

Statics and dynamics of inhomogeneous liquids via the internal-energy functional

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We give a variational formulation of classical statistical mechanics where the one-body density and the local entropy distribution constitute the trial fields. Using Levy's constrained search method, it is shown that the grand potential is a functional of both distributions, that it is minimal in equilibrium, and that the minimizing fields are those at equilibrium. The functional splits into a sum of entropic, external energetic, and internal energetic contributions. Several common approximate Helmholtz free-energy density functionals, such as the Rosenfeld fundamental measure theory for hard-sphere mixtures, are transformed to internal-energy functionals. The variational derivatives of the internal-energy functional are used to generalize dynamical density-functional theory to include the dynamics of the microscopic entropy distribution, as is relevant for studying heat transport and thermal diffusion.

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I. INTRODUCTION

The study of classical many-body systems in equilibrium is often based on the grand potential Ω_0 as a function of its natural variables, which for a one-component system are the chemical potential μ , the temperature T , and the volume V . The mean number of particles, N_0 , is then obtained as a partial derivative $\partial\Omega_0/\partial\mu = -N_0$, while keeping T and V fixed, and the mean particle density is simply N_0/V . When the Hamiltonian contains a contribution due to an external potential, $v(\mathbf{r})$, where \mathbf{r} is the position coordinate, then the density is in general no longer uniform, but becomes position-dependent, hence $\rho_0(\mathbf{r})$, where $\rho_0(\mathbf{r})d\mathbf{r}$ gives the mean number of particles in a volume element $d\mathbf{r}$. Here the difference $\mu - v(\mathbf{r})$ and $\rho_0(\mathbf{r})$ play the role of conjugate thermodynamic fields, and for convenience one often defines (formally) a position-dependent chemical potential $\mu(\mathbf{r}) = \mu - v(\mathbf{r})$. The one-body density distribution can then be obtained as a functional derivative $\delta\Omega_0/\delta\mu(\mathbf{r}) = -\rho_0(\mathbf{r})$.

Density-functional theory (DFT) [1] amounts to generalizing this concept to a functional dependence of the grand potential on the one-body density distribution, i.e., going from $\Omega_0(\mu, T, V)$ to a functional $\Omega([\rho], \mu, T, V)$, where $\rho(\mathbf{r})$ is a trial field. The variational principle of DFT [1,2] states that, for a given thermodynamic state (i.e., fixed values of T , μ , and V), the density distribution that minimizes Ω is the physically realized equilibrium density $\rho_0(\mathbf{r})$. The nontrivial (additive) contribution to Ω is the Helmholtz free-energy functional $F([\rho], T, V)$, which is independent of μ and generalizes the equilibrium Helmholtz free energy $F_0(N_0, T, V)$ to a functional dependence on the trial density $\rho(\mathbf{r})$. Inserting the equilibrium density into the functional yields the equilibrium free energy, i.e., $F_0(N_0, T, V) = F([\rho_0], T, V)$, where $N_0 = \int d\mathbf{r} \rho_0(\mathbf{r})$. There is a significant body of literature on the application of this framework to a wide variety of interesting many-body phenomena in liquids and solids [3–5]. Both conceptually and in practical DFT applications, the temperature enters as a mere parameter, often in the form of “thermal energy” $k_B T$, where k_B is the Boltzmann constant. Clearly, this situation is very different from the sophisticated treatment that the chemical potential received via introduction of $\mu(\mathbf{r})$ and its conjugate field $\rho(\mathbf{r})$. One might justify this by the fact

that $\mu(\mathbf{r}) \neq \text{const}$ leads to a well-defined equilibrium when $v(\mathbf{r})$ acts on the system, whereas considering inhomogeneous temperature distributions reeks of nonequilibrium.

In thermodynamics, one can proceed and Legendre transform to the internal energy $E_0(N_0, S, V)$, where the entropy S is an extensive state variable, conjugate to temperature T . The latter is recovered from $T = \partial E_0/\partial S$ at $N_0, V = \text{const}$. Were one to generalize to an internal-energy functional, one needed to introduce (and define) an entropy distribution $s(\mathbf{r})$ that would “localize” (i.e., make dependent on position) the bulk entropy per unit volume, S/V . This program possesses several requirements in order to be rigorous. (i) A microscopic definition of the entropy distribution $s(\mathbf{r})$ needs to be given. (ii) The grand potential functional needs to depend on both the microscopic density and the microscopic entropy, i.e., $\Omega([\rho, s], \mu, T, V)$. Its nontrivial contribution should be an internal energy functional of both microscopic distributions, i.e., $E([\rho, s], V)$. (iii) The generalized grand potential functional should be minimal at the equilibrium values $\rho_0(\mathbf{r})$ and $s_0(\mathbf{r})$. Note that $T = \text{const}$ will be associated in general with a nontrivial spatial dependence $s_0(\mathbf{r}) \neq \text{const}$. This forms a generalization of the simple parametric dependence on temperature in conventional DFT to a proper Euler-Lagrange equation.

In the following, such a framework is established. We formulate the variational principle in Sec. II. Standard DFT approximations are converted to the internal-energy representation in Sec. III. This includes internal-energy functionals for the ideal gas, hard spheres in the fundamental measures approximation [4,6–8], the quadratic mean-field functional [9], etc. Based on the continuity equations for particle density and internal-energy density, and inspired by the framework of linear irreversible thermodynamics, in Sec. IV we formulate a theory for diffusive dynamics that corresponds to dynamical DFT (DDFT) [1,10,11], but includes the dynamics of the entropy current. Conclusions are given in Sec. V.

II. VARIATIONAL PRINCIPLE

We consider a classical system with N particles and Hamiltonian H_N . The equilibrium many-body probability

distribution in the grand ensemble is given by

$$f_0 = \Xi^{-1} \exp\left(-\frac{H_N - \mu N}{k_B T}\right). \quad (1)$$

Here the normalization constant is the grand partition sum,

$$\Xi = \text{Tr} \exp\left(-\frac{H_N - \mu N}{k_B T}\right), \quad (2)$$

with the (classical) trace being defined as

$$\text{Tr} = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \int d\mathbf{p}_1 \cdots d\mathbf{p}_N, \quad (3)$$

where h is Planck's constant, \mathbf{r}_i is the position coordinate, and \mathbf{p}_i is the momentum of particle $i = 1, \dots, N$. Mermin's form [2] for the grand potential as a functional of a trial many-body distribution f is

$$\Omega[f] = \text{Tr} f(H_N - \mu N + k_B T \ln f). \quad (4)$$

Here f is an arbitrary many-body distribution that is normalized, i.e., that satisfies

$$\text{Tr} f = 1. \quad (5)$$

Inserting the equilibrium distribution (1) into Eq. (4) yields

$$\Omega[f_0] = \text{Tr} f_0(H_N - \mu N + k_B T \ln f_0) \quad (6)$$

$$= \text{Tr} f_0 \left[H_N - \mu N - k_B T \left(\ln \Xi + \frac{H_N - \mu N}{k_B T} \right) \right] \quad (7)$$

$$= -k_B T \ln \Xi \quad (8)$$

$$\equiv \Omega_0, \quad (9)$$

where Ω_0 is the equilibrium grand potential. From the Gibbs inequality, it is straightforward to show [1,12] that for any $f \neq f_0$ the inequality $\Omega[f] > \Omega[f_0]$ holds and hence

$$\Omega_0 = \min_f \text{Tr} f(H_N - \mu N + k_B T \ln f), \quad (10)$$

We use the conventional definition of the density operator [1,12],

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (11)$$

where $\delta(\cdot)$ is the (three-dimensional) Dirac distribution, and express the one-body density distribution in equilibrium as the average

$$\rho_0(\mathbf{r}) = \text{Tr} \hat{\rho}(\mathbf{r}) f_0. \quad (12)$$

We also define a position-dependent entropy density (per unit volume) as

$$s_0(\mathbf{r}) = -k_B \text{Tr} \frac{\hat{\rho}(\mathbf{r})}{N} f_0 \ln f_0. \quad (13)$$

Note that the integral $-T \int d\mathbf{r} s_0(\mathbf{r}) = \text{Tr} k_B T f_0 \ln f_0$ equals the entropic contribution to the grand potential; cf. the last term in Eq. (6).

We use Levy's constrained search method [13,14], as proved useful for classical systems [15], and express Eq. (10)

as a two-stage minimization,

$$\Omega_0 = \min_{\rho,s} \min_{f \rightarrow \rho,s} \text{Tr} f(H_N - \mu N + k_B T \ln f), \quad (14)$$

where the inner minimization is performed for all trial f under the constraint that these generate the given density distribution $\rho(\mathbf{r})$ and the given local entropy distribution $s(\mathbf{r})$ via

$$\rho(\mathbf{r}) = \text{Tr} \hat{\rho}(\mathbf{r}) f, \quad (15)$$

$$s(\mathbf{r}) = -k_B \text{Tr} \frac{\hat{\rho}(\mathbf{r})}{N} f \ln f. \quad (16)$$

The relationships (15) and (16) are indicated as $f \rightarrow \rho,s$ in the notation of Eq. (14).

In the following, we restrict ourselves to Hamiltonians that consist of kinetic energy and internal and external contributions to the potential energy, i.e., that are of the form

$$H_N = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^N v(\mathbf{r}_i), \quad (17)$$

where $p_i^2 = \mathbf{p}_i \cdot \mathbf{p}_i$, m is the particle mass, U is the interparticle interaction potential, and $v(\mathbf{r})$ is an external potential that acts on the system. Hence Eq. (14) is more explicitly

$$\Omega_0 = \min_{\rho,s} \min_{f \rightarrow \rho,s} \text{Tr} f \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^N v(\mathbf{r}_i) - \mu N + k_B T \ln f \right). \quad (18)$$

In the expression above, several contributions can be written as space integrals over averaged one-body quantities. First, the terms due to the external and the chemical potential are

$$\text{Tr} f \left(\sum_{i=1}^N v(\mathbf{r}_i) - \mu N \right) = \int d\mathbf{r} \rho(\mathbf{r}) [v(\mathbf{r}) - \mu], \quad (19)$$

because $f \rightarrow \rho$ via Eq. (15). Furthermore, the last term in Eq. (18) is

$$\text{Tr} f k_B T \ln f = -T \int d\mathbf{r} s(\mathbf{r}), \quad (20)$$

because Eq. (16) implies that $f \rightarrow s$. Hence the terms (19) and (20) are constants with respect to the inner minimization in Eq. (14). Hence we can separate them out and arrive at

$$\Omega_0 = \min_{\rho,s} \left\{ E[\rho,s] + \int d\mathbf{r} \{ \rho(\mathbf{r}) [v(\mathbf{r}) - \mu] - T s(\mathbf{r}) \} \right\}, \quad (21)$$

where we have defined the internal energy as a functional of the density and entropy distributions as

$$E[\rho,s] = \min_{f \rightarrow \rho,s} \left[f \left(\sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \right) \right], \quad (22)$$

where, once more, the minimization ("search" [13]) is constrained to all trial f that generate the given $\rho(\mathbf{r})$ and $s(\mathbf{r})$ via Eqs. (15) and (16), respectively. Here and in the following we suppress the dependence on volume V in the notation.

The grand potential functional is the object inside of the minimization in Eq. (21), defined as

$$\Omega([\rho, s], \mu, T) = E[\rho, s] - T \int d\mathbf{r} s(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) [v(\mathbf{r}) - \mu]. \quad (23)$$

Equation (21) then becomes

$$\Omega_0 = \min_{\rho, s} \Omega([\rho, s], \mu, T), \quad (24)$$

which implies that the following functional derivatives vanish at equilibrium

$$\left. \frac{\delta \Omega([\rho, s], \mu, T)}{\delta \rho(\mathbf{r})} \right|_{\rho_0, s_0} = 0 \quad \text{and} \quad \left. \frac{\delta \Omega([\rho, s], \mu, T)}{\delta s(\mathbf{r})} \right|_{\rho_0, s_0} = 0. \quad (25)$$

The density and entropy distribution that satisfy Eq. (25) are indeed $\rho_0(\mathbf{r})$ and $s_0(\mathbf{r})$, as can be seen from their definitions, Eqs. (12) and (13), and the fact that f_0 minimizes $\Omega[f]$. This implies that

$$\begin{aligned} \Omega_0(\mu, T) &= \Omega([\rho_0, s_0], \mu, T) \\ &= E[\rho_0, s_0] - T \int d\mathbf{r} s_0(\mathbf{r}) \\ &\quad + \int d\mathbf{r} \rho_0(\mathbf{r}) [v(\mathbf{r}) - \mu], \end{aligned} \quad (26)$$

and that the internal energy in equilibrium is

$$E_0(N_0, S_0) = E[\rho_0, s_0], \quad (27)$$

where $S_0 = \int d\mathbf{r} s_0(\mathbf{r})$.

Using the definition (23), the Euler-Lagrange equations (25) can be cast in the form

$$\left. \frac{\delta E[\rho, s]}{\delta \rho(\mathbf{r})} \right|_{\rho_0, s_0} = \mu - v(\mathbf{r}), \quad (28)$$

$$\left. \frac{\delta E[\rho, s]}{\delta s(\mathbf{r})} \right|_{\rho_0, s_0} = T. \quad (29)$$

For completeness, the Helmholtz free-energy functional, on which DFT is conventionally built, is obtained as

$$F([\rho], T) = \min_s \left(E[\rho, s] - T \int d\mathbf{r} s(\mathbf{r}) \right) \quad (30)$$

$$= E[\rho, s_\rho] - T \int d\mathbf{r} s_\rho(\mathbf{r}), \quad (31)$$

where $s_\rho(\mathbf{r})$ denotes the entropy distribution at the minimum in Eq. (30), which hence satisfies

$$\left. \frac{\delta E[\rho, s]}{\delta s(\mathbf{r})} \right|_{\rho, s_\rho} = T, \quad (32)$$

where $\rho(\mathbf{r})$ is the (trial) density distribution on the left-hand side of Eq. (30).

Equations (28) and (29) constitute a closed system of equations for the determination of $\rho_0(\mathbf{r})$ and $s_0(\mathbf{r})$ for given thermodynamic statepoint μ, T and given external potential $v(\mathbf{r})$. In practical applications, one is required to use an approximation for $E[\rho, s]$. Hence it is interesting to formulate

common free-energy DFT approximations in the internal-energy picture, as we do in the next section.

III. EXAMPLES FOR INTERNAL-ENERGY FUNCTIONALS

We start with the ideal gas, where $U(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$. The Helmholtz free-energy functional can be derived from the fact that the absence of interactions decouples all volume elements of the system [1, 12]. In each volume element, the (bulk) ideal gas properties hold. Hence the free-energy functional is an integral over a local free-energy density,

$$F_{\text{id}}([\rho], T) = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\rho(\mathbf{r}) \Lambda^3] - 1 \}, \quad (33)$$

where the thermal de Broglie wavelength depends on T and is given by

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}, \quad (34)$$

and $\hbar = h/(2\pi)$. Corresponding reasoning leads to the internal-energy functional either by starting directly from the Sackur-Tetrode expression for the bulk internal energy of the ideal gas, or by Legendre transforming the integrand in Eq. (33). One arrives at the result

$$E_{\text{id}}[\rho, s] = \frac{3\pi\hbar^2}{e^{5/3}m} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} \exp\left(\frac{2s(\mathbf{r})}{3k_B\rho(\mathbf{r})}\right), \quad (35)$$

where e is the exponential constant. This result is the same as that obtained from Legendre transforming each volume element. The functional (35) is local and nonlinear. Note that \hbar^2/m carries units of energy \times length², as is consistent with the integrand that has units of length⁻⁵. Clearly, the comparison of Eq. (35) to Eq. (33) points to the quite striking density power of 5/3 in Eq. (35), and the fact that the entropy density per unit volume, $s(\mathbf{r})$, appears in effect as an entropy density per particle, $s(\mathbf{r})/\rho(\mathbf{r})$.

Evaluating the derivatives in the Euler-Lagrange equations (28) and (29) and rearranging yields

$$\rho_0(\mathbf{r}) = \Lambda^{-3} \exp\left(-\frac{\mu - v(\mathbf{r})}{k_B T}\right), \quad (36)$$

$$s_0(\mathbf{r}) = -k_B \rho_0(\mathbf{r}) \{ \ln[\rho_0(\mathbf{r}) \Lambda^3] - 5/2 \}, \quad (37)$$

and insertion into Eq. (35) gives the internal energy of the ideal gas, solely due to kinetic contributions, $E_{\text{id}}[\rho_0, s_0] = 3k_B T \int d\mathbf{r} \rho_0(\mathbf{r})/2$, a result which is certainly as expected.

For interacting systems, the total Helmholtz free energy is usually split into an ideal and an excess (over ideal) contribution as

$$F([\rho], T) = F_{\text{id}}([\rho], T) + F_{\text{exc}}([\rho], T), \quad (38)$$

where $F_{\text{id}}([\rho], T)$ is given by Eq. (33) and $F_{\text{exc}}([\rho], T)$ describes the effects of interparticle interactions. For hard spheres, most approximate functionals can be written in the form

$$F_{\text{exc}}([\rho], T) = k_B T \int d\mathbf{r} \Phi(\mathbf{r}), \quad (39)$$

where $\Phi(\mathbf{r})$ is a scaled excess free-energy density per unit volume, which is independent of T . Temperature enters only via the global scaling factor $k_B T$. For nonlocal functionals, $\Phi(\mathbf{r})$ is a functional of $\rho(\mathbf{r})$, typically via convolution. When such additional convolution integrals are present in the functional, the choice which integral features as the “outer” integral in Eq. (40) is not necessarily unique; see Appendix A for a discussion of a suitable choice in fundamental-measure theory [6,7]. Consider the following form of the internal energy functional:

$$E_{\text{HS}}[\rho, s] = \frac{3\pi\hbar^2}{e^{5/3}m} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} \exp\left(\frac{s(\mathbf{r}) - s_{\text{HS}}([\rho], \mathbf{r})}{3k_B\rho(\mathbf{r})/2}\right), \quad (41)$$

where $s_{\text{HS}}([\rho], \mathbf{r}) = -k_B\Phi(\mathbf{r})$ is the hard-sphere contribution to the entropy. Equation (41) is equivalent to Eq. (40) as can be seen from evaluating the Euler-Lagrange equations (29) and (30), which yield

$$s_0(\mathbf{r}) = -k_B\rho_0(\mathbf{r})[\ln(\rho_0(\mathbf{r})\Lambda^3) - 5/2] + s_{\text{HS}}([\rho_0], \mathbf{r}), \quad (42)$$

$$\rho_0(\mathbf{r}) = \Lambda^{-3} \exp\left(\frac{\mu - v(\mathbf{r})}{k_B T} + c_{\text{HS}}^{(1)}([\rho_0], \mathbf{r})\right), \quad (43)$$

where $c_{\text{HS}}^{(1)}$ is equivalent to the one-body direct correlation function for hard spheres and obtained here as

$$c_{\text{HS}}^{(1)}([\rho], \mathbf{r}) = k_B^{-1} \frac{\delta}{\delta\rho(\mathbf{r})} \int d\mathbf{r}' s_{\text{HS}}([\rho], \mathbf{r}'). \quad (44)$$

The common random phase approximation (RPA) [12] consists of splitting a given interparticle pair interaction potential $\phi(r)$, where r is the particle-particle distance and $U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i<j} \phi(|\mathbf{r}_i - \mathbf{r}_j|)$, into a short-ranged repulsive, say hard-sphere part $\phi_{\text{HS}}(r)$ and a long-ranged and slowly varying contribution $\phi_*(r)$, so that $\phi(r) = \phi_{\text{HS}}(r) + \phi_*(r)$. The corresponding internal-energy functional is

$$E_{\text{RPA}}[\rho, s] = E_{\text{HS}}[\rho, s] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \times \rho(\mathbf{r}') \phi_*(|\mathbf{r} - \mathbf{r}'|), \quad (45)$$

where the effects of $\phi_{\text{HS}}(r)$ are described by the hard-sphere functional (41). Equation (45) leads to the same “entropic” Euler-Lagrange equation (42) as for hard spheres, because $\delta E_{\text{RPA}}/\delta s(\mathbf{r}) = \delta E_{\text{HS}}/\delta s(\mathbf{r})$, and generates an additional contribution $-\int d\mathbf{r}' \rho(\mathbf{r}') \phi_*(|\mathbf{r} - \mathbf{r}'|)/(k_B T)$ inside of the exponential in the “density” Euler-Lagrange equation (43).

For any system where the bulk internal energy $E_0(N_0, S, V)$ is known, division by volume yields an internal energy density $\epsilon_0(\rho, s) = E_0(N_0/V, S/V)/V$, from which in a local density approximation (LDA) the functional

$$E_{\text{LDA}}[\rho, s] = \int d\mathbf{r} \epsilon_0[\rho(\mathbf{r}), s(\mathbf{r})] \quad (46)$$

follows. This is expected to be a good approximation when the smallest length scale over which $\rho(\mathbf{r})$ and $s(\mathbf{r})$ vary is much larger than all correlation lengths in the system.

A further “generic” approximation, analogous to the Ramakrishnan-Youssouf (RY) [16] quadratic approximation, is to truncate the functional Taylor expansion around a homogeneous state with $\rho(\mathbf{r}) = \rho_b = \text{const}$ and $s(\mathbf{r}) = s_b = \text{const}$

at second order in density,

$$E_{\text{RY}}[\rho, s] = E_b(\rho_b, s_b) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' [\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')b_{\rho\rho}(|\mathbf{r} - \mathbf{r}'|) + 2\Delta\rho(\mathbf{r})\Delta s(\mathbf{r}')b_{\rho s}(|\mathbf{r} - \mathbf{r}'|) + \Delta s(\mathbf{r})\Delta s(\mathbf{r}')b_{ss}(|\mathbf{r} - \mathbf{r}'|)], \quad (47)$$

where $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_b$ and $\Delta s(\mathbf{r}) = s(\mathbf{r}) - s_b$ are the deviations from the respective bulk values, the subscript b indicates bulk quantities, and the $b_{\rho\rho}(r)$, $b_{\rho s}(r)$, and $b_{ss}(r)$ are the second functional derivatives of $E[\rho, s]$ evaluated in the homogeneous bulk,

$$b_{ab}(|\mathbf{r} - \mathbf{r}'|) = \left. \frac{\delta^2 E[\rho, s]}{\delta a(\mathbf{r})\delta b(\mathbf{r}')} \right|_{\rho_b, s_b}, \quad a, b = \rho, s. \quad (48)$$

In general,

$$b_{\rho\rho}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 E[\rho, s]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right|_{\rho_0, s_0}, \quad (49)$$

$$b_{\rho s}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 E[\rho, s]}{\delta\rho(\mathbf{r})\delta s(\mathbf{r}')} \right|_{\rho_0, s_0}, \quad (50)$$

$$b_{ss}(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta^2 E[\rho, s]}{\delta s(\mathbf{r})\delta s(\mathbf{r}')} \right|_{\rho_0, s_0}. \quad (51)$$

Note that the first-order terms in Eq. (47) vanish, as one expands around equilibrium and hence the Euler-Lagrange equations (29) and (30) hold [in the case $v(\mathbf{r}) = 0$].

Note that Eqs. (49)–(51) are analogous to the usual two-body direct correlation function obtained from the excess Helmholtz free-energy functional as

$$c_2(\mathbf{r}, \mathbf{r}') = -(k_B T)^{-1} \left. \frac{\delta^2 F_{\text{exc}}([\rho], T)}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right|_{\rho_0}. \quad (52)$$

IV. DIFFUSIVE DYNAMICS

Using the equilibrium framework developed in Sec. II, we find it interesting to use it in a dynamical context, similar in spirit to dynamical density-functional theory (DDFT), which rests on the equilibrium Helmholtz free-energy functional. Much current research activity is aimed at applying and developing DDFT, which provides a dynamical equation for the time evolution of the density profile $\rho(\mathbf{r}, t)$, where t is time. In order to derive such an equation, the continuity equation for the density profile, which is exact, is supplemented by approximations for the “thermodynamic driving force” that acts on the density. As compared to a diffusion equation, gradients in chemical potential are replaced by gradients in the functional (density) derivative of the Helmholtz free-energy density. Starting from a more microscopic point of view, DDFT can also be derived from the Smoluchowski equation [10].

Here, we spell out a similar framework for the joint time evolution of $\rho(\mathbf{r}, t)$ and the time- and position-dependent entropy distribution $s(\mathbf{r}, t)$. We keep the discussion at a phenomenological level and make no attempts at a derivation from first principles, albeit paying attention that fundamental symmetry relations, i.e., the Onsager reciprocal relations, are satisfied. Hence the strategy consists of taking the appropriate

dynamic equations from linear irreversible thermodynamics [17,18] and replacing the temperature and density fields in the continuum description by the microscopic (functional) derivatives of the internal-energy functional.

We impose two continuity equations, one for the density $\rho(\mathbf{r},t)$ and one for the internal-energy density $\epsilon(\mathbf{r},t)$,

$$\dot{\rho}(\mathbf{r},t) = -\nabla \cdot \mathbf{J}_\rho(\mathbf{r},t), \quad (53)$$

$$\dot{\epsilon}(\mathbf{r},t) = -\nabla \cdot \mathbf{J}_\epsilon(\mathbf{r},t), \quad (54)$$

where the dot denotes a partial time derivative, i.e., $\dot{\rho} = \partial\rho/\partial t$ and $\dot{\epsilon} = \partial\epsilon/\partial t$. Solving the Gibbs-Duhem relation $d\epsilon = Tds + \mu d\rho$ for the differential entropy per unit volume, ds , gives

$$ds = \frac{1}{T}d\epsilon - \frac{\mu}{T}d\rho, \quad (55)$$

from which the prefactors of the differentials on the right-hand side are identified as the ‘‘driving forces’’ for the internal-energy current \mathbf{J}_ϵ and for the particle density current \mathbf{J}_ρ . Hence

$$\mathbf{J}_\rho = D\rho \nabla \frac{-\mu}{k_B T} + D_T \epsilon \nabla \frac{1}{k_B T}, \quad (56)$$

$$\mathbf{J}_\epsilon = D_T \epsilon \nabla \frac{-\mu}{k_B T} + D_{\text{th}} \frac{\epsilon^2}{\rho} \nabla \frac{1}{k_B T}, \quad (57)$$

where we have omitted the arguments \mathbf{r},t , and have introduced the particle diffusion coefficient D , the thermal diffusion coefficient D_T , and the thermal conductivity D_{th} , all of which possess dimensions of length²/time. The powers of ρ and ϵ in the prefactors of the gradients in Eqs. (56) and (57) can be determined from dimensional analysis, by observing that the left-hand side of Eq. (56) possesses units of 1/(time \times length²) and that of Eq. (57) has units of energy/(time \times length²). Note that the ‘‘cross terms,’’ i.e., the prefactor of the second gradient in Eq. (56) and of the first gradient in Eq. (57) are identical as requested by the Onsager reciprocal relations. See Appendix B for a derivation of Eqs. (56) and (57) starting from a dissipation function. The change in entropy is obtained via the Gibbs-Duhem relation (55) as

$$\dot{s} = \frac{1}{T}\dot{\epsilon} - \frac{\mu}{T}\dot{\rho} \quad (58)$$

$$= -\frac{1}{T}\nabla \cdot \mathbf{J}_\epsilon + \frac{\mu}{T}\nabla \cdot \mathbf{J}_\rho, \quad (59)$$

where Eq. (59) follows from the continuity equations (53) and (54).

Bearing in mind the structure of the Euler-Lagrange equations (29) and (30), we replace μ by $\delta E[\rho,s]/\delta\rho(\mathbf{r},t) + v(\mathbf{r},t)$ and T by $\delta E[\rho,s]/\delta s(\mathbf{r},t)$. Here we have allowed the external potential to be time dependent, in order to model a corresponding external influence on the system. Hence we rewrite Eqs. (53) and (54) as

$$\mathbf{J}_\rho = -\frac{D}{k_B}\rho\nabla \frac{b_\rho + v}{b_s} + \frac{D_T}{k_B}\epsilon\nabla \frac{1}{b_s}, \quad (60)$$

$$\mathbf{J}_\epsilon = -\frac{D_T}{k_B}\epsilon\nabla \frac{b_\rho + v}{b_s} + \frac{D_{\text{th}}}{k_B}\frac{\epsilon^2}{\rho}\nabla \frac{1}{b_s}, \quad (61)$$

where we have used the short-hand notation for the first functional derivatives of the internal-energy functional,

$$b_\rho = \left. \frac{\delta E[\rho,s]}{\delta\rho(\mathbf{r})} \right|_{\rho(\mathbf{r},t),s(\mathbf{r},t)}, \quad (62)$$

$$b_s = \left. \frac{\delta E[\rho,s]}{\delta s(\mathbf{r})} \right|_{\rho(\mathbf{r},t),s(\mathbf{r},t)}. \quad (63)$$

Performing the replacement of the local temperature and the local chemical potential by the corresponding functional derivatives in Eq. (59) yields

$$\dot{s} = -\frac{1}{b_s}\nabla \cdot \mathbf{J}_\epsilon + \frac{b_\rho + v}{b_s}\nabla \cdot \mathbf{J}_\rho. \quad (64)$$

The equations for the currents (60) and (61) together with the continuity equation for the particle density (53) and for the energy density (54), along with Eq. (64), form a closed set of equations for the time evolution of $\rho(\mathbf{r},t)$ and $s(\mathbf{r},t)$, for given $v(\mathbf{r},t)$ and initial conditions $\rho(\mathbf{r},0)$ and $s(\mathbf{r},0)$ at time $t = 0$. In general, the diffusion coefficients D, D_T , and D_{th} will depend on $\rho(\mathbf{r},t)$ and $s(\mathbf{r},t)$; assuming them to be constant would be the simplest approximation.

V. CONCLUSIONS

In summary, we have developed a variational formulation of classical statistical mechanics, which is centered around the internal energy as a functional of the one-body density distribution $\rho(\mathbf{r})$ and the position-dependent entropy distribution $s(\mathbf{r})$. Although the definition of $s(\mathbf{r})$ is not unique [cf. Eq. (13) for the equilibrium value $s_0(\mathbf{r})$], the current choice possesses two important properties that make it a suitable variable in the variational framework: (i) the space integral of $s(\mathbf{r})$ is the macroscopic entropy and (ii) the definition is local in the sense that it probes the entropy under the condition that a particle resides at the space point \mathbf{r} considered. One of the Euler-Lagrange equations for the minimization of the grand potential is very similar to that of DFT based on the Helmholtz theory, i.e., the functional derivative with respect to the density field is related to a local chemical potential; cf. Eq. (29). Physically, such a situation can be realized by an external potential acting on the system. The internal energy functional $E[\rho,s]$ depends on the local density $\rho(\mathbf{r})$ and on the entropy distribution $s(\mathbf{r})$. The functional derivative with respect to $s(\mathbf{r})$ gives the (constant) temperature in equilibrium; cf. Eq. (30). Having this further Euler-Lagrange equation is to be considered a strength of the theory, when it comes to applications using an approximate functional. Rather than having to implement the physics of $T = \text{const}$ on the level of the approximation for the free-energy functional, the internal-energy functional offers an additional mechanism to relax to equilibrium via an inhomogeneous entropy distribution.

In Levy’s constrained search method, which we used for formulating the variational framework, there is no need for introducing a field that is conjugate to the local entropy distribution. Hence the situation is different from the local chemical potential that is conjugate to the one-body density. The relationship between these thermodynamic fields plays a crucial role in the standard Mermin-Evans formulation

of DFT. However, in equilibrium, there is at least no simple conjugate to the entropy distribution. Such a role would be played by an position-dependent temperature, which we deliberately avoided in the derivation presented in Sec. II.

Obtaining dynamical equations for the density and entropy distributions is straightforward when using linear irreversible thermodynamics in a continuum description as a starting point and replacing the fields for temperature and chemical potential by the appropriate functional derivatives of the internal-energy functional; cf. Eqs. (56) and (57). This approach is phenomenological and we have made no attempts at deriving the dynamics from first principles under controlled approximations for the microscopic dynamics. While the structure of the dynamic equations is a straightforward extension of dynamical DFT, there is also an important distinction: when using the Helmholtz free-energy functional, in principle any (nonpathological) density field is a physically realizable one via the choice of an appropriate external potential. The situation is different when considering the internal-energy functional and prescribing both the density field and the entropy field. In general, no corresponding equilibrium situation will exist, i.e., one cannot choose an external potential and a temperature, cf. Eqs. (29) and (30), so that the given trial fields $\rho(\mathbf{r})$ and $s(\mathbf{r})$ become equilibrium quantities. This effect is far less subtle than that of representability of trial density fields; cf. the discussion in Ref. [15].

Clearly, true hydrodynamic effects, that originate from local momentum and angular momentum conservation, are neglected in the treatment of Sec. IV. However, there remains a wide range of interesting physics associated entirely with diffusive dynamics in (complex) liquids [19,20]; see, e.g., Dhont's treatment of thermodiffusion [21,22].

We have formulated a variety of standard DFT approximations in internal-energy language. The mathematical structure of some of these functionals appear unfamiliar in a variational context; cf. the form of the ideal gas internal-energy functional and the way in which the ideal gas and interaction contributions are coupled in the case of hard spheres; cf. Eq. (41). Other approximations are consistent with expectation, i.e., the addition of a mean-field energy contribution (45), the local density approximation (46), and the Taylor expansion up to second order around a homogeneous (fluid) state (47).

The potential importance of the current work lies (i) in the additional insights that can be gained from studying the entropy distribution in applications within existing approximations such as these described in Sec. III and (ii) in the possibility to construct internal-energy functionals that couple the density and entropy contributions in novel ways. Investigating the implications for the dynamical test particle limit [23,24] is an interesting topic for future work, as is considering quenched-annealed mixtures [25–27] and the dynamics of atomic liquids [28]. Finally, note that changing the thermodynamical potential as we have done here is very different from changing to a different ensemble; see, e.g. [29] for DFT in the canonical ensemble.

Note added in proof. The current theory possess similarities, but also significant differences to the approach by P. Attard [31]. His theory is, broadly speaking, based on the entropy functional with the internal energy being a variable.

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APPENDIX A: FUNDAMENTAL-MEASURE THEORY

Although Rosenfeld's functional [for a hard sphere mixture with one-body density profile $\rho_i(\mathbf{r})$ of species i] possesses the structure of Eq. (40),

$$F_{\text{exc}}[\{\rho_i\}] = \int d\mathbf{x} \Phi(\mathbf{x}), \quad (\text{A1})$$

the position coordinate \mathbf{x} is very different from the argument \mathbf{r} of the entropy distribution (16). Rather than corresponding to a particle position, \mathbf{x} is a mere convolution integral that couples the fundamental-measure theory (FMT) weight functions in order to represent the hard sphere Mayer bond and, for third and higher orders in density, constitutes the center of star diagrams that are formed by weight function bonds [30].

Both the definition of the entropy field (16) and in the ratio of entropy and density distribution in the exponential of the hard sphere internal-energy functional (41), one expects a particle to be located at the position considered. In FMT, there is no shortage of position integrals over the density; hence the problem is to single out one of them in a nonbiased, "symmetric" way.

In order to achieve this, we start from the power series of FMT [30], which reads

$$F_{\text{exc}}[\{\rho_i\}] = k_B T \int d\mathbf{x} \sum_{m=2}^{\infty} \frac{1}{m(m-1)} [\mathbf{N}(\mathbf{x})]^m, \quad (\text{A2})$$

where $[\mathbf{N}(\mathbf{x})]^m$ is the m th matrix power of

$$\mathbf{N}(\mathbf{x}) = \begin{pmatrix} n_3(\mathbf{x}) & n_2(\mathbf{x}) & n_1(\mathbf{x}) & n_0(\mathbf{x}) \\ 0 & n_3(\mathbf{x}) & \frac{n_2(\mathbf{x})}{4\pi} & n_1(\mathbf{x}) \\ 0 & 0 & n_3(\mathbf{x}) & n_2(\mathbf{x}) \\ 0 & 0 & 0 & n_3(\mathbf{x}) \end{pmatrix}. \quad (\text{A3})$$

Here the weighted densities $n_\alpha(\mathbf{x})$ are obtained by convolution,

$$n_\alpha(\mathbf{x}) = \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) w_\alpha^{(i)}(\mathbf{r} - \mathbf{x}), \quad (\text{A4})$$

where the $w_\alpha(\cdot)$ are the Kierlik-Rosinberg FMT weight functions [7], and the sum is over all hard-sphere species i . Note that $F_{\text{exc}}[\{\rho_i\}]$ in Eq. (A2) is a 4×4 matrix and that the physically relevant entry $F_{\text{exc}}[\{\rho_i\}]$ is that in the first row and last column [30].

We rewrite the integrand in Eq. (A2) as

$$\mathbf{N}(\mathbf{x}) \sum_{m=2}^{\infty} \frac{1}{m(m-1)} [\mathbf{N}(\mathbf{x})]^{m-1} \quad (\text{A5})$$

$$= \sum_i \int d\mathbf{r} \mathbf{W}^{(i)}(\mathbf{x} - \mathbf{r}) \rho_i(\mathbf{r}) \times \sum_{m=2}^{\infty} \frac{1}{m(m-1)} [\mathbf{N}(\mathbf{x})]^{m-1}, \quad (\text{A6})$$

where the matrix of weight functions is defined as

$$\mathbf{W}^{(i)}(\mathbf{x}) = \begin{pmatrix} w_3^{(i)}(\mathbf{x}) & w_2^{(i)}(\mathbf{x}) & w_1^{(i)}(\mathbf{x}) & w_0^{(i)}(\mathbf{x}) \\ 0 & w_3^{(i)}(\mathbf{x}) & \frac{w_2^{(i)}(\mathbf{x})}{4\pi} & w_1^{(i)}(\mathbf{x}) \\ 0 & 0 & w_3^{(i)}(\mathbf{x}) & w_2^{(i)}(\mathbf{x}) \\ 0 & 0 & 0 & w_3^{(i)}(\mathbf{x}) \end{pmatrix}. \quad (\text{A7})$$

Reintroducing the \mathbf{x} integral and rearranging in Eq. (A6) gives

$$\begin{aligned} F_{\text{exc}}[\{\rho_i\}] &= k_B T \int d\mathbf{r} \sum_i \rho_i(\mathbf{r}) \int d\mathbf{x} \mathbf{W}_i(\mathbf{x} - \mathbf{r}) \\ &\quad \times \sum_{m=2}^{\infty} \frac{1}{m(m-1)} [\mathbf{N}(\mathbf{x})]^{m-1}, \end{aligned} \quad (\text{A8})$$

$$\equiv k_B T \int d\mathbf{r} \sum_i \rho_i(\mathbf{r}) \Psi_i(\mathbf{r}), \quad (\text{A9})$$

where we have defined the free-energy density (per particle) for species i as

$$\Psi_i(\mathbf{r}) = \int d\mathbf{x} \mathbf{W}_i(\mathbf{x} - \mathbf{r}) \sum_{m=2}^{\infty} \frac{1}{m(m-1)} [\mathbf{N}(\mathbf{x})]^{m-1}. \quad (\text{A10})$$

Hence we single out the entry in the top right corner of the matrix in Eq. (A9), and rewrite it as

$$F_{\text{exc}}[\{\rho_i\}] = \int d\mathbf{r} \sum_i \rho_i(\mathbf{r}) \sum_{\alpha=0}^3 (w_{\alpha}^{(i)} * \phi_{\alpha})(\mathbf{r}), \quad (\text{A11})$$

where the asterisk denotes the convolution, and explicit expressions for the $\phi_{\alpha}(\mathbf{x})$ are as follows:

$$\phi_0 = 1 + \left(\frac{1}{n_3} - 1 \right) \ln(1 - n_3), \quad (\text{A12})$$

$$\phi_1 = -\frac{n_2}{n_3} - \frac{n_2}{n_3^2} \ln(1 - n_3), \quad (\text{A13})$$

$$\phi_2 = \left(\frac{n_2^2}{4\pi n_3^3} - \frac{n_1}{n_3^2} \right) \ln(1 - n_3) - \frac{n_1}{n_3} + \frac{n_2^2(2 - n_3)}{8\pi n_3^2(1 - n_3)}, \quad (\text{A14})$$

$$\begin{aligned} \phi_3 &= -\left(\frac{n_0}{n_3^2} - \frac{2n_1 n_2}{n_3^3} + \frac{n_2^3}{4\pi n_3^4} \right) \ln(1 - n_3) \\ &\quad - \frac{n_0}{n_3} + \frac{n_1 n_2(2 - n_3)}{n_3^2(1 - n_3)} - \frac{n_2^3(2n_3^2 - 9n_3 + 6)}{24\pi n_3^3(1 - n_3)^2}. \end{aligned} \quad (\text{A15})$$

In summary, the integrand in Eq. (A11) forms a suitable choice for the desired quantity, i.e.,

$$s_{\text{HS}}([\{\rho_i\}], \mathbf{r}) = -k_B \Phi(\mathbf{r}) \quad (\text{A16})$$

$$= -k_B \sum_i \rho_i(\mathbf{r}) \sum_{\alpha=0}^3 (w_{\alpha}^{(i)} * \phi_{\alpha})(\mathbf{r}). \quad (\text{A17})$$

APPENDIX B: DISSIPATION FUNCTION

As a consistency check on Eqs. (56) and (57) [and hence Eqs. (60) and (61)], we derive the currents from a (scaled) dissipation function R [17,18], which we assume to be given by

$$\begin{aligned} R &= \frac{D\rho}{2} \left(\nabla \frac{-\mu}{k_B T} \right)^2 + D_T \epsilon \left(\nabla \frac{-\mu}{k_B T} \right) \cdot \left(\nabla \frac{1}{k_B T} \right) \\ &\quad + \frac{D_{\text{th}} \epsilon^2}{2\rho} \left(\nabla \frac{1}{k_B T} \right)^2. \end{aligned} \quad (\text{B1})$$

Here R is a scaled object with dimensions of (length \times time) $^{-1}$. One can verify explicitly that Eq. (B1) generates the expressions (56) and (57) via

$$\mathbf{J}_{\rho} = \frac{\partial R}{\partial \left(\nabla \frac{-\mu}{k_B T} \right)}, \quad (\text{B2})$$

$$\mathbf{J}_{\epsilon} = \frac{\partial R}{\partial \left(\nabla \frac{1}{k_B T} \right)}. \quad (\text{B3})$$

Furthermore, one can show explicitly that for the entropy production,

$$\dot{s} + \nabla \cdot \mathbf{J}_s = 2k_B R \quad (\text{B4})$$

holds, where the entropy current is

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_{\epsilon} - \frac{\mu}{T} \mathbf{J}_{\rho}, \quad (\text{B5})$$

consistent with the Gibbs-Duhem relation (55).

Finally, note that Eqs. (56) and (57) can be written as a matrix product,

$$\begin{pmatrix} \mathbf{J}_{\rho} \\ \mathbf{J}_{\epsilon} \end{pmatrix} = \begin{pmatrix} D\rho & D_T \epsilon \\ D_T \epsilon & D_{\text{th}} \epsilon^2 / \rho \end{pmatrix} \cdot \begin{pmatrix} \nabla \frac{-\mu}{k_B T} \\ \nabla \frac{1}{k_B T} \end{pmatrix}, \quad (\text{B6})$$

where the matrix of kinetic coefficients [on the right-hand side of Eq. (B6)] is symmetric, as requested by the Onsager reciprocal relations [17,18].

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