

# Nonlocal effects in nonisothermal hydrodynamics from the perspective of beyond-equilibrium thermodynamics

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We examine the origins of nonlocality in a nonisothermal hydrodynamic formulation of a one-component fluid of particles that exhibit long-range correlations, e.g., due to a spherically symmetric, long-range interaction potential. In order to furnish the continuum modeling with physical understanding of the microscopic interactions and dynamics, we make use of systematic coarse graining from the microscopic to the continuum level. We thus arrive at a thermodynamically admissible and closed set of evolution equations for the densities of momentum, mass, and internal energy. From the consideration of an illustrative special case, the following main conclusions emerge. There are two different source terms in the momentum balance. The first is a body force, which in special circumstances can be related to the functional derivative of a nonlocal Helmholtz free energy density with respect to the mass density. The second source term is proportional to the temperature gradient, multiplied by the nonlocal entropy density. These two source terms combine into a pressure gradient only in the absence of long-range effects. In the irreversible contributions to the time evolution, the nonlocal contributions arise since the self-correlations of the stress tensor and heat flux, respectively, are nonlocal as a result of the microscopic nonlocal correlations. Finally, we point out specific points that warrant further discussions.

## I. INTRODUCTION

The dynamics of matter can be described on different levels from the atomistic to the continuum. For example, for many applications in the dynamics of low-molecular weight fluids, the long length and time scale behavior is conveniently described by nonisothermal hydrodynamics<sup>1</sup> in terms of the densities of mass, momentum, and internal energy. An implicit assumption underlying such treatments is that the range of particle correlations is much smaller than the spatial resolution of the hydrodynamic field variables. In this paper, we explore from the perspective of nonequilibrium thermodynamics possible ramifications of long-range correlations on the continuum formulation of nonisothermal hydrodynamics. By the term “long range” we mean that the distance over which particle positions are correlated is larger than the size of the infinitesimal volume element that describes the resolution of the continuum field variables.

The extension of density functional theory (DFT) to dynamic situations with application to classical fluids has recently been explored.<sup>2</sup> If flow effects are of interest, a most prominent feature of long-range effects is the occurrence of a body force-like term, either in the fluid’s momentum balance or in the (overdamped) diffusion equation for the density variable, closely related to the functional derivative of a nonlocal Helmholtz free energy functional.<sup>2–8</sup> While this effect is based on the nonlocality in the thermodynamics, there are also ramifications of nonlocality in terms of the kinetics. Par-

ticularly, long-range correlations between the constituent particles give rise to a nonlocal relation between the fluid stress and the deformation rate.<sup>8–13</sup> The corresponding relations are either based on phenomenological arguments or obtained by applying the fluctuation dissipation relation, i.e., nonlocal effects in the kinetics. However, to the authors’ knowledge, in none of these approaches that study nonlocal effects of thermodynamic and kinetic origin, a thermal variable is taken into account, e.g., in the form of a temperature or an internal energy. Therefore, within such a setting, a correct treatment of nonisothermal situations is out of reach. In this work we address this shortcoming and aim to formulate a thermodynamically admissible set of evolution equations for nonisothermal hydrodynamics, paying particular attention to nonlocal effects in both the thermodynamics and the kinetics.

While we consider here a one-component system of particles, there is much interest from both a theoretical and practical standpoint in considering the dynamics of two-component systems. This class includes suspensions of large particles in a solvent of smaller solvent particles. In the event that there is a large separation of time scales this incorporates simple models for colloidal dispersions. In treating the dynamics of such colloidal systems, spatial nonlocality may be taken into account using the dynamical density functional theory (DDFT).<sup>5,14–16</sup> Nonlocality enters this theory via the appearance of a nonlocal Helmholtz free energy functional in an approximate DDFT equation of motion for the density distribution of the colloids based on overdamped colloidal dynamics.<sup>17</sup> As the solvent degrees of freedom are already integrated out at the Smoluchowski level the theory thus

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starts from a coarse grained, effective one-component description of the system. Beyond purely formal developments,<sup>2</sup> recent work has made progress toward incorporating solvent flow,<sup>18</sup> hydrodynamic interactions,<sup>19–21</sup> and temperature gradients<sup>22,23</sup> into the formalism. The DDFT in both its standard and extended forms has been proved successful for describing the relaxational dynamics of colloidal dispersions. Nevertheless, with regard to extending the approach to flow and nonisothermal conditions, a highly desirable proper coupling to the nonisothermal hydrodynamics of the solvent has not yet been achieved.

Although of much physical interest, a systematic coarse graining of the multicomponent system of solvent plus colloidal particles (with long-range correlations) poses a considerable challenge. For the present work we thus concentrate on simpler one-component systems composed of atomistic particles and focus on possible nonlocal effects in the continuum description. For such systems, the relation between the microscopic particle-based and the continuum levels of description may be carried out in a clear and elegant fashion (see also Refs. 7, 24, and 25, and references therein), as demonstrated below. In this way we can illustrate the general principles involved in our coarse-graining strategy and prepare the ground for a future treatment of the two-component colloidal system.

In order to keep our treatment as simple and transparent as possible we restrict the interparticle interactions to pair potentials of spherical symmetry. Throughout this manuscript, also hard sphere systems shall be understood as part of this class, with an interaction range equal to the particle diameter and an infinite energy penalty for overlap. Due to our interest in order of magnitudes, we will use the terms long-range interaction and long-range correlation interchangeably, bearing in mind the more fundamental nature of the correlations in certain respects (e.g., see Refs. 10 and 12). One-component systems with spherically symmetric interaction potentials are a highly important class of system and central to simple liquid-state theory.<sup>26</sup> Indeed, their study laid the foundations for the theoretical treatment of colloidal systems. For example, the canonical hard sphere model, extensively investigated by Boltzmann in the early days of statistical mechanics, was first used to model simple atomic liquids before going on to become a central pillar of modern colloid science.<sup>27</sup>

The paper is organized as follows. In Sec. II we will review briefly the GENERIC (general equation for the non-equilibrium reversible-irreversible coupling) framework and its systematic approach to coarse graining. In Sec. III we will develop all ingredients toward the formulation of a thermodynamically admissible set of evolution equations for a single component fluid with nonlocal and thermal effects. The full set of evolution equations is summarized in Sec. IV and examined for a special case. The main conclusions are discussed in Sec. V.

## II. GENERIC FORMALISM

The techniques of nonequilibrium thermodynamics act as a guard rail, helping the modeler to cast the description of

a complex system in a form that complies with certain principles of thermodynamics. There are a wide variety of approaches to nonequilibrium thermodynamics modeling, and the relations between many of them have been established.<sup>28,29</sup> Here, we choose the GENERIC framework by Grmela and Öttinger.<sup>30–32</sup> This approach applies to nonisothermal situations and allows for systematic coarse graining between different levels of description.

The GENERIC formalism describes closed nonequilibrium systems.<sup>30–32</sup> When attempting to formulate a model in the GENERIC framework, the first step is to choose the variables that describe the situation of interest. Similar to the procedure in equilibrium thermodynamics, the choice of variables must be such that they are independent and sufficient to capture the essential physics. Such a set of variables shall here be denoted by  $x$ . In this study, we are concerned with field variables that depend on the spatial position  $r$ . In other words,  $x$  has both discrete indices for the different fields as well as continuous indices to evaluate the fields at a specific position in space. The time evolution of  $x$  can be written in the form

$$\frac{\partial x_i(\mathbf{r})}{\partial t} = \int L_{ik}(\mathbf{r}, \mathbf{r}') \frac{\delta E}{\delta x_k(\mathbf{r}')} d^3 r' + \int M_{ik}(\mathbf{r}, \mathbf{r}') \frac{\delta S}{\delta x_k(\mathbf{r}')} d^3 r', \quad (1)$$

where the two generators  $E$  and  $S$  are the total energy and entropy, respectively. Both  $E$  and  $S$  are functionals of the state variable  $x$ . The functional derivative with respect to the field  $x$  is denoted by  $\delta/\delta x$ . The two contributions to the time evolution of  $x$  generated by the total energy  $E$  and the entropy  $S$  are called the reversible and irreversible contributions, respectively. The matrix  $L$  describes the kinematics, while the matrix  $M$  accounts for a wealth of irreversible processes, and hence contains material parameters such as diffusion coefficients, viscosities, relaxation times, and reaction constants.<sup>30–32</sup>

The GENERIC structure also imposes certain conditions on the building blocks in Eq. (1). First, Eq. (1) is supplemented by the mutual degeneracy requirements

$$\int L_{ik}(\mathbf{r}, \mathbf{r}') \frac{\delta S}{\delta x_k(\mathbf{r}')} d^3 r' = 0, \quad (2a)$$

$$\int M_{ik}(\mathbf{r}, \mathbf{r}') \frac{\delta E}{\delta x_k(\mathbf{r}')} d^3 r' = 0. \quad (2b)$$

The requirement that the functional derivative of the entropy lies in the null space of  $L$  represents the fact that the entropy is not affected by the operator generating the reversible dynamics. Conversely, the energy is conserved by the irreversible contributions according to Eq. (2b). In addition to these degeneracy requirements,  $L$  must be antisymmetric, whereas  $M$  needs to be positive semidefinite and Onsager–Casimir symmetric. As a result of all these conditions it follows that the evolution equations (1) imply both the conservation of total energy as well as a non-negative entropy production. Finally, the GENERIC structure requires that the Poisson

bracket associated to the matrix  $L$  fulfills the Jacobi identity (see the Appendix for details). This important identity expresses the time-structure invariance of the reversible dynamics.

The complementary degeneracy requirements, symmetry properties, and the Jacobi identity are essential for formulating proper  $L$ - and  $M$ -matrices when modeling concrete non-equilibrium problems. Various applications have shown that the two-generator idea and the criteria on the two matrices have strong implications, e.g., on the form of the stress tensor, on certain closure approximations, and on the advection of structural variables in flow (e.g., see Refs. 30 and 32–34). The GENERIC framework is postulated to hold on any level of description. This postulate is substantiated by systematic procedures for coarse graining, specifically for relating the building blocks  $E$ ,  $S$ ,  $L$ , and  $M$  on a specific level with the building blocks on a more fine-grained level. In the remainder of this paper, we consider coarse graining from the microscopic level of  $N$  interacting point particles (i.e., particles without internal structure) described in terms of their positions and momenta

$$\mathbf{z} = (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) \quad (3)$$

to the continuum level as described by the variables  $\mathbf{x}$  that include the densities of momentum  $\mathbf{u}$ , mass  $\rho$ , and the internal energy  $e$ . Knowing the microscopic interactions, (approximate) expressions for the total energy  $E$  and entropy  $S$  in terms of  $\mathbf{x}$  can be obtained. As this is a classical topic in statistical mechanics, and since we will not derive such expressions in this paper, we shall not delve into this topic. Rather, we refer the reader to Refs. 35–37 in relation to equilibrium statistical mechanics, to Ref. 30 concerning beyond equilibrium situations, and to Refs. 14, 26, and 38 with regard to the DFT of inhomogeneous fluids.

The matrices  $L$  and  $M$  on the continuum level are related to the microscopic description. If the instantaneous values of the fields  $\mathbf{x}(\mathbf{r})$  are expressed in terms of the microscopic state  $\mathbf{z}$ , denoted by  $\Pi_{\mathbf{x}}(\mathbf{z}; \mathbf{r})$ , it can be shown that the elements of the Poisson matrix  $L$  are given by<sup>30</sup>

$$L_{ik}(\mathbf{x})(\mathbf{r}, \mathbf{r}') = \sum_n \left\langle \frac{\partial \Pi_i(\mathbf{z}; \mathbf{r})}{\partial r_n} \cdot \frac{\partial \Pi_k(\mathbf{z}; \mathbf{r}')}{\partial p_n} - \frac{\partial \Pi_i(\mathbf{z}; \mathbf{r})}{\partial p_n} \cdot \frac{\partial \Pi_k(\mathbf{z}; \mathbf{r}')}{\partial r_n} \right\rangle_x, \quad (4)$$

where the average  $\langle \dots \rangle_x$  is taken with respect to a generalized (micro-)canonical distribution of states corresponding to the macrostate  $\mathbf{x}$  (see Refs. 24 and 30 for more details). Equation (4) is an average of the microscopic Poisson bracket. The situation for the friction matrix  $M$  is more involved. Under the assumption of time scale separation between the different levels, the projection operator method<sup>39</sup> has been used to relate a coarse level of description with the microscopic purely reversible dynamics. In particular, it is recognized that fast motions that are not resolved on the coarse level give rise to dissipative effects. Rather than writing the corresponding result of the projection operator procedure in its full form, here we summarize the result in a symbolic notation

$$M_{ik}(\mathbf{x})(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B} \int_0^\tau \langle \dot{\Pi}_{x_i}^f(\mathbf{z}(t); \mathbf{r}) \dot{\Pi}_{x_k}^f(\mathbf{z}(0); \mathbf{r}') \rangle_x dt, \quad (5)$$

where  $\dot{\Pi}_{x_i}^f(\mathbf{z}(t); \mathbf{r})$  denotes the fast, fluctuating part of the time derivative of  $\Pi_{x_i}$  at time  $t$  according to the dynamics of the microscopic degrees of freedom (see Refs. 24 and 30 for more details). The upper integration limit  $\tau$  is a time scale intermediate between the characteristic time scales of the fine grained and the coarse grained levels of description. Given a clear separation of time scales, the friction matrix (5) does not depend on the separating time scale  $\tau$ .

### III. NONISOTHERMAL HYDRODYNAMICS WITH LONG-RANGE INTERACTIONS

#### A. Choice of variables

Our aim is to describe a compressible fluid under nonisothermal conditions. On the continuum scale, the flow field is described by the velocity field  $\mathbf{v}$ , while compressibility requires to keep track of the mass density  $\rho$  as well. Finally, the modeling of general nonisothermal situations necessitates the inclusion of a thermal variable, e.g., the internal energy density  $e$ . In summary, we choose as the complete set of dynamic variables on the continuum scale

$$\mathbf{x} = (\mathbf{u}, \rho, e), \quad (6)$$

where the momentum density  $\mathbf{u} = \rho \mathbf{v}$  has been chosen instead of  $\mathbf{v}$  for technical convenience.<sup>30</sup> The instantaneous values of these quantities in terms of the microscopic positions and momenta, Eq. (3), read

$$\Pi_{\mathbf{u}}(\mathbf{z}; \mathbf{r}) = \sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (7a)$$

$$\Pi_{\rho}(\mathbf{z}; \mathbf{r}) = \sum_{i=1}^N m_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (7b)$$

$$\Pi_e(\mathbf{z}; \mathbf{r}) = \sum_{i=1}^N \left( \frac{1}{2m_i} [\mathbf{p}_i - m_i \mathbf{v}(\mathbf{r})]^2 + \frac{1}{2} \sum_j V(r_{ij}) \right) \delta(\mathbf{r} - \mathbf{r}_i), \quad (7c)$$

where the summation runs over all particles. For simplicity we restrict ourselves to pairwise interactions. Note that we attribute to each particle half of the pair interaction energy. Alternatively, smearing out the interaction energy on the connector line between both particles is another possibility, which is, however, not considered here. The instantaneous value for the internal energy density includes the peculiar momenta, i.e., the momenta with respect to the macroscopic flow field  $\mathbf{v}$ , which leads to nonvanishing internal energy even for the ideal gas  $V \equiv 0$ . The average of the microscopic expressions (7) with respect to the generalized (micro-)canonical ensemble leads to the continuum fields<sup>30</sup>

$$\mathbf{x} = \langle \Pi_{\mathbf{x}}(\mathbf{z}; \mathbf{r}) \rangle_x. \quad (8)$$

The flow field used in the definition of the internal energy (7c) is defined as  $\mathbf{v} = \mathbf{u} / \rho$  and can therefore be accessed using the averages (8).

With respect to the spatial resolution of the field variables  $\mathbf{x}(\mathbf{r})$ , the following specification is needed. It is assumed that many particles are to be found within each volume element of size  $d^3r$ , that the fields are smooth and differentiable, and that the size of the volume element is also bound from above. As we are interested in examining the effect of nonlocality on the level described by the continuum fields  $\mathbf{x}(\mathbf{r})$ , one must allow that there are certain contributions to the interaction potentials with a range larger than the size of the volume element.

## B. Generating functionals

In terms of the variables (6), the total energy and the entropy can be written in the form

$$E[\mathbf{x}] = \int \left( \frac{\mathbf{u}^2(\mathbf{r})}{2\rho(\mathbf{r})} + e(\mathbf{r}) \right) d^3r, \quad (9a)$$

$$S[\mathbf{x}] = \int s[\rho, e](\mathbf{r}) d^3r. \quad (9b)$$

Here we consider the entropy density  $s[\rho, e](\mathbf{r})$  as a functional of  $\rho$  and  $e$ , thus neglecting any dependence on the momentum density. We employ the notation  $f[\dots]$  if  $f$  is a functional of its arguments, while  $f(\dots)$  is used to indicate that  $f$  is a function. Using Eq. (8), it can be shown that the average of the microscopic Hamiltonian  $H(\mathbf{z})$  coincides with the expression (9a),  $\langle H(\mathbf{z}) \rangle_{\mathbf{x}} = E[\mathbf{x}]$ . In view of the form (9a) for the continuum energy functional, it is clear that all system dependent thermodynamic information relevant for the evolution equations is contained in the entropy functional  $S[\mathbf{x}]$ . We assume  $S[\mathbf{x}]$  to be given (see Sec. 6.1 in Ref. 30 for the procedure to calculate  $S$  in terms of the fields  $\mathbf{x}(\mathbf{r})$  in the setting of generalized ensembles) either exactly or by a suitable density functional approximation. For constructing the evolution equations according to the thermodynamic framework, Eq. (1), we require the functional derivatives

$$\frac{\delta E}{\delta \mathbf{x}(\mathbf{r})} = \begin{pmatrix} \mathbf{v}(\mathbf{r}) \\ -\frac{1}{2} \mathbf{v}^2(\mathbf{r}) \\ 1 \end{pmatrix}, \quad (10a)$$

$$\frac{\delta S}{\delta \mathbf{x}(\mathbf{r})} = \begin{pmatrix} \mathbf{0} \\ \frac{\delta S}{\delta \rho(\mathbf{r})} \\ \frac{\delta S}{\delta e(\mathbf{r})} \end{pmatrix}, \quad (10b)$$

where we have used  $\mathbf{v} = \mathbf{u}/\rho$ .

## C. Reversible dynamics

The Poisson matrix, which governs the reversible dynamics in Eq. (1), is usually assumed to be local,<sup>30</sup> i.e., it vanishes if  $\mathbf{r} \neq \mathbf{r}'$ . In order to highlight possible ramifications of long-range interactions also in the Poisson operator, we use here the coarse-graining relation (4) and the instantane-

ous expressions (7) for the field variables. In this way, it can be shown that the Poisson matrix is of the form

$$L(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} u_\alpha(\mathbf{r}') \frac{\partial \delta}{\partial r'_\gamma} - \frac{\partial \delta}{\partial r'_\alpha} u_\gamma(\mathbf{r}) - \frac{\partial \delta}{\partial r'_\alpha} \rho(\mathbf{r}) & L^{(u, e)}(\mathbf{r}, \mathbf{r}') \\ \rho(\mathbf{r}') \frac{\partial \delta}{\partial r'_\gamma} & 0 & 0 \\ L^{(e, u)}(\mathbf{r}, \mathbf{r}') & 0 & 0 \end{pmatrix}, \quad (11)$$

where  $\delta = \delta(\mathbf{r} - \mathbf{r}')$  is the Dirac delta function. Subscript  $\alpha$  implies contraction with a vector  $A_\alpha$  multiplied from the left, while subscript  $\gamma$  implies contraction with a vector  $A_\gamma$  multiplied from the right. In general, Einstein's summation convention is used throughout the paper for indices that occur twice, and we will only make this explicit at points where additional clarification is required. It is essential to note that all positional derivatives act only on the delta functions.

In the form (11), all elements are specified except for the upper right and the lower left. While these two elements can, in principle, also be calculated on the basis of Eq. (4) we adopt an alternative strategy.<sup>40</sup> In order to formulate the Poisson matrix, we temporarily consider the entropy density  $s$  instead of  $e$  as a variable. While the temporary change in variables from  $e$  to  $s$  is physically irrelevant, it significantly simplifies the mathematical formulation of the conditions on the Poisson operator. Assuming that the entropy density  $s$  is advected in flow as a scalar density,  $\partial_t s = -\nabla \cdot (s\mathbf{v})$ , one obtains (see Appendix for details)

$$L^{(u, e)}(\mathbf{r}, \mathbf{r}') = -\rho(\mathbf{r}) \frac{\partial}{\partial r'_\alpha} \left( \frac{\delta e[\rho, s](\mathbf{r}')}{\delta \rho(\mathbf{r})} \right) - s(\mathbf{r}) \frac{\partial}{\partial r'_\alpha} \left( \frac{\delta e[\rho, s](\mathbf{r}')}{\delta s(\mathbf{r})} \right), \quad (12a)$$

$$L^{(e, u)}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') \frac{\partial}{\partial r'_\gamma} \left( \frac{\delta e[\rho, s](\mathbf{r})}{\delta \rho(\mathbf{r}')} \right) + s(\mathbf{r}') \frac{\partial}{\partial r'_\gamma} \left( \frac{\delta e[\rho, s](\mathbf{r})}{\delta s(\mathbf{r}')} \right), \quad (12b)$$

which are nonlocal due to the occurrence of the functional derivatives of  $e$ , which must then be evaluated for given  $\rho$  and  $e$ . With the specific elements (12), it can be shown that the Poisson matrix (11) satisfies all GENERIC properties,<sup>30,32</sup> i.e., it is thermodynamically admissible. In the most general case, choices other than Eq. (12) are possible within the limits specified in the Appendix, a subject on which we will comment in Sec. V. We point out that the Poisson matrix is nonlocal when expressed for the variables  $\mathbf{x} = (\mathbf{u}, \rho, e)$ , while it is local when formulated for the variables  $\tilde{\mathbf{x}} = (\mathbf{u}, \rho, s)$ .

## D. Irreversible dynamics

In order to discuss the form of the friction matrix we use the coarse-graining scheme (5). First, the changes in  $\Pi_{x_i}(\mathbf{z}(t); \mathbf{r})$  due to the microscopic dynamics  $\dot{\mathbf{z}}(t)$  must be

calculated, leading to  $\dot{\Pi}_{x_i}(z(t);r)$ . Second, only the fast fluctuating part is needed, which is achieved by applying a projection operator  $\mathcal{Q}$  perpendicular to the slow variables, i.e.,  $\mathcal{Q}\Pi_{x_i}(z(t);r)=0$ , which leads to the fluctuations  $\dot{\Pi}_{x_i}^f(z(t);r) \equiv \mathcal{Q}\dot{\Pi}_{x_i}(z(t);r)$ .<sup>30</sup> With the definitions (7), the result of this procedure can be written in the form (see also Ref. 25)

$$\dot{\Pi}_u^f(z;r) = \frac{\partial}{\partial r} \cdot \mathcal{Q}\Pi_\sigma(z;r) \equiv \frac{\partial}{\partial r} \cdot \sigma^f(z;r), \quad (13a)$$

$$\dot{\Pi}_\rho^f(z;r) = 0, \quad (13b)$$

$$\begin{aligned} \dot{\Pi}_e^f(z;r) &= -\frac{\partial}{\partial r} \cdot \mathcal{Q}\Pi_q(z;r) + \mathcal{Q}\Pi_\sigma(z;r):\kappa(r) \\ &\equiv -\frac{\partial}{\partial r} \cdot q^f(z;r) + \sigma^f(z;r):\kappa(r), \end{aligned} \quad (13c)$$

with the transposed velocity gradient  $\kappa = (\partial v / \partial r)$ , and where we have introduced the symbols  $\sigma^f$  and  $q^f$  for the fluctuating contributions to the instantaneous stress tensor  $\Pi_\sigma$  and the instantaneous heat flux  $\Pi_q$ , respectively. The latter two are given by

$$\Pi_\sigma(z;r) = -\sum_{i=1}^N \frac{1}{m_i} \tilde{p}_i(r) \tilde{p}_i(r) \delta(r-r_i) + \frac{1}{2} \sum_{i,j} r_{ij} \frac{\partial V_{ij}}{\partial r_{ij}} \mathcal{O}_{ij}, \quad (14a)$$

$$\begin{aligned} \Pi_q(z;r) &= \sum_{i=1}^N \left( \frac{\tilde{p}_i^2(r)}{2m_i} + \frac{1}{2} \sum_j V_{ij} \right) \frac{\tilde{p}_i(r)}{m_i} \delta(r-r_i) \\ &\quad - \frac{1}{2} \sum_{i,j=1}^N r_{ij} \frac{\partial V_{ij}}{\partial r_{ij}} \cdot \frac{\tilde{p}_i(r)}{m_i} \mathcal{O}_{ij}, \end{aligned} \quad (14b)$$

with peculiar momenta  $\tilde{p}_i(r) = p_i - m_i v(r)$ , distance vectors  $r_{ij} = r_i - r_j$ , and with<sup>41,42</sup>

$$\mathcal{O}_{ij} = \sum_{k=1}^{\infty} \frac{1}{k!} \left( r_{ij} \cdot \frac{\partial}{\partial r} \right)^{k-1} \delta(r-r_i). \quad (15)$$

The microscopic expressions for the stress tensor and the heat flux (14) are in full agreement with literature.<sup>11,42,43</sup> We will comment in detail about the long-range nature of these objects in Sec. V.

As the last step in exploiting the coarse-graining expression (5), the mutual and self-correlations of the fluctuations must be discussed. Here, we assume that the quantities  $\sigma^f$  and  $q^f$  are mutually uncorrelated,<sup>44</sup> which lead to the friction matrix of the form

$$M(x)(r,r') = \begin{pmatrix} M^{u\alpha e}(r,r') & 0 & M^{u\alpha e}(r,r') \\ 0 & 0 & 0 \\ M^{e\alpha\gamma}(r,r') & 0 & M^{ee}(r,r') \end{pmatrix}, \quad (16a)$$

with the entries

$$M^{u\alpha e}(r,r') = \frac{\partial}{\partial r_\mu} \frac{\partial}{\partial r'_\nu} C_{\alpha\mu\gamma\nu}^{\sigma\sigma}(r,r'), \quad (16b)$$

$$M^{u\alpha e}(r,r') = \frac{\partial}{\partial r_\mu} \kappa_{\nu\gamma}(r') C_{\alpha\mu\gamma\nu}^{\sigma\sigma}(r,r'), \quad (16c)$$

$$M^{e\alpha\gamma}(r,r') = \kappa_{\mu\alpha}(r) \frac{\partial}{\partial r'_\nu} C_{\alpha\mu\gamma\nu}^{\sigma\sigma}(r,r'), \quad (16d)$$

$$\begin{aligned} M^{ee}(r,r') &= \kappa_{\mu\alpha}(r) \kappa_{\nu\gamma}(r') C_{\alpha\mu\gamma\nu}^{\sigma\sigma}(r,r') \\ &\quad + \frac{\partial}{\partial r_\mu} \frac{\partial}{\partial r'_\nu} C_{\mu\nu}^{qq}(r,r'), \end{aligned} \quad (16e)$$

and correlation functions

$$C_{\alpha\mu\gamma\nu}^{\sigma\sigma}(r,r') = \frac{1}{k_B} \int_0^\tau \langle \sigma_{\alpha\mu}^f(z(t);r) \sigma_{\gamma\nu}^f(z(0);r') \rangle_x dt, \quad (17a)$$

$$C_{\mu\nu}^{qq}(r,r') = \frac{1}{k_B} \int_0^\tau \langle q_\mu^f(z(t);r) q_\nu^f(z(0);r') \rangle_x dt. \quad (17b)$$

In the general case, it is to be expected that both correlation functions are finite for values of  $|r-r'|$  smaller than the range of interaction (since both fluctuating quantities contain the interaction potential). In the absence of nonlocal correlations, the correlation functions are proportional to the Dirac  $\delta$ -function, i.e., one can write them in the form

$$C_{\alpha\mu\gamma\nu}^{\sigma\sigma,\text{local}}(r,r') = \eta_{\alpha\mu\gamma\nu}(r) T(r) \delta(r-r'), \quad (18a)$$

$$C_{\mu\nu}^{qq,\text{local}}(r,r') = \lambda_{\mu\nu}^q(r) T^2(r) \delta(r-r'), \quad (18b)$$

with the temperature  $T$  as defined in detail in Sec. IV B, Eq. (23a), below. There, it is also shown that  $\eta_{\alpha\mu\gamma\nu}$  and  $\lambda_{\mu\nu}^q$  play the role of the anisotropic viscosity tensor and the heat conductivity tensor, respectively. As it can be shown in general that the coarse-grained form (5) of the friction matrix satisfies all required thermodynamic properties,<sup>30,45</sup> this is automatically the case for Eqs. (16) and (17). The nonlocal correlations (17) present an extension of an earlier, similar, coarse-graining study where the locality assumption (18) was invoked.<sup>7</sup>

## IV. EVOLUTION EQUATIONS

### A. General set

The full set of evolution equations (1) for the variable  $x$  is obtained by applying the Poisson (11) and (12) and friction matrices (16) and (17) to the functional derivatives (10). This yields

$$\begin{aligned} \frac{\partial u(r)}{\partial t} &= -\frac{\partial}{\partial r} \cdot (u(r)v(r)) - \rho(r) \frac{\partial}{\partial r} \int \frac{\delta e[\rho,s](r')}{\delta \rho(r)} d^3 r' \\ &\quad - s(r) \frac{\partial}{\partial r} \int \frac{\delta e[\rho,s](r')}{\delta s(r)} d^3 r' + \frac{\partial}{\partial r} \cdot \tau^p(r), \end{aligned} \quad (19a)$$

$$\frac{\partial \rho(r)}{\partial t} = -\frac{\partial}{\partial r} \cdot (\rho(r)v(r)), \quad (19b)$$

$$\begin{aligned} \frac{\partial e(\mathbf{r})}{\partial t} = & \int \rho(\mathbf{r}') \mathbf{v}(\mathbf{r}') \cdot \frac{\partial}{\partial \mathbf{r}'} \left( \frac{\delta e[\rho, s](\mathbf{r})}{\delta \rho(\mathbf{r}')} \right) d^3 r' \\ & + \int s(\mathbf{r}') \mathbf{v}(\mathbf{r}') \cdot \frac{\partial}{\partial \mathbf{r}'} \left( \frac{\delta e[\rho, s](\mathbf{r})}{\delta s(\mathbf{r}')} \right) d^3 r' \\ & + \boldsymbol{\kappa}(\mathbf{r}) : \boldsymbol{\tau}^\nu(\mathbf{r}) - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q}(\mathbf{r}), \end{aligned} \quad (19c)$$

with the definitions

$$\boldsymbol{\tau}^\nu(\mathbf{r}) = \int \mathbf{C}^{\sigma\alpha}(\mathbf{r}, \mathbf{r}') : \boldsymbol{\kappa}(\mathbf{r}') \frac{\delta \mathcal{S}}{\delta e(\mathbf{r}')} d^3 r', \quad (20a)$$

$$\mathbf{q}(\mathbf{r}) = \int \mathbf{C}^{qa}(\mathbf{r}, \mathbf{r}') \cdot \frac{\partial}{\partial \mathbf{r}'} \frac{\delta \mathcal{S}}{\delta e(\mathbf{r}')} d^3 r', \quad (20b)$$

where in Eq. (20b) boundary terms occurring as a result of integration by parts have been neglected. The entities  $\boldsymbol{\tau}^\nu$  and  $\mathbf{q}$  that account for all irreversible effects can be identified by inspection with the viscous stress and the heat flux, respectively, while the other terms will be discussed below. It is noteworthy that the constitutive relations (20) are nonlocal in space while at the same time they are instantaneous. This is a consequence of, first, the choice of hydrodynamic variables (6), and, second, the Markovian assumption in the GENERIC framework. Therefore, the current description is applicable to situations where spatially nonlocal effects are noticeable while temporal memory kernels can be neglected.

## B. Special case: "Athermal nonlocal" effects

To illustrate the general set of evolution equations more clearly, we split the energy density into local and nonlocal contributions,  $e_l$  and  $e_{nl}$ , respectively, with  $e = e_l + e_{nl}$ . It is understood that  $e_l$  originates from short range interactions while  $e_{nl}$  captures the long-range interactions between particles. For example, for point particles interacting by a long-range potential  $V$ , one may employ a typical mean-field approximation for the nonlocal energy density,  $e_{nl}(\mathbf{r}) = \frac{1}{2} \int \rho(\mathbf{r}') V(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') d^3 r'$ , in neglect of spatial correlations which cannot be captured by the variables in Eq. (6). A commonly studied model of this type is a one-component fluid of particles interacting via a repulsive Gaussian pair potential (a simple model for globular polymer solutions).<sup>46</sup> Conversely, it is also reasonable to split the entropy into local and nonlocal contributions. For example, for systems with strongly repulsive hard-sphere interactions the nonlocal entropy density  $s_{nl}$  may assume the approximate Rosenfeld form.<sup>47-49</sup> Using  $e_l$  instead of  $e$ , we write

$$e = e_l + e_{nl}[\rho], \quad (21a)$$

$$s = s_l(\rho, e_l) + s_{nl}[\rho], \quad (21b)$$

tacitly assuming that such local-nonlocal splitting is well defined. A similar splitting has been used in Ref. 6 for the case  $s_{nl} = 0$ , where  $s_l(\rho, e - e_{nl})$  was derived for a van der Waals fluid. In this study, the local thermodynamics described by the relation  $s_l(\rho, e_l)$  can be of the most general form. In contrast, it has been assumed in Eq. (21) that the nonlocal contributions to the energy density and the entropy density are

functionals of  $\rho$  only, i.e., they are independent of  $e_l$ . Therefore, we refer to this as the athermal nonlocal case.

In the following, we calculate the functional derivatives which occur in the general evolution equations (19). On the one hand, one can consider all terms in Eq. (21) as functionals of  $e$  and  $\rho$  and assume that one can write the local entropy density  $s_l$  as a function of the mass density  $\rho$  and the local energy density  $e_l = e - e_{nl}$ , i.e.,  $s_l(\rho, e_l)$ . The latter form can be used to introduce the following abbreviations for the partial derivatives:

$$\frac{\partial s_l[\rho, e_l](\mathbf{r})}{\partial e_l(\mathbf{r})} = \frac{1}{T(\mathbf{r})}, \quad (22a)$$

$$\frac{\partial s_l[\rho, e_l](\mathbf{r})}{\partial \rho(\mathbf{r})} = -\frac{\mu(\mathbf{r})}{T(\mathbf{r})}, \quad (22b)$$

with a local temperature  $T$  and the chemical potential  $\mu$  in accordance with the common definitions when nonlocal effects are absent. Using the chain rule for functional derivatives, one obtains

$$\frac{\delta \mathcal{S}[\rho, e]}{\delta e(\mathbf{r}')} = \frac{1}{T(\mathbf{r}')}, \quad (23a)$$

i.e., the conjugate variable of the total internal energy density with respect to the total entropy equals the conjugate variable of the local internal energy density with respect to the local entropy. Equation (23a) can be inserted into the definitions of the viscous stress and the heat flux, Eq. (20). For the spatially uncorrelated fluctuations (18), one obtains from Eq. (20) the well known anisotropic forms of Newton's law and Fourier's law of heat conduction,  $\tau_{\alpha\beta}^\nu = \eta_{\alpha\beta\mu\nu} \kappa_{\mu\nu}$  and  $q_\alpha = -\lambda_{\alpha\beta}^q (\partial T / \partial r_\beta)$ .

On the other hand, all quantities in Eq. (21) can also be written in terms of  $s$  and  $\rho$ , and, correspondingly, the local energy density  $e_l$  becomes a function of the mass density  $\rho$  and the local entropy density  $s_l = s - s_{nl}$ , i.e.,  $e_l(\rho, s_l)$ . Again using the chain rule it can be shown that

$$\frac{\delta e[\rho, s](\mathbf{r})}{\delta s(\mathbf{r}')} = T(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'), \quad (23b)$$

$$\begin{aligned} \frac{\delta e[\rho, s](\mathbf{r})}{\delta \rho(\mathbf{r}')} = & \mu(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \\ & + \left( \frac{\delta e_{nl}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}')} - T(\mathbf{r}) \frac{\delta s_{nl}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}')} \right). \end{aligned} \quad (23c)$$

It must be pointed out that by virtue of Eq. (22a), the temperature depends in general on the mass density. Therefore, the underlined term in Eq. (23c) could *only* be written as the functional derivative of a Helmholtz free energy-like quantity  $a_{nl} \equiv e_{nl} - T s_{nl}$  if  $T$  itself was chosen as the thermal variable instead of  $e$  or  $s$ . However, that choice should only be made with great care since the concept of temperature is cumbersome in beyond-equilibrium situations.<sup>50,51</sup>

We are now in the position to arrive at the main conclusion of the paper, namely, the thermodynamically admissible set of evolution equations for nonisothermal hydrodynamics with nonlocal effects for the special case of Eq. (21). Insert-

ing the functional derivatives (23) and the friction matrix (16) into the evolution equations (19), one finds

$$\frac{\partial \mathbf{u}(\mathbf{r})}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{u}(\mathbf{r})\mathbf{v}(\mathbf{r})) + \frac{\partial}{\partial \mathbf{r}} \cdot (-p(\mathbf{r})\mathbf{1} + \boldsymbol{\tau}^p(\mathbf{r})) + \rho(\mathbf{r}) \int \mathbf{f}_{\text{nl}}(\mathbf{r}, \mathbf{r}') d^3 r' - s_{\text{nl}}(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} T(\mathbf{r}), \quad (24a)$$

$$\frac{\partial \rho(\mathbf{r})}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot (\rho(\mathbf{r})\mathbf{v}(\mathbf{r})), \quad (24b)$$

$$\begin{aligned} \frac{\partial e(\mathbf{r})}{\partial t} = & -\frac{\partial}{\partial \mathbf{r}} \cdot (e_l(\mathbf{r})\mathbf{v}(\mathbf{r})) + (-p(\mathbf{r})\mathbf{1} + \boldsymbol{\tau}^p(\mathbf{r})) : \boldsymbol{\kappa}(\mathbf{r}) \\ & - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q}(\mathbf{r}) - \int \rho(\mathbf{r}') \mathbf{v}(\mathbf{r}') \cdot \mathbf{f}_{\text{nl}}(\mathbf{r}', \mathbf{r}) d^3 r' \\ & - T(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \cdot (s_{\text{nl}}(\mathbf{r})\mathbf{v}(\mathbf{r})), \end{aligned} \quad (24c)$$

with the pressure  $p$  and the body force  $\mathbf{f}_{\text{nl}}$  defined by

$$p(\mathbf{r}) = -e_l(\mathbf{r}) + \rho(\mathbf{r})\mu(\mathbf{r}) + s_l(\mathbf{r})T(\mathbf{r}), \quad (25a)$$

$$\mathbf{f}_{\text{nl}}(\mathbf{r}, \mathbf{r}') = -\frac{\partial}{\partial \mathbf{r}} \left( \frac{\delta e_{\text{nl}}[\rho](\mathbf{r}')}{\delta \rho(\mathbf{r})} - T(\mathbf{r}') \frac{\delta s_{\text{nl}}[\rho](\mathbf{r}')}{\delta \rho(\mathbf{r})} \right), \quad (25b)$$

with  $p$  defined exclusively in terms of local thermodynamic quantities.

The second to last term on the right hand side (r.h.s.) of the momentum balance (24a) is in the form of a body force, which will be discussed further below, while the last term is present exclusively in nonisothermal situations. In specific applications of these equations, it may be useful to replace the evolution equation for  $e$  (24c) by one for the local energy density  $e_l$ . In order to achieve that, one can link the evolution of the nonlocal energy  $e_{\text{nl}}$  to the one for  $\rho$ , which is then used in combination with Eq. (24c) to obtain

$$\begin{aligned} \frac{\partial e_l(\mathbf{r})}{\partial t} = & -\frac{\partial}{\partial \mathbf{r}} \cdot (e_l(\mathbf{r})\mathbf{v}(\mathbf{r})) + (-p(\mathbf{r})\mathbf{1} + \boldsymbol{\tau}^p(\mathbf{r})) : \boldsymbol{\kappa}(\mathbf{r}) \\ & - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q}(\mathbf{r}) - T(\mathbf{r}) \left[ \frac{\partial s_{\text{nl}}(\mathbf{r})}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot (s_{\text{nl}}(\mathbf{r})\mathbf{v}(\mathbf{r})) \right], \end{aligned} \quad (25c)$$

where we have neglected boundary terms that occur as a result of integration by parts with respect to  $\mathbf{r}'$ . The first three of the four contributions on the r.h.s. are of the form known to usual (local) nonisothermal hydrodynamics with the important caveat that here both the viscous stresses and the heat flux contain the nonlocal correlation functions (17). The fourth explicitly nonlocal term on the r.h.s. of Eq. (25c) is absent only if the nonlocal entropy density  $s_{\text{nl}}$  is advected as a scalar density (i.e., as the density  $\rho$  is).

## V. DISCUSSION

For describing nonlocal effects in nonisothermal hydrodynamics, we have formulated a thermodynamically admissible set of evolution equations for the densities of mass,

momentum, and internal energy. The general form of the evolution equations (19) shows that the approach taken in this paper is suitable to give a unified view on the different origins of nonlocal effects, namely, due to the generating functionals  $E$  and  $S$ , the Poisson matrix  $L$ , and the correlations of the fluctuations in the friction matrix  $M$ . While the mass balance assumes the usual form, the evolution equations for the momentum density and the internal energy density deserve special attention.

It is striking to see in Eq. (19) that the source terms in the momentum balance contain, without further ado, terms of the form  $\rho \nabla \dots$  and  $s \nabla \dots$  in the first place. Particularly, the former of the two is indicative of body forces. Only after separating local and nonlocal contributions to the generating functionals, as done in the athermal special case in Sec. IV B, the difference and similarities to known (local) hydrodynamics become clear. On the one hand, it is observed that the local contributions to  $e$  and  $s$  can be captured in the form of a pressure gradient. On the other hand, the remaining nonlocal contributions can be cast into, first, a body-force contribution, and, second, a term proportional to the temperature gradient. It has been discussed above that the energetic and entropic contributions to the body force can be summarized if the local temperature  $T$  is used (with caution) as an independent variable. Since a body force derived from a Helmholtz free energy is in agreement with earlier ansatzes in the literature, we must be clear what has been gained. First, we have rederived that result within a framework that is capable of treating nonisothermal situations, and second, the last term in the momentum balance (24a) has not been observed so far. It is there particularly in nonisothermal situations and can hardly be obtained by a straightforward generalization of an isothermal treatment. While body forces comparable to Eq. (25b) have been derived and used in the literature,<sup>3-5,8</sup> it is to the authors' knowledge the first time that such expressions are examined in the context of extended nonisothermal hydrodynamics. A famous example for the relevance of body forces is Vlasov's equation which is frequently used in plasma physics.<sup>52,53</sup> Furthermore, it has been shown earlier that nonlocal pressure terms or body forces in the momentum balance give rise to surface tension effects.<sup>7,54</sup> This study here shows clearly that the resulting surface tension has got both an energetic and an entropic contribution due to  $e_{\text{nl}}$  and  $s_{\text{nl}}$ , respectively. Although the latter two functionals are "athermal" as stated earlier, the resulting surface tension derived from Eq. (25b) attains a temperature dependence.

The approach presented in this paper is both systematic and general, which has led to a transparent formulation of the effect of nonlocal interactions. Particularly, we have clearly separated thermodynamic from kinetic effects. This procedure allows us to pinpoint the three major issues that warrant further examination in future work, as discussed in the following.

First, it has been assumed in Eq. (9b) that the entropy density does not depend on the velocity  $\mathbf{v} = \mathbf{u}/\rho$ . If the size of the volume element was significantly larger than any interaction range present in the system, and in a situation of local equilibrium, a justification of that assumption goes as follows. Since the entropy is associated with counting mi-

crostates that agree with a given macrostate, translating the entire system with a constant velocity must not change the entropy. Hence, Galilean invariance requires in this case that the entropy density does not depend on the velocity field. In contrast, the situation is more involved if there are interactions with a range larger than the size of the volume element, in which case the internal energy density  $e(\mathbf{r})$  depends on the positions of particles located in different volume elements,  $\mathbf{r}$  and  $\mathbf{r}'$ . In turn, this means that variations in the flow field from one volume element at  $\mathbf{r}$  to the next at  $\mathbf{r}'$  may affect the entropy density  $s[\rho, e](\mathbf{r})$  since not all interacting particles experience the same displacement. Thus, it seems that such effects could give rise to a dependence of the entropy density on the velocity gradient  $\nabla \mathbf{v}$  for weakly inhomogeneous flow fields, where higher order derivatives can be neglected.

Second, the advection behavior of the entropy density  $s$  can be investigated in more detail. Here, we have assumed that it is advected in flow as a scalar density,  $\partial_t s = -\nabla \cdot (s\mathbf{v})$ , i.e., the choice (A3) with  $\hat{\mathcal{Q}} = \mathbf{0}$  (see the Appendix). Other choices may be possible, although only within the bounds set by the three conditions (A4), (A7), and (A10). Specifically, we now comment on two choices for  $\hat{\mathcal{Q}}$ , which seem attractive on first sight but are found to be in contradiction with the thermodynamic principles on second sight. To begin with, we calculate the additional contribution in the momentum balance (19a) due to a nonvanishing  $\hat{\mathcal{Q}}$ ,

$$\frac{\partial \mathbf{u}(\mathbf{r})}{\partial t} \Big|_{\hat{\mathcal{Q}}} = \int \int \hat{\mathcal{Q}}(\mathbf{r}, \mathbf{r}'') \frac{\delta e[\rho, s](\mathbf{r}')}{\delta s(\mathbf{r}'')} d^3 r' d^3 r''. \quad (26a)$$

Let us discuss now the athermal nonlocal case examined in Sec. IV B, with the useful relation (23b) for the functional derivative in Eq. (26a). The special choice

$$\hat{\mathcal{Q}}(\mathbf{r}, \mathbf{r}') = \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} s_{nl}(\mathbf{r}) \quad (26b)$$

leads to a cancellation of the last term in the momentum balance (24a); however, it is not in agreement with the thermodynamic condition (A10) derived in the Appendix. Another possible choice for  $\hat{\mathcal{Q}}$  seems to be

$$\hat{\mathcal{Q}}(\mathbf{r}, \mathbf{r}') = \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} s_{nl}(\mathbf{r}) - \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \left( \frac{\delta s_{nl}[\rho](\mathbf{r}')}{\delta \rho(\mathbf{r})} \right), \quad (26c)$$

since (i) it leads to the local entropy density  $s_l$  being advected as a scalar density,  $\partial_t s_l = -\nabla \cdot (s_l \mathbf{v})$ , and (ii) it also cancels the last term in the momentum balance (24a). However, also this choice for  $\hat{\mathcal{Q}}$  is thermodynamically inadmissible since the condition (A4) of the Appendix is not fulfilled. The discussion of these two seemingly obvious alternatives to  $\hat{\mathcal{Q}} = \mathbf{0}$  (i) shows that the local entropy density is not advected as a scalar density, in contrast to the usual local hydrodynamic theory, and (ii) substantiates the unusual momentum source term  $-s_{nl} \nabla T$  in Eq. (24a). However, further systematic analysis of the conditions (A4), (A7), and (A10) must be undertaken.

Third, the irreversible terms in the evolution equations (19) are explicitly nonlocal due to the correlation functions in the friction matrix (16). There is also an implicit depen-

dence on long-range interaction effects through the entropy functional. However, for the special case treated in Sec. IV B, only the local temperature enters into the expressions for the stress tensor and heat flux defined in Eq. (20). As a matter of fact, it is more interesting to discuss the correlation functions, particularly the stress-stress correlations  $\mathbf{C}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ . Nonlocal relations between the viscous stress and the deformation rate, as obtained above, have also been used by others.<sup>8-11,13</sup> However, a critical and more deep discussion is needed at this place. The fact that  $\mathbf{C}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$  is not automatically vanishing for  $\mathbf{r} \neq \mathbf{r}'$  goes back to the occurrence of the long-range interactions and the nonlocal quantity  $\mathcal{O}_{ij}$  (15) in the microscopic expression for the stress tensor (14), which in turn affects the friction matrix (16). The effect of  $\mathcal{O}_{ij}$  is to distribute the interaction contributions in Eq. (14) on the connector line between the interacting particles. The above writing (13) of the fluctuations has artificially written all contributions in terms of the divergence of a stress tensor. However, this is not necessarily useful as the following discussion shows. The definition of the stress tensor is based on the concept of continuum mechanics, the latter resolving phenomena down to some characteristic length scale denoted by  $\ell$ . If all interactions had a range significantly less than  $\ell$ ,  $\mathcal{O}_{ij}$  could be approximated by its first term in Eq. (15). Particle separations that satisfy  $|\mathbf{r}_i - \mathbf{r}_j| \geq \ell$  contribute only if the range of the interaction potential is significantly larger than  $\ell$ .<sup>55</sup> However, in that case, particles located in different volume elements  $d^3 r$  interact with each other, which has the following important ramifications. In the momentum balance, such interactions are naturally interpreted (and written in the form of) body forces. For pairwise interaction  $V$  between particles, the corresponding contributions to the r.h.s. of the momentum balance (13a), before projection with  $\mathcal{Q}$ , can be written in the two forms

$$\frac{\partial}{\partial \mathbf{r}} \cdot [\Pi_{\sigma}]_V(\mathbf{z}; \mathbf{r}) = -\Pi_n(\mathbf{z}; \mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \int V(\mathbf{r} - \mathbf{r}') \Pi_n(\mathbf{z}; \mathbf{r}') d^3 r', \quad (27a)$$

where  $\Pi_n(\mathbf{z}; \mathbf{r}) = \sum \delta(\mathbf{r} - \mathbf{r}_i)$  denotes the number density of particles, with  $\Pi_n = \Pi_p/m$  if all particles have the same mass  $m$ . If the interaction potentials are short range, the r.h.s. of Eq. (27a) is ill defined as it contains products of delta functions. In this case the form (14) with keeping only the first term on the r.h.s. of Eq. (15) is more appropriate to represent the interactions. On the other hand, for long-range interactions, the right side in Eq. (27a) is to be preferred. In this case, the integral smears out one of the two distribution functions. Clearly, the integral takes the meaning of a mean-field potential built by the particles in the vicinity of  $\mathbf{r}$ . So, in summary, the interaction effects in the evolution equation for the momentum density take two different forms depending on whether the interaction is either long-range or short-range. As a consequence, there is in principle a contribution of the mean-field type in the momentum balance. Since the long-range interaction smooths the number density in the integral, it is reasonable to assume, as a first approximation, that the application of the projection  $\mathcal{Q}$  acts only on the other number density, leading to the modification of Eq. (13a),

$$\begin{aligned} \dot{\Pi}_n^f(\mathbf{z};\mathbf{r}) &= \frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\sigma}_{\text{short}}^f(\mathbf{z};\mathbf{r}) \\ &- [\mathcal{Q}\Pi_n(\mathbf{z};\mathbf{r})] \frac{\partial}{\partial \mathbf{r}} \int V(|\mathbf{r}-\mathbf{r}'|)_{\text{long}} \Pi_n(\mathbf{z};\mathbf{r}') d^3 r', \end{aligned} \quad (27b)$$

and a corresponding modification in  $\dot{\Pi}_e^f(\mathbf{z};\mathbf{r})$  in order to ensure conservation of energy. However, if all particles contained in the mass density  $\rho$  have the same mass  $m$ , then one can write  $\mathcal{Q}\Pi_n = m^{-1}\mathcal{Q}\Pi_\rho = 0$ , with the effect that the long-range interactions do not contribute to the fluctuations. In the light of this discussion, it is thus a reasonable scenario to neglect the additional mean-field contribution in Eq. (27b), which is the route followed in this manuscript, in accordance with earlier studies.<sup>7</sup> However, if fluctuations in the mean-field potential are considered relevant and/or in the presence of different particle masses, certain contributions in the friction matrix may be written more usefully by splitting the momentum fluctuations into local and nonlocal (body force-like) terms.

Microscopic simulations in this field are without any doubt of highest relevance, particularly for executing the above scheme to link the particle-based level with the continuum description. For the sake of presenting the theory in a clean form, simulation results have not been included in the present study. However, given the various microscopic expressions for the continuum mechanics building blocks above, one can anticipate the substantial benefit of future nonequilibrium molecular dynamics simulations.

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## APPENDIX: POISSON OPERATOR

In this Appendix, we elaborate on the conditions on and the construction of the entries  $L^{(u,\alpha^e)}(\mathbf{r},\mathbf{r}')$  and  $L^{(e,u,\gamma)}(\mathbf{r},\mathbf{r}')$  in the Poisson operator (11). To that end, we first consider the set of variables  $\bar{\mathbf{x}} = (\mathbf{u}, \rho, \theta)$  with  $\theta$  as a thermal variable. For that set of variables, the upper-left  $2 \times 2$ -subblock of the Poisson operator (11) is still valid. Furthermore, the  $\theta$ -row and column are of the form as indicated in Eq. (11), and so one can concentrate on formulating the elements  $\tilde{L}^{(u,\alpha^e)}(\mathbf{r},\mathbf{r}')$  and  $\tilde{L}^{(e,u,\gamma)}(\mathbf{r},\mathbf{r}')$ . Once they are determined, a transformation of variables from  $\bar{\mathbf{x}}$  to  $\mathbf{x}$  as defined in Eq. (6) can be used to obtain the corresponding Poisson operator for the set of variable  $\mathbf{x}$ . Specifically, with the transformation “matrix”

$$\frac{\delta \mathbf{x}(\mathbf{r})}{\delta \bar{\mathbf{x}}(\mathbf{r}')} = \begin{pmatrix} \delta(\mathbf{r}-\mathbf{r}')\mathbf{1} & 0 & 0 \\ 0 & \delta(\mathbf{r}-\mathbf{r}') & 0 \\ 0 & \frac{\delta e(\mathbf{r})}{\delta \rho(\mathbf{r}')} & \frac{\delta e(\mathbf{r})}{\delta \theta(\mathbf{r}')} \end{pmatrix}, \quad (A1)$$

the Poisson operator for the variable  $\mathbf{x}$  is given by

$$L(\mathbf{r},\mathbf{r}') = \int \int \frac{\delta \mathbf{x}(\mathbf{r})}{\delta \bar{\mathbf{x}}(\mathbf{r}'')} \cdot \tilde{L}(\mathbf{r}'',\mathbf{r}''') \cdot \left( \frac{\delta \mathbf{x}(\mathbf{r}')}{\delta \bar{\mathbf{x}}(\mathbf{r}''')} \right)^T d^3 r'' d^3 r''' \quad (A2)$$

with contraction with  $\bar{\mathbf{x}}$  in the denominator. Hence, in order to construct the remaining entries  $L^{(u,\alpha^e)}(\mathbf{r},\mathbf{r}')$  and  $L^{(e,u,\gamma)}(\mathbf{r},\mathbf{r}')$  in the Poisson operator (11) one can choose a most convenient variable  $\theta$  for the determination of  $\tilde{L}$  and thereafter make the transformation to  $L$ .

To execute that procedure, we choose for  $\theta$  the entropy density  $s$ . In accordance with the above arguments, the Poisson operator is written in the form

$$\tilde{L}(\mathbf{r},\mathbf{r}') = \begin{pmatrix} u_\alpha(\mathbf{r}') \frac{\partial \delta}{\partial r'_\gamma} - \frac{\partial \delta}{\partial r'_\alpha} u_\gamma(\mathbf{r}') & -\frac{\partial \delta}{\partial r'_\alpha} \rho(\mathbf{r}') & \mathcal{Q}_\alpha(\mathbf{r},\mathbf{r}') \\ \rho(\mathbf{r}') \frac{\partial \delta}{\partial r'_\gamma} & 0 & 0 \\ -\mathcal{Q}_\gamma(\mathbf{r}',\mathbf{r}) & 0 & 0 \end{pmatrix}, \quad (A3a)$$

with the only assumption that the yet undetermined function  $\mathcal{Q}$  does not depend on the momentum density  $\mathbf{u}$ . In order to simplify the further discussion, we write  $\mathcal{Q}$  in the form

$$\mathcal{Q}_\alpha(\mathbf{r},\mathbf{r}') = -\frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial r'_\alpha} s(\mathbf{r}) + \hat{\mathcal{Q}}_\alpha(\mathbf{r},\mathbf{r}'). \quad (A3b)$$

While  $\tilde{L}(\mathbf{r},\mathbf{r}')$  is antisymmetric by construction, we derive the following three conditions on the function  $\hat{\mathcal{Q}}$ .

**Condition 1:** Degeneracy condition (2a). With the above choice of variables, one obtains  $\delta S / \delta \bar{\mathbf{x}} = (\mathbf{0}, 0, 1)$ , and in turn the degeneracy condition (2a) becomes

$$\int \hat{\mathcal{Q}}_\alpha(\mathbf{r},\mathbf{r}') d^3 r' = 0. \quad (A4)$$

**Condition 2:** Jacobi identity. Based on the Poisson operator  $\tilde{L}$ , a Poisson bracket can be defined as

$$\{A,B\} = \int \int \sum_{ij} \frac{\delta A}{\delta \bar{x}_i(\mathbf{r})} \tilde{L}_{ij}(\mathbf{r},\mathbf{r}') \frac{\delta B}{\delta \bar{x}_j(\mathbf{r}')} d^3 r d^3 r', \quad (A5)$$

with  $A$  and  $B$  as two arbitrary real-valued functionals of  $\bar{\mathbf{x}}$ . For the so-defined Poisson bracket, the Jacobi identity is written as

$$\{A,\{B,C\}\} + \{B,\{C,A\}\} + \{C,\{A,B\}\} = 0 \quad (A6)$$

and expresses the time-structure invariance of the reversible dynamics (see Ref. 30 for details). If applied to the system of interest here, the Jacobi identity imposes a condition on the function  $\hat{\mathcal{Q}}$ . Particularly, one finds after lengthy calculations that the condition

$$\sum_{i=1}^5 (J_{A,B,C}^{(i)} + J_{B,C,A}^{(i)} + J_{C,A,B}^{(i)}) = 0, \quad (A7a)$$

with the definitions

$$J_{A,B,C}^{(1)} = - \int \hat{Q}_\alpha(\mathbf{q}, \mathbf{q}') A_{u_\alpha(\mathbf{q})} \left[ B_{u_\gamma(\mathbf{q}')} \frac{\partial C_{s(\mathbf{q}')}}{\partial q'_\gamma} - \frac{\partial B_{s(\mathbf{q}')}}{\partial q'_\gamma} C_{u_\gamma(\mathbf{q}')} \right] d^3 q d^3 q', \quad (\text{A7b})$$

$$J_{A,B,C}^{(2)} = - \int \hat{Q}_\alpha(\mathbf{q}, \mathbf{q}') A_{s(\mathbf{q}')} \left[ \frac{\partial B_{u_\alpha(\mathbf{q})}}{\partial q_\gamma} C_{u_\gamma(\mathbf{q}')} - \frac{\partial C_{u_\alpha(\mathbf{q})}}{\partial q_\gamma} B_{u_\gamma(\mathbf{q}')} \right] d^3 q d^3 q', \quad (\text{A7c})$$

$$J_{A,B,C}^{(3)} = - \int \rho(\mathbf{r}) A_{u_\alpha(\mathbf{r})} [B_{u_\gamma(\mathbf{q})} C_{s(\mathbf{q}')} - B_{s(\mathbf{q}')} C_{u_\gamma(\mathbf{q})}] \frac{\partial}{\partial r_\alpha} \left[ \frac{\delta \hat{Q}_\gamma(\mathbf{q}, \mathbf{q}')}{\delta \rho(\mathbf{r})} \right] d^3 q d^3 q' d^3 r, \quad (\text{A7d})$$

$$J_{A,B,C}^{(4)} = - \int s(\mathbf{r}) A_{u_\alpha(\mathbf{r})} [B_{u_\gamma(\mathbf{q})} C_{s(\mathbf{q}')} - B_{s(\mathbf{q}')} C_{u_\gamma(\mathbf{q})}] \frac{\partial}{\partial r_\alpha} \left[ \frac{\delta \hat{Q}_\gamma(\mathbf{q}, \mathbf{q}')}{\delta s(\mathbf{r})} \right] d^3 q d^3 q' d^3 r, \quad (\text{A7e})$$

$$J_{A,B,C}^{(5)} = \int \hat{Q}_\alpha(\mathbf{q}, \mathbf{q}') \frac{\delta \hat{Q}_\gamma(\mathbf{r}, \mathbf{r}')}{\delta s(\mathbf{q}')} A_{u_\alpha(\mathbf{q})} [B_{u_\gamma(\mathbf{r})} C_{s(\mathbf{r}')} - B_{s(\mathbf{r}')} C_{u_\gamma(\mathbf{r})}] d^3 q d^3 q' d^3 r d^3 r', \quad (\text{A7f})$$

with  $A$ ,  $B$ , and  $C$  arbitrary real-valued functionals of  $\vec{x}$ , is equivalent to the Jacobi identity. To simplify the notation, we have abbreviated the functional derivatives, e.g.,  $A_{u_\alpha(\mathbf{q})} = \delta A / \delta u_\alpha(\mathbf{q})$ .

**Condition 3:** Conservation of total momentum. Since GENERIC deals with closed systems, the total momentum

$$U = \int \mathbf{u}(\mathbf{r}) d^3 r, \quad (\text{A8})$$

must be conserved. With the Poisson operator (A3), one obtains, after neglecting boundary terms,

$$\begin{aligned} \frac{dU_\alpha}{dt} &= \int \frac{\partial u_\alpha(\mathbf{r})}{\partial t} d^3 r \\ &= \int \left( \frac{\partial u_\gamma(\mathbf{r})}{\partial r_\alpha} \frac{\delta E}{\delta u_\gamma(\mathbf{r})} + \frac{\partial \rho(\mathbf{r})}{\partial r_\alpha} \frac{\delta E}{\delta \rho(\mathbf{r})} + \frac{\partial s(\mathbf{r})}{\partial r_\alpha} \frac{\delta E}{\delta s(\mathbf{r})} \right) d^3 r + \int \int \hat{Q}_\alpha(\mathbf{r}, \mathbf{r}') \frac{\delta E}{\delta s(\mathbf{r}')} d^3 r d^3 r'. \end{aligned} \quad (\text{A9})$$

On the other hand, it is a central conclusion in physics that the translation invariance of the total energy is the only requirement needed to ensure the momentum conservation of a (reversible) system. It can be shown that the translation invariance of the energy  $E$  requires that the first of the two

terms on the r.h.s. of Eq. (A9) vanishes identically. Therefore, the conservation of the total momentum of the system is equivalent to the condition

$$\int \int \hat{Q}_\alpha(\mathbf{r}, \mathbf{r}') \frac{\delta E}{\delta s(\mathbf{r}')} d^3 r d^3 r' = 0. \quad (\text{A10})$$

In the main part of the manuscript, we make the choice  $\hat{Q} = \mathbf{0}$ , which is manifestly in accordance with all three conditions (A4), (A7), and (A10). With this choice, the transformation of  $\tilde{L}$  according to Eq. (A2) leads to the Poisson operator (11) with Eq. (12). Furthermore, the choice of  $\hat{Q} = \mathbf{0}$  is equivalent to requiring that the entropy density is advected as a scalar density, since

$$\frac{\partial s(\mathbf{r})}{\partial t} = - \int Q_\gamma(\mathbf{r}', \mathbf{r}) \frac{\delta E}{\delta u_\gamma(\mathbf{r}')} d^3 r' = - \frac{\partial}{\partial \mathbf{r}} \cdot (s(\mathbf{r}) \mathbf{v}(\mathbf{r})), \quad (\text{A11})$$

where we have used  $\delta E / \delta u_\gamma = v_\gamma$ . However, for completeness, we point out that other choices for  $\hat{Q}$  may be possible if they are in agreement with the three conditions (A4), (A7), and (A10).

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