Gamma}_t,t)$ corresponding to the Hamiltonian (66) of the considered system is

$$\hat{\mathcal{L}} = \sum_{i=0}^{n}\sum_{k=1}^{N_i}\big(\vec{\nabla}_{\vec{p}^{(i)}_k}\hat{H}\big)\cdot\vec{\nabla}_{\vec{r}^{(i)}_k} - \big(\vec{\nabla}_{\vec{r}^{(i)}_k}\hat{H}\big)\cdot\vec{\nabla}_{\vec{p}^{(i)}_k}. \tag{68}$$

A. Relevant variables

As relevant variables $\hat{a}_i(\vec{r},t)$ of the colloidal mixture, we choose the n concentrations

$$\hat{c}_i(\vec{r},t) = \sum_{k=1}^{N_i}\delta\big(\vec{r}-\vec{r}^{(i)}_k(t)\big) \tag{69}$$

with $i \in \{1, \dots, n\}$ and the internal energy density

$$\hat{\varepsilon}(\vec{r},t) = \sum_{i=0}^{n}\sum_{k=1}^{N_i}\hat{H}^{(i)}_k(\hat{\Gamma}_t,t)\delta\big(\vec{r}-\vec{r}^{(i)}_k(t)\big). \tag{70}$$

Their averages are denoted as $c_i(\vec{r},t) = \mathrm{Tr}(\rho(0)\hat{c}_i(\vec{r},t))$ and $\varepsilon(\vec{r},t) = \mathrm{Tr}(\rho(0)\hat{\varepsilon}(\vec{r},t))$ in the following.

By considering only the n concentrations $\hat{a}_1(\vec{r},t) = \hat{c}_1(\vec{r},t), \dots, \hat{a}_n(\vec{r},t) = \hat{c}_n(\vec{r},t)$ and the internal energy density $\hat{a}_{n+1}(\vec{r},t) = \hat{\varepsilon}(\vec{r},t)$ as relevant variables, we assume that the momentum variables $\vec{p}^{(i)}_k(t)$ relax much faster to local thermodynamic equilibrium than the position variables $\vec{r}^{(i)}_k(t)$ so that the momentum density can be neglected as a further dynamic variable on the characteristic time scale of the concentrations and of the internal energy density. By this choice of relevant variables, we further assume that the concentration $\hat{c}_0(\vec{r},t)$ of the molecular solvent relaxes much faster than the concentrations $\hat{c}_i(\vec{r},t)$, $i > 0$, of the colloidal particles.

The concentrations $\hat{c}_i(\vec{r},t)$ and the internal energy density $\hat{\varepsilon}(\vec{r},t)$ are even under parity and time reversal. Furthermore, they are locally conserved, if there are no sources and sinks of particles and energy in the system.

The corresponding currents follow from the Liouville equations $\dot{\hat{a}}_i + \{\hat{H},\hat{a}_i\} = 0$ [see Eq. (9)] by comparison with Eq. (57).[95] They are the particle number current

$$\hat{\vec{J}}^{c_i}(\vec{r},t) = \sum_{k=1}^{N_i}\frac{\vec{p}^{(i)}_k}{m_i}\,\delta\big(\vec{r}-\vec{r}^{(i)}_k\big) \tag{71}$$

and the internal energy current

$$\begin{aligned}\hat{\vec{J}}^{\varepsilon}(\vec{r},t) ={}& \sum_{i=0}^{n}\sum_{k=1}^{N_i}\frac{\vec{p}^{(i)}_k}{m_i}\hat{H}^{(i)}_k\,\delta\big(\vec{r}-\vec{r}^{(i)}_k\big)\\ &-\frac{1}{4}\sum_{\substack{i,j=0\\(k,i)\neq(l,j)}}^{n}\sum_{k=1}^{N_i}\sum_{l=1}^{N_j}\big(\vec{\nabla}_{\vec{r}^{(ij)}_{kl}}U^{(ij)}_2\big(\vec{r}^{(ij)}_{kl}\big)\big)\\ &\cdot\Big(\frac{\vec{p}^{(i)}_k}{m_i}+\frac{\vec{p}^{(j)}_l}{m_j}\Big)\\ &\times\vec{r}^{(ij)}_{kl}\int_0^1\!\mathrm{d}\lambda\,\delta\big(\vec{r}-\vec{r}^{(i)}_k+\lambda\vec{r}^{(ij)}_{kl}\big)\end{aligned} \tag{72}$$

with the dyadic product $\otimes$ and the notation $\vec{r}^{(ij)}_{kl} = \vec{r}^{(i)}_k - \vec{r}^{(j)}_l$, where all $\vec{r}^{(i)}_k$, $\vec{r}^{(ij)}_{kl}$, $\vec{p}^{(i)}_k$, and $\hat{H}^{(i)}_k$ in Eqs. (71) and (72) are to be taken at time t.

Since $\hat{\vec{J}}^{c_i}(\vec{r},t)$ and $\hat{\vec{J}}^{\varepsilon}(\vec{r},t)$ are of odd order in the momentum $\vec{p}_k^{(i)}(t)$, the averages $\mathrm{Tr}(\rho(t)\hat{\vec{J}}^{c_i})=0$ and $\mathrm{Tr}(\rho(t)\hat{\vec{J}}^{\varepsilon})=0$ vanish. This leads to the important invariance properties $\hat{\mathcal{Q}}_t\hat{\vec{J}}^{c_i}=\hat{\vec{J}}^{c_i}$ and $\hat{\mathcal{Q}}_t\hat{\vec{J}}^{\varepsilon}=\hat{\vec{J}}^{\varepsilon}$ [see Eq. (8)].

B. Transport equations

Since the concentration fields $c_i(\vec{r},t)$ and the internal energy density $\varepsilon(\vec{r},t)$ are locally conserved, the EDDFT equation (58) and the corresponding transport equation (60), respectively, can be applied. Due to the invariance of $\hat{c}_i(\vec{r},t)$ and $\hat{\varepsilon}(\vec{r},t)$ under time-reversal, the frequency matrix and therefore also the first term on the right-hand-side of Eq. (58) vanish.

1. Non-equilibrium dynamics

Application of Eq. (58) results in the following *extended DDFT equations for colloidal mixtures*:

$$\dot{c}_i(\vec{r},t)=\sum_{j=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r'\,\beta D^{(ij)}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_j^{\natural}(\vec{r}\,',t)$$

$$+\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r'\,\beta D^{(i\varepsilon)}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}\varepsilon^{\natural}(\vec{r}\,',t),\qquad(73)$$

$$\dot{\varepsilon}(\vec{r},t)=\sum_{j=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r'\,\beta D^{(\varepsilon j)}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_j^{\natural}(\vec{r}\,',t)$$

$$+\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r'\,\beta D^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}\varepsilon^{\natural}(\vec{r}\,',t).\qquad(74)$$

Let us briefly comment on the thermodynamic conjugate quantities appearing in Eqs. (73) and (74). The thermodynamic conjugate of a concentration $c_i(\vec{r},t)$ is the associated chemical potential, denoted in the present context by $c_i^{\natural}(\vec{r},t)$. In the literature, this quantity is sometimes also called $\mu_{c_i}(\vec{r},t)$. For the thermodynamic conjugate associated with the internal energy density, the situation is somewhat more delicate. This question will be discussed in detail in a forthcoming paper incorporating the entropy density into EDDFT.[96] It turns out that the internal energy density as a variable and the energy conservation law can be taken care of by assuming that the local formulation of the first law of thermodynamics is valid. In this case, there is a relation between the internal energy density, the entropy density, and the other variables. Thus one of these variables can be expressed by a linear combination of the other variables and their thermodynamic conjugates. Frequently this is done by satisfying energy conservation by requirements on the structure of the reversible and irreversible parts of the internal energy current. Such a program has been carried out in the past for the hydrodynamic regime (compare, for example, Ref. 97 for a comprehensive description of this approach).

The diffusion tensors $D^{(ij)}(\vec{r},\vec{r}\,',t)$, $D^{(i\varepsilon)}(\vec{r},\vec{r}\,',t)=(D^{(\varepsilon i)}(\vec{r},\vec{r}\,',t))^{\mathrm{T}}$, and $D^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,',t)$ in the EDDFT equations (73) and (74) are given by

$$D_{kl}^{(ij)}(\vec{r},\vec{r}\,',t)=\int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}\big(\rho(t)\hat{J}_k^{c_i}(\vec{r},t')\hat{J}_l^{c_j}(\vec{r}\,',0)\big),\qquad(75)$$

$$D_{kl}^{(i\varepsilon)}(\vec{r},\vec{r}\,',t)=\int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}\big(\rho(t)\hat{J}_k^{c_i}(\vec{r},t')\hat{J}_l^{\varepsilon}(\vec{r}\,',0)\big),\qquad(76)$$

$$D_{kl}^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,',t)=\int_0^\infty\!\mathrm{d}t'\;\mathrm{Tr}\big(\rho(t)\hat{J}_k^{\varepsilon}(\vec{r},t')\hat{J}_l^{\varepsilon}(\vec{r}\,',0)\big).\qquad(77)$$

They are associated with particle diffusion ($D^{(ij)}$), (inverse) thermodiffusion ($D^{(i\varepsilon)}$: Ludwig-Soret effect, $D^{(\varepsilon i)}$: Dufour effect), and heat conduction ($D^{(\varepsilon\varepsilon)}$), respectively. From a hydrodynamic point of view, Eqs. (75)–(77) can be interpreted as generalized diffusion tensors that reduce to the corresponding diffusion constants in the hydrodynamic limit (see Sec. III E 2 for details). The EDDFT equations (73) and (74) in combination with the diffusion tensors (75)–(77) constitute the main result of this paper.

2. Equilibrium correlations

If the transport equation (60) is applied, one obtains dynamical equations for the time correlation functions

$$C_{ij}(\vec{r},\vec{r}\,',t)=\big\langle\Delta\hat{c}_i^{\mathrm{eq}}(\vec{r},t)\big|\Delta\hat{c}_j^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}},\qquad(78)$$

$$C_{i\varepsilon}(\vec{r},\vec{r}\,',t)=\big\langle\Delta\hat{c}_i^{\mathrm{eq}}(\vec{r},t)\big|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}},\qquad(79)$$

$$C_{\varepsilon\varepsilon}(\vec{r},\vec{r}\,',t)=\big\langle\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r},t)\big|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}.\qquad(80)$$

These dynamical equations are given by

$$\dot{C}_{ij}(\vec{r},\vec{r}\,',t)=\sum_{k=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(ik)}(\vec{r},\vec{r}\,'')C_{kj}(\vec{r}\,'',\vec{r}\,',t)$$

$$+\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(i\varepsilon)}(\vec{r},\vec{r}\,'')C_{\varepsilon j}(\vec{r}\,'',\vec{r}\,',t),\qquad(81)$$

$$\dot{C}_{i\varepsilon}(\vec{r},\vec{r}\,',t)=\sum_{k=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(ik)}(\vec{r},\vec{r}\,'')C_{k\varepsilon}(\vec{r}\,'',\vec{r}\,',t)$$

$$+\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(i\varepsilon)}(\vec{r},\vec{r}\,'')C_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,',t),\qquad(82)$$

$$\dot{C}_{\varepsilon\varepsilon}(\vec{r},\vec{r}\,',t)=\sum_{k=1}^{n}\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(\varepsilon k)}(\vec{r},\vec{r}\,'')C_{k\varepsilon}(\vec{r}\,'',\vec{r}\,',t)$$

$$+\vec{\nabla}_{\vec{r}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3r''\,L_{\mathrm{eq}}^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,'')C_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,',t)\qquad(83)$$

with the total transport matrices

$$L_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,')=\Omega_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,')+\Gamma_{\mathrm{eq}}^{(ij)}(\vec{r},\vec{r}\,'),\qquad(84)$$

$$L_{\mathrm{eq}}^{(i\varepsilon)}(\vec{r},\vec{r}\,')=\Omega_{\mathrm{eq}}^{(i\varepsilon)}(\vec{r},\vec{r}\,')+\Gamma_{\mathrm{eq}}^{(i\varepsilon)}(\vec{r},\vec{r}\,'),\qquad(85)$$

$$L_{\mathrm{eq}}^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,')=\Omega_{\mathrm{eq}}^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,')+\Gamma_{\mathrm{eq}}^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,')\qquad(86)$$

consisting of the contributions

$$\Omega^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = -\sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(ik)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{kj}(\vec{r}\,'',\vec{r}\,') - \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{\varepsilon j}(\vec{r}\,'',\vec{r}\,'), \tag{87}$$

$$\Omega^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = -\sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(ik)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{k\varepsilon}(\vec{r}\,'',\vec{r}\,') - \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,'), \tag{88}$$

$$\Omega^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = -\sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(\varepsilon k)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{k\varepsilon}(\vec{r}\,'',\vec{r}\,') - \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\, B^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\chi^{\mathrm{eq}-1}_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,') \tag{89}$$

and

$$\Gamma^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(ik)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{kj}(\vec{r}\,'',\vec{r}\,') + \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{\varepsilon j}(\vec{r}\,'',\vec{r}\,'), \tag{90}$$

$$\Gamma^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(ik)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{k\varepsilon}(\vec{r}\,'',\vec{r}\,') + \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,'), \tag{91}$$

$$\Gamma^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \sum_{k=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(\varepsilon k)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{k\varepsilon}(\vec{r}\,'',\vec{r}\,') + \int_{\mathbb{R}^3}\!\mathrm{d}^3r''\,\beta D^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,'')\,\vec{\nabla}_{\vec{r}\,''}\chi^{\mathrm{eq}-1}_{\varepsilon\varepsilon}(\vec{r}\,'',\vec{r}\,'). \tag{92}$$

Equations (87)–(92) in turn depend on the equilibrium drift tensors

$$B^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \beta\big\langle\hat{\vec{J}}^{c_i}(\vec{r},0)\big|\Delta\hat{c}^{\mathrm{eq}}_j(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}, \tag{93}$$

$$B^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \beta\big\langle\hat{\vec{J}}^{c_i}(\vec{r},0)\big|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}, \tag{94}$$

$$B^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \beta\big\langle\hat{\vec{J}}^{\varepsilon}(\vec{r},0)\big|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}, \tag{95}$$

on the equilibrium diffusion tensors

$$D^{(ij)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \int_0^\infty\!\mathrm{d}t'\,\big\langle\hat{\vec{J}}^{c_i}(\vec{r},0)\big|\hat{\vec{J}}^{c_j}(\vec{r}\,',t')\big\rangle_{\mathrm{eq}}, \tag{96}$$

$$D^{(i\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \int_0^\infty\!\mathrm{d}t'\,\big\langle\hat{\vec{J}}^{c_i}(\vec{r},0)\big|\hat{\vec{J}}^{\varepsilon}(\vec{r}\,',t')\big\rangle_{\mathrm{eq}}, \tag{97}$$

$$D^{(\varepsilon\varepsilon)}_{\mathrm{eq}}(\vec{r},\vec{r}\,') = \int_0^\infty\!\mathrm{d}t'\,\big\langle\hat{\vec{J}}^{\varepsilon}(\vec{r},0)\big|\hat{\vec{J}}^{\varepsilon}(\vec{r}\,',t')\big\rangle_{\mathrm{eq}}, \tag{98}$$

and on the static equilibrium susceptibility matrices

$$\chi^{\mathrm{eq}}_{ij}(\vec{r},\vec{r}\,') = \beta\big\langle\Delta\hat{c}^{\mathrm{eq}}_i(\vec{r},0)\big|\Delta\hat{c}^{\mathrm{eq}}_j(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}, \tag{99}$$

$$\chi^{\mathrm{eq}}_{i\varepsilon}(\vec{r},\vec{r}\,') = \beta\big\langle\Delta\hat{c}^{\mathrm{eq}}_i(\vec{r},0)\big|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\big\rangle_{\mathrm{eq}}, \tag{100}$$

$$\chi^{\mathrm{eq}}_{\varepsilon\varepsilon}(\vec{r},\vec{r}\,') = \beta\langle\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r},0)|\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r}\,',0)\rangle_{\mathrm{eq}} \tag{101}$$

with the equilibrium fluctuations $\Delta\hat{c}^{\mathrm{eq}}_i(\vec{r},t) = \hat{c}_i(\vec{r},t) - c^{\mathrm{eq}}_i(\vec{r})$ and $\Delta\hat{\varepsilon}^{\mathrm{eq}}(\vec{r},t) = \hat{\varepsilon}(\vec{r},t) - \varepsilon^{\mathrm{eq}}(\vec{r})$.

C. Approximation of the diffusion tensors

For an application of the EDDFT equations (73) and (74) to a particular system, suitable expressions for the diffusion tensors (75)–(77) are needed. A possibility to determine these diffusion tensors is the implementation of particle-resolved computer simulations.[98] Alternatively, analytical approximations for the diffusion tensors $D^{(ij)}(\vec{r},\vec{r}\,',t)$, $D^{(i\varepsilon)}(\vec{r},\vec{r}\,',t)$, and $D^{(\varepsilon\varepsilon)}(\vec{r},\vec{r}\,',t)$ can be applied. Such approximate expressions are given in the following.

1. No hydrodynamic interactions

As first approximation, it is assumed that the considered system is sufficiently close to local thermodynamic equilibrium so that the relevant probability density $\rho(t)$ can be approximated by the equilibrium probability density ρ^{eq} [see Eq. (27)] in Eqs. (75)–(77). Second, we assume that the position variables relax much more slowly to local thermodynamic equilibrium than the momentum variables and that the external potential is approximately constant on microscopic length scales. Third, we suppose that the position and momentum variables are statistically independent. Furthermore, the considered suspension shall be sufficiently dilute so that hydrodynamic interactions between the colloidal particles can be neglected and the momenta of different particles are uncorrelated. Finally, we assume orientational isotropy for the momentum variables, i.e., $\langle\vec{p}\otimes\vec{p}\rangle_{\mathrm{eq}} = \frac{1}{3}\mathbf{1}\langle\vec{p}\cdot\vec{p}\rangle_{\mathrm{eq}}$ and neglect the pair-interaction potential $U^{(ij)}_2(\vec{r}^{\,(i)}_k - \vec{r}^{\,(j)}_l)$ in Eqs. (67) and (72).

With these assumptions, the diffusion tensors (75)–(77) can be approximated by

$$D^{(ij)}_{\mathrm{NH}}(\vec{r},\vec{r}\,',t) = D^{(i)}_0\,\mathbf{1}\,\delta_{ij}\,\delta(\vec{r}-\vec{r}\,')c_i(\vec{r},t), \tag{102}$$

$$D^{(i\varepsilon)}_{\mathrm{NH}}(\vec{r},\vec{r}\,',t) = \kappa^{(i)}_{\mathrm{S}}\,\mathbf{1}\,\delta(\vec{r}-\vec{r}\,')c_i(\vec{r},t), \tag{103}$$

$$D^{(\varepsilon\varepsilon)}_{\mathrm{NH}}(\vec{r},\vec{r}\,',t) = \sum_{i=0}^{n}\kappa^{(i)}_{\mathrm{H}}\,\mathbf{1}\,\delta(\vec{r}-\vec{r}\,')c_i(\vec{r},t) \tag{104}$$

with the transport coefficients

$$D^{(i)}_0 = \frac{1}{3}\int_0^\infty\!\mathrm{d}t'\,\langle\vec{v}_i(t')\cdot\vec{v}_i(0)\rangle_{\mathrm{eq}}, \tag{105}$$

$$\kappa_{\mathrm{S}}^{(i)} = \frac{1}{3}\int_0^\infty \!\mathrm{d}t' \, \langle \vec{v}_i(t')\cdot\vec{v}_i(0)\hat{H}_i(0)\rangle_{\mathrm{eq}}, \tag{106}$$

$$\kappa_{\mathrm{H}}^{(i)} = \frac{1}{3}\int_0^\infty \!\mathrm{d}t' \, \langle \vec{v}_i(t')\cdot\vec{v}_i(0)\hat{H}_i(t')\hat{H}_i(0)\rangle_{\mathrm{eq}}, \tag{107}$$

where $\vec{v}_i(t) = \vec{p}^{(i)}(t)/m_i$ is the velocity of a colloidal particle of species i and $\hat{H}_i(t)$ is its energy. These coefficients are associated with particle diffusion, thermodiffusion, and heat conduction, respectively. Notice that the diffusion tensor (102) is diagonal and that all diffusive cross-couplings in Eq. (73) vanish, if there are no hydrodynamic interactions between the colloidal particles.

2. Hydrodynamic interactions

A better approximation for the diffusion tensor (75), that takes also diffusive cross-couplings into account, can be derived, if hydrodynamic interactions between the colloidal particles are taken into account. In order to do so, the derivation of the DDFT equation for a one-component suspension of colloidal particles with hydrodynamic interactions in Refs. 30 and 31 is generalized and compared with Eq. (73). This derivation starts from the Smoluchowski equation[18]

$$\dot{P}(\vec{r}^N,t) + \sum_{i=1}^{n}\sum_{k=1}^{N_i} \vec{\nabla}_{\vec{r}_k^{(i)}}\cdot \vec{J}_{\mathrm{P},k}^{(i)}(\vec{r}^N,t) = 0 \tag{108}$$

with the N-particle probability density $P(\vec{r}^N,t)$, where $\vec{r}^N = (\vec{r}_1^{(1)},\dots,\vec{r}_{N_n}^{(n)})$ are the positions of all particles, the probability currents

$$\vec{J}_{\mathrm{P},k}^{(i)}(\vec{r}^N,t) = -\sum_{j=1}^{n}\sum_{l=1}^{N_j} \mathrm{D}_{kl}^{(ij)}(\vec{r}^N)\vec{f}_l^{(j)}(\vec{r}^N,t), \tag{109}$$

and the force densities

$$\vec{f}_l^{(j)}(\vec{r}^N,t) = \vec{\nabla}_{\vec{r}_l^{(j)}} P(\vec{r}^N,t) + P(\vec{r}^N,t)\vec{\nabla}_{\vec{r}_l^{(j)}}(\beta U(\vec{r}^N,t)). \tag{110}$$

Here, $\mathrm{D}_{kl}^{(ij)}(\vec{r}^N)$ is a short-time diffusion tensor and $U(\vec{r}^N,t)$ denotes the total potential energy of the system. If the considered suspension is not too dense so that the particle distances are sufficiently large, the hydrodynamic interactions can be approximated on the two-particle level and higher order hydrodynamic interactions are negligible.

In case of only hydrodynamic pair-interactions, the short-time diffusion tensors $\mathrm{D}_{kl}^{(ij)}(\vec{r}^N)$ can be written in the exact form[18,99]

$$\begin{aligned}\mathrm{D}_{kl}^{(ij)}(\vec{r}^N) = {}& D_0^{(i)}\delta_{ij}\delta_{kl}\mathbf{1} + D_0^{(i)}\delta_{ij}\delta_{kl}\sum_{q=1}^{n}\sum_{p=1}^{N_q}(1-\delta_{kp}\delta_{iq}) \\ &\times \mathrm{h}_{\mathrm{s}}^{(iq)}\big(\vec{r}_{kp}^{(iq)}\big) + (1-\delta_{ij}\delta_{kl})D_0^{(j)}\mathrm{h}_{\mathrm{c}}^{(ij)}\big(\vec{r}_{kl}^{(ij)}\big)\end{aligned} \tag{111}$$

with the self- and cross-interaction functions

$$\mathrm{h}_{\lambda}^{(ij)}(\vec{r}) = A_{\lambda}^{(ij)}(r)\,\hat{r}\otimes\hat{r} + B_{\lambda}^{(ij)}(r)(\mathbf{1}-\hat{r}\otimes\hat{r}) \tag{112}$$

with $\lambda = \mathrm{s}$ for "self" and $\lambda = \mathrm{c}$ for "cross," respectively, and the notation $r = \lVert\vec{r}\rVert$ and $\hat{r} = \vec{r}/r$ for an arbitrary vector $\vec{r}$. The self- and cross-interaction functions depend on the four mobility functions $A_{\lambda}^{(ij)}(r)$ and $B_{\lambda}^{(ij)}(r)$ with $\lambda \in \{\mathrm{s},\mathrm{c}\}$. With the *method of reflections*,[18,99] these mobility functions can be determined up to arbitrary order as an expansion in the inverse inter-particle distances. Up to fourth order, the mobility functions are given by[100]

$$A_{\mathrm{s}}^{(ij)}(r) = \mathcal{O}(r^{-4}), \tag{113}$$

$$B_{\mathrm{s}}^{(ij)}(r) = \mathcal{O}(r^{-4}), \tag{114}$$

$$A_{\mathrm{c}}^{(ij)}(r) = \frac{3}{2}\frac{R_j}{r} - \frac{1}{2}\frac{R_i^2 R_j + R_j^3}{r^3} + \mathcal{O}(r^{-4}), \tag{115}$$

$$B_{\mathrm{c}}^{(ij)}(r) = \frac{3}{4}\frac{R_j}{r} + \frac{1}{4}\frac{R_i^2 R_j + R_j^3}{r^3} + \mathcal{O}(r^{-4}), \tag{116}$$

where R_i denotes the radius of a colloidal particle of species i. Notice that Eqs. (111) and (112) together with the fourth-order approximations (113)–(116) of the mobility functions constitute a *generalized Rotne-Prager approximation* for mixtures.[18,101]

The generalization of the derivation in Refs. 30 and 31 leads to the following approximation of the diffusion tensor (75) for hydrodynamic pair-interactions:

$$\begin{aligned}D_{\mathrm{HI}}^{(ij)}(\vec{r},\vec{r}\,',t) = {}& D_0^{(i)}\delta_{ij}\delta(\vec{r}-\vec{r}\,')\big(\mathbf{1}c_i(\vec{r},t) + \mathrm{c}_{\mathrm{s}}^{(i)}(\vec{r},t)\big) \\ &+ D_0^{(j)}\mathrm{h}_{\mathrm{c}}^{(ij)}(\vec{r}-\vec{r}\,')c_{ij}(\vec{r},\vec{r}\,',t).\end{aligned} \tag{117}$$

Here, we introduced the functions

$$\mathrm{c}_{\mathrm{s}}^{(i)}(\vec{r},t) = \sum_{j=1}^{n}\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\, \mathrm{h}_{\mathrm{s}}^{(ij)}(\vec{r}-\vec{r}\,')c_{ij}(\vec{r},\vec{r}\,',t) \tag{118}$$

and the two-particle concentrations

$$c_{ij}(\vec{r},\vec{r}\,',t) = \mathrm{Tr}(\rho(0)\hat{c}_{ij}(\vec{r},\vec{r}\,',t)) \tag{119}$$

with the corresponding variables

$$\hat{c}_{ij}(\vec{r},\vec{r}\,',t) = \sum_{k=1}^{N_i}\sum_{\substack{l=1\\ l\neq k}}^{N_j}\delta\big(\vec{r}-\vec{r}_k^{(i)}(t)\big)\delta\big(\vec{r}\,'-\vec{r}_l^{(j)}(t)\big). \tag{120}$$

The two-particle variables $\hat{c}_{ij}(\vec{r},\vec{r}\,',t)$ are assumed to relax much faster to local thermodynamic equilibrium than $\hat{c}_i(\vec{r},t)$ and $\hat{\varepsilon}(\vec{r},t)$.

Notice that Eq. (108) is the simplest Smoluchowski equation that describes colloidal mixtures with hydrodynamic interactions appropriately. We chose this equation, since a corresponding DDFT equation can be derived from it so that by comparison with our EDDFT equation (73) the expression (117) for the diffusion tensor (75) could be obtained without a direct microscopic derivation starting from the microscopic expression (75). In general, also contributions from external forces appear in the Smoluchowski equation, but they do not influence the result (117). There exist also more general Smoluchowski equations that take, for example, also temperature gradients into account, but to the best of our knowledge it is in general not possible to derive corresponding DDFT equations from these more complicated Smoluchowski equations. It is therefore not possible to derive relations analogous to Eq. (117) for the diffusion tensors (76) and (77) by a direct generalization of the derivation presented in this section.

D. Approximation of the generalized Helmholtz free-energy functional

In order to determine the generalized Helmholtz free-energy functional $\mathcal{F}[c_1,\dotsc,c_n,T]$, which is needed in the EDDFT equations (73) and (74), it is always possible to expand this functional with respect to $c_i(\vec{r},t)$, $T(\vec{r},t)$, and their gradients taking general symmetry considerations into account.[97] Notice that $\mathcal{F}$ here depends on the absolute temperature $T(\vec{r},t)$ instead of the internal energy density $\varepsilon(\vec{r},t)$. A connection between $T(\vec{r},t)$ and $\varepsilon(\vec{r},t)$ can be established by the local formulation of the first law of thermodynamics.[96]

If the internal energy density can be neglected so that only an approximation for the functional $\mathcal{F}[c_1,\dotsc,c_n]$ is needed, static density functional theory can be applied to derive such an approximation on a microscopic basis. The up to now most accurate approximation for $\mathcal{F}[c_1,\dotsc,c_n]$ was derived in the framework of fundamental measure theory (see Ref. 102 for a review).

E. Special cases of the EDDFT equations

The EDDFT equations (73) and (74) contain several special cases that are known from the literature or that are relevant for particular applications. Two of these special cases are addressed in this section. The first one is an isothermal binary mixture, where only two concentrations are present and the internal energy density can be neglected. As a second example, the hydrodynamic limit of the EDDFT equations is discussed.

1. *Isothermal binary mixture*

If the considered mixture consists only of $n=2$ different species of colloidal particles and the internal energy density can be assumed to be constant, the EDDFT equations (73) and (74) can be simplified to

$$\begin{aligned}\dot{c}_1(\vec{r},t) &= \beta D_0^{(1)}\vec{\nabla}_{\vec{r}}\cdot\big(\mathbf{1}c_1(\vec{r},t)+\mathrm{c}_{\mathrm{s}}^{(1)}(\vec{r},t)\big)\vec{\nabla}_{\vec{r}}\,c_1^{\natural}(\vec{r},t)\\ &\quad+\beta D_0^{(1)}\vec{\nabla}_{\vec{r}}\cdot\!\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\,\mathrm{h}_{\mathrm{c}}^{(11)}(\vec{r}-\vec{r}\,')c_{11}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_1^{\natural}(\vec{r}\,',t)\\ &\quad+\beta D_0^{(2)}\vec{\nabla}_{\vec{r}}\cdot\!\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\,\mathrm{h}_{\mathrm{c}}^{(12)}(\vec{r}-\vec{r}\,')c_{12}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_2^{\natural}(\vec{r}\,',t),\end{aligned}\tag{121}$$

$$\begin{aligned}\dot{c}_2(\vec{r},t) &= \beta D_0^{(2)}\vec{\nabla}_{\vec{r}}\cdot\big(\mathbf{1}c_2(\vec{r},t)+\mathrm{c}_{\mathrm{s}}^{(2)}(\vec{r},t)\big)\vec{\nabla}_{\vec{r}}\,c_2^{\natural}(\vec{r},t)\\ &\quad+\beta D_0^{(1)}\vec{\nabla}_{\vec{r}}\cdot\!\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\,\mathrm{h}_{\mathrm{c}}^{(21)}(\vec{r}-\vec{r}\,')c_{21}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_1^{\natural}(\vec{r}\,',t)\\ &\quad+\beta D_0^{(2)}\vec{\nabla}_{\vec{r}}\cdot\!\int_{\mathbb{R}^3}\!\mathrm{d}^3r'\,\mathrm{h}_{\mathrm{c}}^{(22)}(\vec{r}-\vec{r}\,')c_{22}(\vec{r},\vec{r}\,',t)\vec{\nabla}_{\vec{r}\,'}c_2^{\natural}(\vec{r}\,',t).\end{aligned}\tag{122}$$

Here, the short-time diffusion coefficients (105) can be expressed by

$$D_0^{(i)} = \frac{1}{\beta 6\pi\eta R_i}\tag{123}$$

with the dynamic (shear) viscosity η of the molecular solvent. Hydrodynamic interactions between the colloidal particles are still taken into account by Eqs. (73) and (74). In the fourth-order approximation (113)–(116), the functions $\mathrm{c}_{\mathrm{s}}^{(i)}(\vec{r},t)=\mathbf{0}$ vanish ($\mathbf{0}$ denotes the zero matrix) and the cross-interaction functions $\mathrm{h}_{\mathrm{c}}^{(ij)}(\vec{r})$ are

$$\mathrm{h}_{\mathrm{c}}^{(ij)}(\vec{r}) = \frac{3}{4}\frac{R_j}{\lVert\vec{r}\rVert}\bigg(\mathbf{1}+\frac{\vec{r}\otimes\vec{r}}{\lVert\vec{r}\rVert^2}\bigg)+\frac{1}{4}\frac{R_i^2R_j+R_j^3}{\lVert\vec{r}\rVert^3}\bigg(\mathbf{1}-3\frac{\vec{r}\otimes\vec{r}}{\lVert\vec{r}\rVert^2}\bigg).\tag{124}$$

As closure relations for the two-particle concentrations $c_{ij}(\vec{r},\vec{r}\,',t)$ in the dynamical equation (121), the (exact) generalized Ornstein-Zernike equation for mixtures or simple analytical approximations that are known from the literature can be applied.[30,31]

2. *The hydrodynamic limit*

The derived EDDFT equations (73) and (74) with the space- and time-dependent diffusion tensors (75)–(77) constitute an extension of the corresponding hydrodynamic equations to larger wave vectors $\vec{k}$ and frequencies ω. In the hydrodynamic limit ($\vec{k}\to\vec{0}$, $\omega\to 0$), the EDDFT equations become

$$\dot{c}_i(\vec{r},t) = \sum_{j=1}^{n}\beta D_0^{(ij)}\Delta_{\vec{r}}\,c_j^{\natural}(\vec{r},t)+\beta D_0^{(i\varepsilon)}\Delta_{\vec{r}}\,\varepsilon^{\natural}(\vec{r},t),\tag{125}$$

$$\dot{\varepsilon}(\vec{r},t) = \sum_{j=1}^{n}\beta D_0^{(\varepsilon j)}\Delta_{\vec{r}}\,c_j^{\natural}(\vec{r},t)+\beta D_0^{(\varepsilon\varepsilon)}\Delta_{\vec{r}}\,\varepsilon^{\natural}(\vec{r},t)\tag{126}$$

with the constant diffusion coefficients

$$D_0^{(ij)} = \frac{1}{3}\int_{\mathbb{R}^3}\!\mathrm{d}^3r\int_0^\infty\!\mathrm{d}t\;\mathrm{Tr}\big(\rho(0)\hat{\vec{J}}^{c_i}(\vec{r},t)\cdot\hat{\vec{J}}^{c_j}(\vec{0},0)\big),\tag{127}$$

$$D_0^{(i\varepsilon)} = \frac{1}{3}\int_{\mathbb{R}^3}\!\mathrm{d}^3r\int_0^\infty\!\mathrm{d}t\;\mathrm{Tr}\big(\rho(0)\hat{\vec{J}}^{c_i}(\vec{r},t)\cdot\hat{\vec{J}}^{\varepsilon}(\vec{0},0)\big),\tag{128}$$

$$D_0^{(\varepsilon\varepsilon)} = \frac{1}{3}\int_{\mathbb{R}^3}\!\mathrm{d}^3r\int_0^\infty\!\mathrm{d}t\;\mathrm{Tr}\big(\rho(0)\hat{\vec{J}}^{\varepsilon}(\vec{r},t)\cdot\hat{\vec{J}}^{\varepsilon}(\vec{0},0)\big)\tag{129}$$

and $D_0^{(\varepsilon i)}=D_0^{(i\varepsilon)}$. The hydrodynamic limit of the transport equations (81)–(83) for the time correlation functions (78)-(80) can be obtained analogously.

F. Relation of EDDFT and MCT

The MCT of glass transitions[54,92] is a classical theory for the dynamics of liquids near the glass transition. Originally, MCT was constructed for the underdamped dynamics of atomic and molecular systems,[92] but it can also be derived for the overdamped dynamics of colloidal systems.[55–59] Like

EDDFT, also MCT can be derived from the MZFT. This allows a comparison of these two theories on a common fundamental basis. In the following, we summarize the derivation of MCT and discuss its relation to DDFT and EDDFT.

1. MCT for atomic and molecular systems

The traditional form of MCT applies to a one-component system of equal spherical atoms or molecules of mass m. This system is characterized by a one-particle density field $\hat{c}(\vec{r},t)$ following the conservation law $\dot{\hat{c}}(\vec{r},t)+\vec{\nabla}_{\vec{r}}\cdot\hat{\vec{J}}^{\mathrm{c}}(\vec{r},t)=0$ with the density current $\hat{\vec{J}}^{\mathrm{c}}(\vec{r},t)$. In order to derive MCT, we switch to the Fourier-Laplace space and utilize Eq. (37), where we omit the letters "eq" denoting equilibrium quantities and the tilde ~ denoting quantities in the Fourier-Laplace space for reasons of clarity in this section. Near the glass transition, two variables are taken into account as relevant variables. These are the density field $\hat{c}(\vec{k},z)$ and the longitudinal component $\hat{j}^{\mathrm{L}}(\vec{k},z)=\vec{k}/k\cdot\hat{\vec{J}}^{\mathrm{c}}(\vec{k},z)$ of the density current $\hat{\vec{J}}^{\mathrm{c}}(\vec{k},z)$. The transversal component of the density current, on the other hand, does not couple to density fluctuations and can therefore be neglected. While this was not the case in the context of EDDFT, here also the current associated with the density field has to be regarded as a relevant variable, since there is no separation of time scales between these variables near the glass transition.[92] We further define the concentration time autocorrelation function (dynamic structure factor) $C^{\mathrm{c}}(\vec{k},z)=\langle\Delta\hat{c}(\vec{k},z)|\Delta\hat{c}(\vec{k},0)\rangle$ and the current time autocorrelation function $C^{\mathrm{j}}(\vec{k},z)=\langle\Delta\hat{j}^{\mathrm{L}}(\vec{k},z)|\Delta\hat{j}^{\mathrm{L}}(\vec{k},0)\rangle$ corresponding to the chosen relevant variables. With these definitions, application of Eq. (37) leads directly to a dynamical equation for the normalized density time autocorrelation function $\phi^{\mathrm{c}}(\vec{k},z)=C^{\mathrm{c}}(\vec{k},z)/C^{\mathrm{c}}(\vec{k},0)$. This dynamical equation is the *MCT equation*[92]

$$\phi^{\mathrm{c}}(\vec{k},z)=\left(z+\frac{\Omega_{\mathrm{m}}^{2}(\vec{k})}{z-K^{\mathrm{j}}(\vec{k},z)}\right)^{-1} \tag{130}$$

with the frequency $\Omega_{\mathrm{m}}(\vec{k})$ that must not be confused with the (vanishing) frequency matrix in Eq. (37). This frequency is given by $\Omega_{\mathrm{m}}^{2}(\vec{k})=C^{\mathrm{j}}(\vec{k},0)\vec{k}^{2}/C^{\mathrm{c}}(\vec{k},0)$ and $C^{\mathrm{j}}(\vec{k},0)=1/(\beta m)$. Furthermore, the current memory function $K^{\mathrm{j}}(\vec{k},z)$ in Eq. (130) is defined as $K^{\mathrm{j}}(\vec{k},z)=-\langle\Delta\dot{\hat{j}}^{\mathrm{L}}(\vec{k},0)|\hat{\mathcal{Q}}(z+\hat{\mathcal{L}}_{\hat{\mathcal{Q}}})^{-1}\hat{\mathcal{Q}}|\Delta\dot{\hat{j}}^{\mathrm{L}}(\vec{k},0)\rangle/C^{\mathrm{c}}(\vec{k},0)$.

2. MCT for colloidal systems

In case of a system of spherical colloidal particles that are suspended in a molecular solvent, a simpler MCT equation but with the same long-time behavior as Eq. (130) can be derived. This colloidal system is characterized by the short-time diffusion coefficient D_0 and concentration field $\hat{c}(\vec{k},z)$ of the colloidal particles. A similar derivation as before, but now with the appropriate Smoluchowski operator $\hat{\mathcal{L}}_{\mathrm{S}}$ instead of the Liouvillian $\hat{\mathcal{L}}$, leads to the *MCT equation for colloidal systems*[55,57,58]

$$\phi^{\mathrm{c}}(\vec{k},z)=\left(z+\frac{\Omega_{\mathrm{D}}^{2}(\vec{k})}{1-K^{\mathrm{j}}(\vec{k},z)}\right)^{-1} \tag{131}$$

with $\Omega_{\mathrm{D}}^{2}(\vec{k})=D_0\vec{k}^{2}/C^{\mathrm{c}}(\vec{k},0)$. Notice that Eq. (131) is only of first order in z, while Eq. (130) is of second order.

3. Comparison of EDDFT and MCT

Although the derivation of MCT was only presented for the simple special case of a one-component system here, more general formulations of MCT exist that are like EDDFT, for example, also applicable to (colloidal) mixtures.[92] Even the incorporation of the internal energy density into MCT has already been discussed[103] in the literature. EDDFT and MCT are therefore two different general theories with overlapping fields of application. A possible relation of DDFT and MCT has been mentioned by Archer,[60,61] but was not yet rigorously proven. Archer showed that under certain approximations the traditional DDFT equation[9–11] can be rearranged into a transport equation for the density time autocorrelation function, which matches the standard form (131) of MCT for colloidal systems. However, his derivation, which suggests that MCT can be derived from DDFT, is not rigorous, since it involves a reinterpretation of the one-particle density field as a temporally coarse-grained density field.

In contrast, our derivation of the EDDFT presented in this paper allows to compare both theories from a fundamental point of view. The derivation of EDDFT and MCT on the basis of the MZFT is illustrated in Fig. 1. A comparison of the derivations of these theories makes clear that there are actually strong differences between EDDFT and MCT and that a rigorous derivation of one theory from the other is not possible. An obvious and important difference between EDDFT and MCT results from the different approximations made in their derivations. While the derivation of EDDFT involves a Markovian approximation when slow variables are assumed (see Sec. II C 1), the MCT equations are non-Markovian—a feature that becomes indeed relevant near the glass transition. A more detailed comparison reveals that EDDFT and MCT are rather complementary but not replaceable theories. While EDDFT has proven that it is successfully applicable

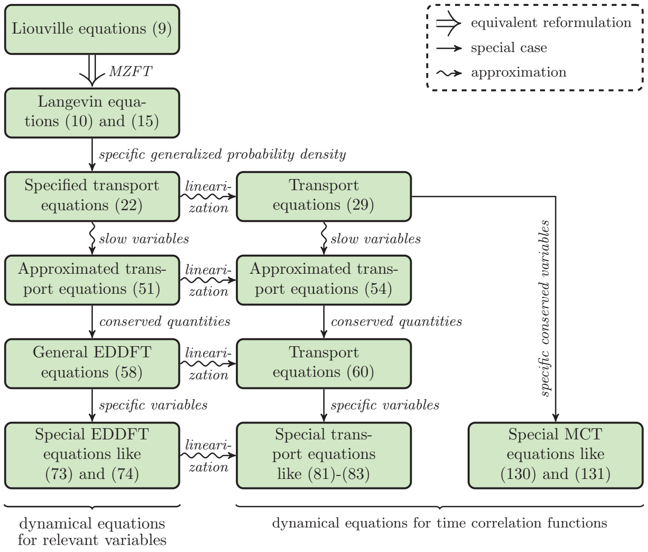

FIG. 1. Illustration of the derivation of EDDFT and MCT using the MZFT.

to describe weakly correlated systems with low concentrations, it cannot be applied to the glassy dynamics of systems at very high densities, since the Markovian approximation in the derivation of the EDDFT equation can only be justified, if effects associated with long time tails can be neglected.[16] To the contrary, the derivation of MCT does not involve a Markovian approximation and has proven to be a useful analytical tool for the description of strongly correlated systems with high concentrations, where long time tails have to be taken into account.[92] However, its derivation involves strong approximations, too, so that MCT fails when it is applied to weakly correlated dilute suspensions.

IV. CONCLUSIONS

In this paper we have generalized classical dynamical density functional theory using the Mori-Zwanzig-Forster projection operator technique by adding concentration fields and the internal energy density as variables. The resulting extended dynamical density functional theory was compared to its hydrodynamic limit and to mode-coupling theory revealing that EDDFT and MCT are complementary theories with different fields of application. Our EDDFT framework shows that the MZFT is a flexible framework to incorporate thermal gradients (and other possible slow fields).

We emphasize that, in principle, our EDDFT equations (73) and (74) treat concentration and temperature gradients on arbitrary length scales even down to microscopic length scales of the average distance between the colloidal particles. The essential input for our EDDFT equations is functional derivatives, which can be obtained from equilibrium correlations, and diffusion tensors, which can be obtained from dynamical correlations. An important challenge for the future is to apply this concept to actual temperature gradients in order to predict the Soret coefficient.

Guided by the application of the MZFT to various hydrodynamic systems including those with macroscopic degrees of freedom associated with spontaneously broken continuous symmetries,[15,74,75] it will also be interesting to see to what extent one can generalize hydrodynamic considerations[77,78] using correlation functions to larger wave vectors and frequencies.

A future generalization of the EDDFT equations should also take anisotropic colloidal particles with macroscopic degrees of freedom into account so that colloidal liquid crystals can be addressed.[26] It will be important to compare such an approach to the results obtained previously for colloidal liquid crystals using a parametrization of the density with spherically symmetric, dipolar, and quadrupolar contributions.[8,104–106] Also the incorporation of the entropy density[107] as a further variable would be an important task for the future.

Another challenge for the future is the potential use of the MZFT for systems driven far from thermodynamic equilibrium for which a generalized thermodynamic potential[108–111] is not known. To address this question appears to be particularly important for active systems, which have increasingly come into focus over the last few years.[112–116]

Recently, a similar approach using the MZFT for the one-particle density and the internal energy density was put forward by Español.[117] This approach is based on an entropy functional formalism and provides explicit expressions for hard spheres. However, mixtures and hydrodynamic interactions are not treated explicitly in this approach.[117]

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APPENDIX: INTEGRAL TRANSFORMATIONS

Since there are different definitions of the Fourier- and Laplace transformations in the literature, here we summarize the definitions that have been used in the context of the work presented. In addition, two useful relations between the Fourier- and Laplace transformation are given.

1. Fourier transformation

The Fourier transformation of a space- and time-dependent function $X(\vec{r},t)$ is given by

$$\begin{aligned}\widetilde{X}(\vec{k},\omega) &= \int_{\mathbb{R}^3}\mathrm{d}^3r\int_{\mathbb{R}}\mathrm{d}t\, X(\vec{r},t)e^{-\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)},\\ X(\vec{r},t) &= \frac{1}{(2\pi)^4}\int_{\mathbb{R}^3}\mathrm{d}^3k\int_{\mathbb{R}}\mathrm{d}\omega\, \widetilde{X}(\vec{k},\omega)e^{\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)}\end{aligned} \tag{A1}$$

with $\vec{k}\in\mathbb{R}^3$ and $\omega\in\mathbb{R}$.

2. Laplace transformation

The Laplace transformation of a time-dependent function $X(t)$ is given by

$$\begin{aligned}\widetilde{X}(z) &= \int_0^\infty \mathrm{d}t\, X(t)e^{-zt},\\ X(t) &= \frac{1}{2\pi\mathrm{i}}\int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty}\mathrm{d}z\,\widetilde{X}(z)e^{zt}\end{aligned} \tag{A2}$$

with $z\in\mathbb{C}$ and the real part $\Re(z)>0$. The expression for the inverse Laplace transformation is known as Bromwich integral and contains a constant $c>z_0$, where z_0 is the convergence abscissa of $\widetilde{X}(z)$.

3. Useful relations

The Fourier transformed function $\widetilde{X}(\omega)$ and the Laplace transformed function $\widetilde{X}(z)$ can directly be transformed into each other. With the residue theorem, the following map from $\widetilde{X}(\omega)$ to $\widetilde{X}(z)$ can be proven:

$$\widetilde{X}(z) = \frac{1}{2\pi\mathrm{i}}\int_{\mathbb{R}}\mathrm{d}\omega\,\frac{\widetilde{X}(\omega)}{\omega-\mathrm{i}z}. \tag{A3}$$

A complementary map from $\widetilde{X}(z)$ to $\widetilde{X}(\omega)$ is given by

$$\widetilde{X}(\omega) = \lim_{\epsilon\to 0^+}\big(\widetilde{X}(z)\big|_{z=-\mathrm{i}\omega+\epsilon} - \widetilde{X}(z)\big|_{z=-\mathrm{i}\omega-\epsilon}\big). \tag{A4}$$

It follows directly from the (special) *Sokhotski-Plemelj theorem*[17,118]

$$\lim_{\epsilon\to 0^+} \frac{1}{x \mp \mathrm{i}\epsilon} = \mathrm{P}\frac{1}{x} \pm \mathrm{i}\pi\,\delta(x), \qquad \text{(A5)}$$

where P denotes the Cauchy principal value.

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[79] In order to keep the following expressions simple, the Hamiltonian $\hat{H}(\hat{\Gamma}_t)$ is assumed to be not explicitly time-dependent. Nevertheless, it is possible to consider also systems with a time-dependent external potential $U_1(\vec{r},t)$ in the framework of the MZFT as it is described here, if the external potential varies sufficiently slowly with time so that it is approximately constant on microscopic time scales.

[80] In case of a classical system, the commutator $[X,Y]/(\mathrm{i}\hbar)$ should be replaced by the Poisson brackets $\{X,Y\}$ for any variables X and Y.

[81] The abbreviating notation $X_i(t) \equiv X_i(\vec{r},t) \equiv X_i(\hat{\Gamma}_t;\vec{r})$ is used for several symbols X in this paper. Summation about an index i implies also integration over $\vec{r}$ for such symbols: $X_iY_i \equiv \sum_i \int \mathrm{d}^3r\, X_i(\vec{r},t)Y_i(\vec{r},t)$. (Einstein's sum convention is used throughout this paper.)

[82] Notice that $a_i(t) \equiv a_i(\vec{r},t)$ does not depend on the total ensemble $\hat{\Gamma}_t$, but the generalized summation rule defined in Ref. 81 applies also here.

[83] The internal energy density is an exception that has to be treated separately (see Sec. III B 1).

[84] This functional $\mathcal{F}[\vec{a}] = \mathcal{F}[a_1,\dots,a_n]$ is also called *density functional* in the context of DDFT.

[85] Equivalently, one could also choose a linearly dependent set of relevant variables $\hat{a}_i(t)$ and construct a projector that maps onto the space spanned by these variables. In this case, the unity id is only indirectly taken into account as a basis element and the corresponding contribution – the first term on the right-hand-side of Eq. (8) – has to be omitted (see, for example, Ref. 17).

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[87] For abbreviation, elements of inverse matrices are denoted as $\mathrm{M}^{-1}_{ij} \equiv (\mathrm{M}^{-1})_{ij}$ with an arbitrary matrix M in this paper.

[88] This expression follows directly from the operator identity[16,17]

$$\frac{\mathrm{d}}{\mathrm{d}x}e^{A(x)} = \int_0^1 \mathrm{d}\lambda\, e^{\lambda A(x)}\frac{\mathrm{d}A(x)}{\mathrm{d}x}e^{-\lambda A(x)}e^{A(x)}$$

with a linear operator $A(x)$.

[89] While the first equality in Eq. (32) follows directly from Eq. (23), the second equality holds only in the linear regime near equilibrium and can be derived by linearization of the first term on the right-hand-side of Eq. (15) and comparison with the equivalent Eq. (22).

[90] In Eq. (33), a redundant $\hat{\mathcal{Q}}^{\mathrm{eq}}$ is often inserted directly in front of $\hat{\dot{a}}_i$ in order to obtain a more symmetric expression.

[91] The expression (41) has been symmetrized by insertion of redundant operators $\hat{\mathcal{Q}}^{\mathrm{eq}}$.

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[94] Notice that the meaning of n in this section is different from its meaning in the previous section.

[95] For the derivation of $\hat{\vec{J}}^{\varepsilon}(\vec{r},t)$, the equation[16]

$$\delta(\vec{r}-\vec{r}\,')-\delta(\vec{r}-\vec{r}\,'') = -\vec{\nabla}_{\vec{r}}\cdot\Big((\vec{r}\,'-\vec{r}\,'')\int_0^1 \mathrm{d}\lambda\,\delta(\vec{r}-\vec{r}\,'+\lambda(\vec{r}\,'-\vec{r}\,''))\Big)$$

is helpful.

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