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Generalized energy-conserving dissipative particle dynamics revisited: Insight from the thermodynamics of the mesoparticle leading to an alternative heat flow model

Josep Bonet Avalos,[1,*] Martin Lísal,[2,3,†] James P. Larentzos,[4,‡] Allan D. Mackie,[1,§] and John K. Brennan[4,¶]
[1]*Department d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Tarragona 43007, Spain*
[2]*Department of Molecular and Mesoscopic Modelling, The Czech Academy of Sciences,*
Institute of Chemical Process Fundamentals, Prague 165 01, Czech Republic
[3]*Department of Physics, Faculty of Science, J. E. Purkinje University, Ústí n. Lab. 400 96, Czech Republic*
[4]*Weapons and Materials Research Directorate, U.S. Army CCDC Army Research Laboratory, Aberdeen Proving Ground,*
Maryland 21005, USA

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Recently we introduced the generalized energy-conserving dissipative particle dynamics method (GenDPDE) [J. Bonet Avalos, M. Lísal, J. P. Larentzos, A. D. Mackie, and J. K. Brennan, Phys. Chem. Chem. Phys. **21**, 24891 (2019)], which has been formulated for an emerging class of density- and temperature-dependent coarse-grain models. In the original work, GenDPDE was formulated to ensure a fundamental link is maintained with the underlying physical system at the higher resolution scale. In this paper, we revisit the formulation of the GenDPDE method, and rederive the particle thermodynamics to ensure consistency at the opposing scale extreme, i.e., between the local thermodynamics in the mesoscopic systems and the corresponding macroscopic properties. We demonstrate this consistency by introducing unambiguous, physically meaningful definitions of the heat and work, which lead to the formulation of an alternative heat flow model that is analogous to Fourier's law of heat conduction. We present further analysis of the internal, unresolved degrees-of-freedom of the mesoparticles by considering the thermodynamics of an individual mesoparticle within the GenDPDE framework. Several key outcomes of the analysis include: (i) demonstration that the choice of the independent variables alters the particle thermodynamic description; (ii) demonstration that the mesoscopic thermodynamic transformations introduce additional terms of the order of the size of the local fluctuations, which prevent an unambiguous definition of both the heat and work; (iii) an emphasis on the importance of the choice of the proper estimators of the thermodynamic properties that are embedded in the chosen thermodynamic description; and (iv) a clearly defined path for determining any thermodynamic quantity dressed by the fluctuations. The further insight provided by this deeper analysis is useful for both readers interested in the GenDPDE theoretical framework, as well as readers interested in the practical ramifications of the analysis, namely, the alternative heat flow model.

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I. INTRODUCTION

The recently proposed generalized energy-conserving dissipative particle dynamics (GenDPDE) method [1] allows for isoenergetic simulations of many-body models, which are an appealing class of density- and temperature-dependent coarse-grain models that have recently emerged (e.g., Refs. [2–7]). These models have several key attributes that allow them to overcome common coarse-grain model deficiencies, including scaling consistency and transferability. In the GenDPDE method, the force between mesoparticles is a function of the local particle density n [8,9]. GenDPDE allows simulations of coarse-grain models for which the density-dependent force is dependent on the thermodynamic state of the mesoparticle, particularly, the *fluctuating* particle temperature θ. From that perspective, GenDPDE is unique because it allows a description of the particle temperature and the local particle density such that they are entangled in the coarse-grain model through a complete definition of what we refer to as the *particle thermodynamics*. For comparison, it is worth noting that in the energy-conserving dissipative particle dynamics (DPDE) method [10,11], such particle thermodynamics is restricted to a linear relation between the stored internal energy u and the particle temperature θ. Moreover, the force between DPDE particles is a function of the inter-particle distance only; thus, the force is independent of the mesoparticle thermodynamic state.

In the introductory work [1], GenDPDE was formulated to ensure a fundamental link is maintained with the underlying physical system at the higher resolution scale. However, a direct link to the macroscale was not established, partly due to the following. In the GenDPDE method, particles are considered as mesoscopic objects, *a priori* containing many degrees-of-freedom (DoF), which are defined through the particle thermodynamics. However, by construction, the variables defining the particle state are fluctuating due to the mesoscopic size of the particles. As such, defining the local

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[*] josep.bonet@urv.cat
[†] lisal@icpf.cas.cz
[‡] james.p.larentzos.civ@mail.mil
[§] allan.mackie@urv.cat
[¶] john.k.brennan.civ@mail.mil

thermodynamics in mesoscopic systems poses several challenges related to the influence of system fluctuations on the interpretation of the analogous macroscopic properties. In this work, we consider the appropriate framework that consistently describes the mesoparticle with internal (unresolved) DoF in contact with the environment. Interestingly, we encounter uncertainty in the distinction between *heat* and *work* at the mesoparticle level, which does not exist at the thermodynamic limit.

In this paper, we revisit the formulation of the GenDPDE method, and rederive the mesoparticle thermodynamic transformations to ensure consistency at the macroscale, i.e., between the local thermodynamics in the mesoscopic systems and the corresponding macroscopic properties. We demonstrate that we can establish this link by introducing unambiguous, physically meaningful definitions of the heat and work. These lead to the formulation of an alternative heat flow model that is a mesoscopic counterpart of Fourier's law of heat conduction, and that differs from the heat flow model traditionally used in DPDE. This insight is useful for both readers interested in the theoretical framework, as well as readers interested in the practical ramifications of the analysis, particularly the alternative heat flow model.

While the formulation emulates that of the original work [1], a deeper analysis of the thermodynamics of the individual mesoparticle provides new insight into the mesoscopic thermodynamic transformations. In this work, we define *particle thermodynamics* as the formal relation describing the energy exchange between the unresolved DoF within the particle and the resolved DoF, where we assume a separation of timescales exists between these DoF [12]. The latter DoF include the particle volume, internal energy, center-of-mass position and total momentum for the simple case analyzed here. Unlike their macroscopic counterparts, these resolved variables can fluctuate according to the Laws of Statistical Mechanics due to the reduced size of the particle as a system. *Macroscopic thermodynamics* relies on the thermodynamic potentials and the transformations between ensembles, which are defined from the given reservoirs that maintain constant intensive variables (e.g., the temperature or chemical potentials) or maintain constraints that fix some extensive variables (e.g., volume or energy content). These variables will be referred to as *control parameters*. Legendre transformations permit changing from one ensemble to the other without loss of thermodynamic information. Contrastingly, for particle thermodynamics, the thermodynamic information is not embedded in a function under the form of a given thermodynamic potential, but instead in a distribution. Not only does the thermodynamic ensemble need to be specified, but also those variables that independently fluctuate and those that do not. Therefore, when changing from one set of independent variables to another within the same macroscopic ensemble, transformation rules need to be considered that involve additional terms depending on the size of the fluctuations.[1]

The formulation of a particle thermodynamic description also affects the dynamic properties of the system through the relationship between the thermodynamic forces and the dissipative fluxes. In the model presented here, the former are differences in the velocities and in the particle temperatures, which are fluctuating variables, while the latter correspond to the frictional forces and the interparticle heat exchange, respectively. In this formulation, the dynamics of the particle variables are required to satisfy the principles of nonequilibrium thermodynamics [15] when fluctuations are absent. In other words, the fluctuations in these mesoscopic systems are constructed such that the nonequilibrium thermodynamic description instantaneously holds at the particle level with the particle properties derived from $s(u, \mathcal{V})$ or $u(s, \mathcal{V})$ together with the dynamics of the resolved DoF.

In this work, we introduce a set of ansatzes that allow us to cast the dynamic formulation under Onsager's nonequilibrium thermodynamics framework [15] at the particle level, taking into account the *dressing* effect of the fluctuations. In this context, linear Langevin equations [16,17] can be introduced, based on the appropriate thermodynamic forces, leading to an ultimately complete and consistent framework for the simulation of complex systems.

The paper is organized as the following. In Sec. II, we revisit the theoretical framework of the GenDPDE method, providing an analysis into both the particle thermodynamics and dynamics in the context of the unresolved DoF of the individual mesoparticle, after which the equations of motion (EoM) are given in Sec. II C. In Sec. III A, we demonstrate the consistency of the alternative heat flow model, followed by a discussion of the implications of the analysis of the particle thermodynamics within the GenDPDE framework. We conclude by providing a summary of the work along with a brief discussion of possible novel extensions arising from the new insight of the mesoparticle thermodynamic transformations within the GenDPDE framework. A list of symbols and notation used throughout the manuscript is provided in the Supplemental Material [18].

II. THEORETICAL FRAMEWORK: FURTHER ANALYSIS FROM THE PARTICLE THERMODYNAMICS

In this section, we provide a formulation of the GenDPDE method that follows the formulation presented in the original work [1]. However, a deeper analysis of the thermodynamics of the unresolved DoF of an individual mesoparticle reveals insight that allows us to link the particle thermodynamics with the corresponding macroscopic properties. In Sec. II A, the theoretical framework of the thermodynamics is formulated by first considering the particle entropy as the dependent variable, followed by a formulation using the particle internal energy as the dependent variable. The analysis of the latter highlights that the mesoscopic thermodynamic transformations introduce additional terms of the order of the size of

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[1] Interestingly, in agreement with our description, a similar dependence on the set of independent variables has been experimentally observed for DNA strands operated with optical traps [13,14]. These authors observed that the relationship between force $\bar{F}$ and elongation x of an externally stretched DNA strand depends on whether the force is fixed and the elongation measured, or inversely, whether the elongation is fixed and the force measured. In other words, given $\langle \bar{F} \rangle = f(x)$, it is found that $\langle x \rangle \neq f^{-1}(\bar{F})$.

the local fluctuations, which prevent an unambiguous definition of both the mesoscopic heat and work. To overcome this ambiguity within the GenDPDE framework, in Sec. II B, we formulate the particle dynamics by assuming a heat flow model that has a linear relation between the fluxes and the forces, where this particular form is consistent with Fourier's law of heat conduction. Finally, to conclude Sec. II, a summary of the EoM is given at the end of Sec. II C, which is intended for more application-oriented readers with less interest in the formulation of the GenDPDE theoretical framework. The numerical discretization of the EoM is presented in Appendix B.

A. Thermodynamics of the mesoparticle unresolved degrees-of-freedom

1. Entropic thermodynamic description

The GenDPDE method was based upon the original DPDE method, which itself is based on Einstein's formulation of thermodynamic fluctuations that is an entropy-centered perspective [10,19]. Following the formulation of the entropic form presented in the original GenDPDE work [1], we define the physical model by assuming that each particle i ($i = 1, \ldots, N$; N is the number of particles) is an individual mesoscopic system composed of $\mathcal{N}$ physical entities. The mesoscopic system is characterized by a Hamiltonian $\mathcal{H}(\tilde{\mathbf{r}}^{\mathcal{N}}, \tilde{\mathbf{p}}^{\mathcal{N}})$ with $(\tilde{\mathbf{r}}^{\mathcal{N}}, \tilde{\mathbf{p}}^{\mathcal{N}})$ being a point in the $6\mathcal{N}$-dimensional internal phase space of mesoparticle i. (In this section, the statements refer to the properties related to an individual mesoparticle i; for notational simplicity, the subscript i is not explicitly used unless necessary to avoid confusion.) The vectors $\tilde{\mathbf{r}}^{\alpha}$ and $\tilde{\mathbf{p}}^{\alpha}$ with $\alpha = 1, \ldots, \mathcal{N}$ are, respectively, the positions and momenta (both refer to the center-of-mass of the mesoparticle) of the underlying physical entities embedded into mesoparticle i. For our purposes, let us consider that the resolved mesoparticle variables are the particle internal energy content u_i, the material content $\mathcal{N}_i$, and the particle volume $\mathcal{V}_i$, together with the position of its center-of-mass $\mathbf{r}_i$ and its total momentum $\mathbf{p}_i$.

u_i is specifically defined as the particle internal energy, i.e., the energy stored in the unresolved DoF. Hence, u_i is obtained by subtracting from the total energy of the mesoparticle: (a) the energy due to the *mechanical* DoF, i.e., the kinetic energy $\mathcal{K}_i = \mathbf{p}_i^2/(2m_i)$; and (b) any potential energy field Ψ related to the particle positions $\{\mathbf{r}_i\}_{i=1}^N$ (e.g., gravitational or electromagnetic fields) or any interparticle interactions *not* associated with changes in the particle volume and particle temperature.

The *volume* of a mesoparticle is defined as $\mathcal{V} = 1/n$, where n is the local particle density, estimated from the positions of neighboring mesoparticles via a weighting function w as

$$n_i = \sum_{j=1, j\neq i}^{N} w_{ij}, \tag{1}$$

where $w_{ij} \equiv w(r_{ij})$ is a smooth, monotonically decreasing, nonnegative, spherically symmetric weighting function, vanishing for the particle separation distance $r_{ij} \geqslant R_{\text{cut}}$, and normalised such that $4\pi \int_0^{R_{\text{cut}}} w(r)\, r^2\, dr = 1$; R_{cut} is the cutoff range.

Owing to the relatively small size of the mesoparticle, contributions due to the interfacial area, particle rotations, or deformations may be considered when addressing particular physical systems. Here, for simplicity, we consider that any contribution can be reduced to a function of the particle volume. Although, for example, surface contributions may eventually lead to the nonextensiveness of the particle thermodynamic functions. Also, for the sake of simplicity, we consider only the case of constant $\mathcal{N}$.

Let us consider mesoparticles at rest, i.e., $\{\mathbf{p}_i\}_{i=1}^N = 0$, and all the positions $\{\mathbf{r}_i\}_{i=1}^N$ fixed in space. In equilibrium, the density-of-states of a thermally isolated mesoparticle at rest is given by

$$g(u, \mathcal{V}) = \frac{1}{\mathcal{N}!\, h^{3\mathcal{N}}} \int_{u-\Delta u/2<u<u+\Delta u/2;\mathcal{V}} d\tilde{\mathbf{r}}^{\mathcal{N}} d\tilde{\mathbf{p}}^{\mathcal{N}}, \tag{2}$$

where, from a thermodynamic perspective, Eq. (2) contains all the relevant information. In particular, we can define the *bare* entropy [20] as

$$\tilde{s}(u, \mathcal{V}) = k_B \ln g(u, \mathcal{V}), \tag{3}$$

where k_B is the Boltzmann constant. As such, $\tilde{s}$ is the true entropy of the mesoparticle under *isolated* conditions, which is defined by fixing the control parameters u and $\mathcal{V}$. Due to our assumption that there are no additional resolved variables other than $\mathcal{V}$ and u, $\tilde{s}$ can be defined in a thermodynamic sense only if the internal dynamic processes associated with the $\mathcal{N}$ physical entities in the mesoparticle are relaxed to their thermodynamic equilibrium. Therefore, for an isolated mesoscopic system, no fluctuations are observed in the nonmechanical resolved variables. Finally, because $\tilde{s}$ has the classical meaning of entropy, we can assume that $\partial\tilde{s}/\partial u|_{\mathcal{V}} = 1/\tilde{\theta} > 0$, i.e., the positiveness of the bare temperature $\tilde{\theta}$ of the mesoscopic system is assumed.

Note that we have changed the nomenclature from our original work [1] with respect to $\tilde{s}$, where $\tilde{s}$ here is denoted as the bare entropy rather than the dressed entropy. The reader is referred to both footnote[2] for further discussion of this

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[2] In our previous work [1], we introduced z as the dressed entropy and s as the bare entropy. For the work presented in this manuscript, we have inverted the nomenclature regarding all corresponding dressed and bare quantities. Note that the physical expression for these quantities do not change, rather only a nomenclature change has been introduced. The switch in nomenclature is based on the following. In our previous work [1], we began our formulation by postulating s as a central quantity, from which we obtained z. However, in the revision of the formulation presented here, we first established a direct connection between z and the statistical mechanics of the system. From this connection, physical intuition suggests z as a bare quantity, while dressed quantities are those that are 'dressed' by the fluctuations of the mesoscopic system. As such, the natural variables of the mesoparticles are the dressed quantities, where all variables denoted by the bare and dressed nomenclature have been inverted from the original work [1]. Further, in an attempt to simplify the notation, we have also changed the bare entropy notation from z to $\tilde{s}$, and the bare particle temperature notation from τ to $\tilde{\theta}$. In summary, in this manuscript and hereafter, we will denote quantities with a *tilde* as a bare quantity, otherwise it will be taken as a dressed quantity.

nomenclature change and the list of symbols provided in the Supplemental Material [18].

When the mesoscopic system is in contact with a heat reservoir of temperature T, the thermodynamic behavior is determined by the ensemble average yielding the Helmholtz free energy, i.e.,

$$e^{-F/(k_BT)} = \int du\, g(u,\mathcal{V})\, e^{-u/(k_BT)}, \tag{4}$$

where the control parameters of the ensemble are T and $\mathcal{V}$. Analogous to Eq. (3), Eq. (4) contains all the relevant information, where given the state of the mesoparticle, the canonical probability distribution becomes

$$\begin{aligned} P_{eq}(u,\mathcal{V})\, du\, d\mathcal{V} &\sim g(u,\mathcal{V}) e^{-u/(k_BT)}\, du\, d\mathcal{V} \\ &= e^{[T\tilde{s}(u,\mathcal{V})-u]/(k_BT)} du\, d\mathcal{V}. \end{aligned} \tag{5}$$

Equation (5) is the starting point in the classical treatment of fluctuations [19]. Indeed, the formulation of the DPDE method is based on Eq. (5). In this classical treatment, the removal of the adiabatic condition for the mesoscopic particle causes fluctuations in the resolved variables, weighted by the function $\tilde{s}$, which is no longer a measure of the entropy of the system. Because the independent variables of Eq. (5) are u and $\mathcal{V}$, then without loss of generality, we have

$$d\tilde{s} = \left.\frac{\partial\tilde{s}}{\partial u}\right|_{\mathcal{V}} du + \left.\frac{\partial\tilde{s}}{\partial\mathcal{V}}\right|_{u} d\mathcal{V} \equiv \frac{1}{\tilde{\theta}} du + \frac{\tilde{\pi}}{\tilde{\theta}} d\mathcal{V}. \tag{6}$$

The variables $1/\tilde{\theta}$ and $\tilde{\pi}/\tilde{\theta}$ ($\tilde{\pi}$ is the bare particle pressure) are defined via Eq. (6). These are analogous to the intensive variables in macroscopic thermodynamics, which are the natural variables for the entropic thermodynamic description [19]. However, in the fluctuating system, these variables play the role of *estimators* of the macroscopic quantities of the ensemble. For example, in the canonical ensemble, $1/\tilde{\theta}$ is the *proper estimator* of $1/T$, i.e.,

$$\left\langle \frac{1}{\tilde{\theta}} \right\rangle_T = \int du\, \frac{1}{\tilde{\theta}}\, P_{\mathrm{eq}}(u,\mathcal{V}) = \frac{1}{T}. \tag{7}$$

However, if the system is coupled to a barostat of pressure P, then

$$\left\langle \frac{\tilde{\pi}}{\tilde{\theta}} \right\rangle_{TP} = \int du\, d\mathcal{V}\, \frac{\tilde{\pi}}{\tilde{\theta}}\, P_{\mathrm{eq}}(u,\mathcal{V})\, e^{-P\mathcal{V}/(k_BT)} = \frac{P}{T}. \tag{8}$$

In this context, *proper* refers to the ensemble average, which gives the corresponding macroscopic quantity. It is important to realize that $\langle\tilde{\theta}\rangle_T \neq T$ and $\langle\tilde{\pi}\rangle_{TP} \neq P$, which we demonstrate below. Last, because the estimators depend upon the particle thermodynamics, they are defined for each mesoparticle independently.

2. *Energetic thermodynamic description*

Analogous to the formulation of the energetic form presented in the original GenDPDE work [1], rather than working with $(u,\mathcal{V})$, let us work with $(s,\mathcal{V})$ instead, and use u as the dependent variable; s is the *dressed* entropy defined below. The equilibrium behavior of the system is still contained in Eq. (5), but now is cast under a different form,

$$P_{\mathrm{eq}}(s,\mathcal{V})\, ds\, d\mathcal{V} \sim e^{[T\tilde{s}-u(s,\mathcal{V})]}|J|\, ds\, d\mathcal{V}, \tag{9}$$

where J is the Jacobian of the transformation, $J = \partial u/\partial s|_{\mathcal{V}} > 0$, and $|J|$ is its determinant. Formally, $J > 0$ sets the properties of s that are consistent with the macroscopic thermodynamic definition. The dressed entropy is then defined as

$$s = \tilde{s} + k_B \ln \left.\frac{\partial u}{\partial s}\right|_{\mathcal{V}}. \tag{10}$$

Equation (10) is a differential equation that links the dressed entropy with the statistical mechanical information contained in $g(u,\mathcal{V})$. Note that we assume $\partial u/\partial s|_{\mathcal{V}} > 0$ without loss of generality, as the formal solution of Eq. (10) indicates that

$$s(u,\mathcal{V}) = k_B \ln \frac{1}{k_B} \int_0^u du\, e^{\tilde{s}(u,\mathcal{V})/k_B} \tag{11}$$

is a monotonously increasing function of the particle internal energy, in agreement with the behavior of the macroscopic entropy [19].

We can now establish the central equation of our thermodynamic formulation:

$$P_{\mathrm{eq}}(s,\mathcal{V})\, ds\, d\mathcal{V} \sim e^{[Ts-u(s,\mathcal{V})]/(k_BT)}\, ds\, d\mathcal{V}. \tag{12}$$

Although the physics of the system remains the same, we can introduce a different, but equivalent thermodynamic description of the mesoscopic system in the so-called energetic form [19]:

$$du = \left.\frac{\partial u}{\partial s}\right|_{\mathcal{V}} ds + \left.\frac{\partial u}{\partial\mathcal{V}}\right|_{s} d\mathcal{V} \equiv \theta ds - \pi d\mathcal{V}. \tag{13}$$

For the energetic form, Eq. (13) defines a new set of proper estimators of the macroscopic quantities of the ensemble. The particle temperature θ is the proper estimator of the (macroscopic) temperature, i.e.,

$$\langle\theta\rangle_T = \int ds\, \theta\, P_{\mathrm{eq}}(s,\mathcal{V}) = T, \tag{14}$$

and the particle pressure π is the proper estimator of the (macroscopic) pressure, i.e.,

$$\langle\pi\rangle_{TP} = \int ds\, d\mathcal{V}\, \pi\, P_{\mathrm{eq}}(s,\mathcal{V})\, e^{-P\mathcal{V}/(k_BT)} = P. \tag{15}$$

3. *Identification of the heat and work: Comparison of the entropic and energetic thermodynamic descriptions*

We have arrived at a key juncture in the formulation, which requires identifying the heat and work in the GenDPDE framework. Comparing Eqs. (6) and (13), and using the *First Law of Thermodynamics*, we have

$$du = \tilde{\theta} d\tilde{s} - \tilde{\pi} d\mathcal{V} = \theta ds - \pi d\mathcal{V} = \text{đ}q + \text{đ}W, \tag{16}$$

where q and W are the heat and work, respectively, and the crossbar notation in the last equality indicates an inexact differential.

In the original formulation of GenDPDE [1], we demonstrated that the relationship between the estimators is

$$\tilde{\theta} = \frac{\theta}{\left(1 - \frac{k_B}{C_V}\right)} \simeq \theta\left[1 + \frac{k_B}{C_V} + \mathcal{O}\left(\frac{k_B}{C_V}\right)^2\right] \tag{17}$$

$$\tilde{\pi} = \pi + \frac{k_B\tilde{\theta}}{C_V}\frac{\alpha}{\beta} \simeq \pi + \frac{k_B\theta}{C_V}\frac{\alpha}{\beta} + \mathcal{O}\left(\frac{k_B}{C_V}\right)^2, \tag{18}$$

where α is the thermal expansion coefficient, β is the isothermal compressibility, and C_V is the constant-volume heat capacity. (The coefficients α, β, and C_V are given by standard thermodynamic relations, but replaced with mesoparticle thermodynamic variables.) However, comparing Eqs. (16), (17), and (18), it is evident that both $\tilde{\theta} d\tilde{s} \neq \theta ds$ and $\tilde{\pi} d\mathcal{V} \neq \pi d\mathcal{V}$ due to the additional terms introduced by the mesoscopic thermodynamic transformations. This is a key finding of this work, which indicates that there is not an unambiguous definition of both the heat and work exerted on the mesoparticle.

It is important to note that this ambiguity is not related to either the chosen scale of the thermodynamic description [21], or to a change in the statistical mechanical ensemble. Rather it is intrinsic to the particle thermodynamics being defined through the probability distributions. Therefore, the thermodynamic description of the mesoscopic system is completely contained in a thermodynamic potential relating the resolved DoF with the unresolved DoF. However, such a thermodynamic potential depends not only on the reservoir properties (e.g., the temperature T or the pressure P), but also on the set of independently fluctuating variables. If there is a change in the independent variables, then the mesoscopic thermodynamic potential is transformed as a distribution. The transformation from the original DPDE entropic description $\tilde{s}(u, \mathcal{V})$ into an energetic description does not involve the inversion of the function $\tilde{s}(u, \mathcal{V}) \rightarrow u(\tilde{s}, \mathcal{V})$, but instead $\tilde{s}(u, \mathcal{V}) \rightarrow u(s, \mathcal{V})$ with s given by Eq. (10). In fluctuating systems, the mesoscopic thermodynamic parameters are then *dressed* by the fluctuations permitted by the chosen ensemble. In addition, this influences the formulation of the dynamic properties since the *thermodynamic forces* will depend on the chosen potentials and also crucially on the choice of the independently fluctuating variables.

To further elucidate the ambiguous relation between the definitions of the heat and work at the mesoscopic and macroscopic levels, consider the following. Consider the ensemble average of the reversible mechanical work for a mesoscopic system at constant temperature under a quasistatic volume change. According to Eqs. (4), (5), and (9), the Helmholtz free energy of the system F can be expressed by both

$$\begin{aligned} F &= -k_B T \ln \left[\int ds\, e^{[Ts - u(s,\mathcal{V})]/(k_B T)} \right] \\ &= -k_B T \ln \left[\int du\, e^{[T\tilde{s}(u,\mathcal{V}) - u]/(k_B T)} \right]. \end{aligned} \tag{19}$$

Considering the first equality in Eq. (19), from Eq. (13) the system pressure is related to the estimator π by

$$P = -\left.\frac{\partial F}{\partial \mathcal{V}}\right|_T = \langle \pi \rangle. \tag{20}$$

Therefore, for a quasistatic reversibly varying volume,

$$\langle dW^C \rangle = -P d\mathcal{V} = -\langle \pi \rangle d\mathcal{V}, \tag{21}$$

where W^C is the mesoscopic reversible work. Note that in Eq. (21), we used the fact that $\mathcal{V}$ is a control parameter of the ensemble as well as of the state of the particle, i.e., it is nonfluctuating. Based on this, it is reasonable to define the *instantaneous* W^C as

$$dW^C = -\pi d\mathcal{V}, \tag{22}$$

which is defined in terms of system variables only and is independent of the reservoir quantities such as T. In view of Eq. (21), the ensemble average of Eq. (22) effectively is the macroscopic work. Since Eq. (22) is independent of the macroscopic ensemble used, the expression is taken as the definition of the mesoscopic reversible work. Alternatively, starting from the first law of thermodynamics and using the definition of the instantaneous work Eq. (22), together with Eq. (13), we can write the expression of the instantaneous reversible heat

$$dq = du - dW^C = \theta ds. \tag{23}$$

Equation (23) also serves as the definition of the instantaneous heat transferred into the system irrespective of the macroscopic ensemble, since it does not depend on reservoir variables.

Finally, for comparison, we determine an equivalent formulation in terms of the entropic parameters. Considering Eq. (8) and the second equality in Eq. (19), the instantaneous W^C can also be written as

$$dW^C = -T \frac{\tilde{\pi}}{\tilde{\theta}} d\mathcal{V}, \tag{24}$$

which satisfies $\langle dW^C \rangle = -P d\mathcal{V}$. However, it is important to realize that within this formulation, dW^C is not defined in terms of particle properties alone, but depends also on the ensemble temperature T. Hence, this formulation cannot be directly applied to microcanonical simulations. Then, considering the first law of thermodynamics again, we can write

$$dq = du + T \frac{\tilde{\pi}}{\tilde{\theta}} d\mathcal{V} = \tilde{\theta} d\tilde{s} + \left(\frac{T}{\tilde{\theta}} - 1 \right) \tilde{\pi} d\mathcal{V}. \tag{25}$$

Although $\langle dq \rangle = \langle \tilde{\theta} d\tilde{s} \rangle_{\mathcal{V}}$, we cannot identify the *instantaneous* mesoscopic heat as $\tilde{\theta} d\tilde{s}$ in a general process due to the existence of the additional term $(T/\tilde{\theta} - 1)\tilde{\pi} dV$, whose average is nonzero.

In summary, we have demonstrated that if the instantaneous heat and work are defined in terms of the system variables only, then this permits the use of the model for a simulation in any ensemble. This demonstration has only been possible by using the energetic formulation, which involves the renormalization of the bare entropy $\tilde{s}$ into the dressed entropy s, due to the fact that the particle thermodynamic potentials transform as distributions rather than as functions. Moreover, the identification of the mesoscopic heat and work from the energetic formulation is crucial for the construction of an algorithm in which the processes of particle volume change and heat exchange are separated. Finally, as described next, the energetic formulation permits us to define an effective mesoscopic Hamiltonian, from which all the reversible dynamics can be derived.

B. Dynamics of mesoparticles

As a result of the ambiguities discussed above, the construction of a consistent mesoscopic model with arbitrary particle thermodynamics requires the introduction of additional assumptions. These assumptions and considerations are itemized and discussed during the presentation of the formulation. Note that in the previous subsection, we defined the single-particle properties, while in this section we analyze a system of N mesoparticles, which requires explicit use of the subscript i in the corresponding quantities.

(1) The interactions between N mesoparticles are defined in terms of the mesoparticle variables only; namely, the interactions are independent of the properties that characterize the ensemble, and dependent only on the local properties.

(2) The equilibrium probability distribution of an ensemble of N moving mesoparticles is given by

$$P_{\rm eq}(\{\mathbf{p}_i\},\{\mathbf{r}_i\},\{s_i\})\Gamma \sim e^{-\sum_i\left[\frac{p_i^2}{2m_i}+u_i(s_i,n_i)-Ts_i\right]\big/(k_BT)}d\Gamma, \quad (26)$$

where m_i is the mass of a mesoparticle, and $\Gamma \equiv (\mathbf{p}^N,\mathbf{r}^N,s^N)$ is a point in a $7N$-dimensional phase space. For convenience, we use $n_i(\{\mathbf{r}_j\})$, instead of the particle volume $\mathcal{V}_i = 1/n_i$ from this point onward in the formulation. The link between Eq. (26) and the underlying physical properties is given by Eqs. (3) and (4), together with the definition given in Eq. (10). The function

$$H(\{\mathbf{p}_i\},\{\mathbf{r}_i\}) = \sum_i\left[\frac{p_i^2}{2m_i}+u_i(s_i,n_i)\right] \quad (27)$$

is the *effective Hamiltonian*, defining the system reversible dynamics, with the internal energy u given as a function of the mesoparticle coordinates through $n(\{\mathbf{r}_j\})$, and depending parametrically on the dressed entropy s. The mesoparticle positions and momenta are referred to as the *mechanical* (resolved) DoF since they are directly associated with the reversible work and the kinetic energy of the particle, respectively. Note that it is possible to add to the Hamiltonian [Eq. (27)] and the associated probability distribution [Eq. (26)] a position-dependent potential energy $\Psi(\mathbf{r}_j)$, which describes, for example, electrostatic interactions, or to include a contribution depending solely on the particle position such as an external gravitational field. However, here for the sake of simplicity, we do not consider such contributions. By switching dependent variables from s to u, the distribution in Eq. (26) is equivalent to

$$P_{\rm eq}(\{\mathbf{p}_i\},\{\mathbf{r}_i\},\{u_i\})d\tilde{\Gamma} \sim e^{-\sum_i\left[\frac{p_i^2}{2m_i}+u_i-T\tilde{s}_i(u_i,n_i)\right]\big/(k_BT)}d\tilde{\Gamma}, \quad (28)$$

which, therefore, can also be used to evaluate the ensemble averages when needed; $\tilde{\Gamma} \equiv (\mathbf{p}^N,\mathbf{r}^N,u^N)$.

(3) The *reversible* interactions are distinguished from the *irreversible* interactions via their behavior under time-reversibility. In other words, the reversible interactions are even, while the irreversible interactions are odd.

1. Reversible, conservative interactions

Let us begin by formulating the reversible (conservative) interactions. Implicit in the choice of the independent variables, $\tilde{\Gamma} \equiv (\mathbf{p}^N,\mathbf{r}^N,u^N)$, and the form of the Hamiltonian in Eq. (27) is the identification of both the reversible work and the adiabatic condition. As such, the reversible interactions follow straightforwardly from the Hamilton EoM:

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \quad (29)$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = \sum_{j\neq i}\left(\left.\frac{\partial u_i}{\partial \mathbf{r}_j}\right|_{s_i} - \left.\frac{\partial u_j}{\partial \mathbf{r}_i}\right|_{s_j}\right) \quad (30)$$

In Eq. (30), we have used the translational invariance of u_i, which imposes $\sum_j \partial u_i/\partial \mathbf{r}_j = 0$. This allows us to write $\partial u_i/\partial \mathbf{r}_i = -\sum_{j\neq i}\partial u_i/\partial \mathbf{r}_j$ when the contribution due to mesoparticle i is separated from the Hamiltonian. Equations (29) and (30) need to be supplemented by the adiabatic condition

$$\dot{s}_i = 0. \quad (31)$$

The conservative force is derived using Eqs. (1) and (13), $ds_i = 0$, and the requirement that the thermodynamic function of the mesoparticle $u(s,n)$ is both Galilean and solid-body rotation invariant. These criteria lead to the conservation of the linear and angular momenta [22,23], whereby we can express W^C due to the conservative interactions as

$$\begin{aligned} dW^C &= \sum_i\sum_{j\neq i}\left.\frac{\partial u_i}{\partial \mathbf{r}_j}\right|_{s_i} d\mathbf{r}_j \\ &= \sum_i\sum_{j<i}\left(\left.\frac{\partial u_i}{\partial \mathbf{r}_j}\right|_{s_i} - \left.\frac{\partial u_j}{\partial \mathbf{r}_i}\right|_{s_j}\right)d\mathbf{r}_{ij} \\ &= \frac{1}{2}\sum_i\sum_{j\neq i}\mathbf{f}_{ij}^C d\mathbf{r}_{ij} \equiv \sum_i dW_i^C, \end{aligned} \quad (32)$$

with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. From the last equation, we obtain an expression for the reversible, conservative work exerted on mesoparticle i, i.e.,

$$dW_i^C = \frac{1}{2}\sum_{j\neq i}\mathbf{f}_{ij}^C d\mathbf{r}_{ij}, \quad (33)$$

where the conservative force is then given as

$$\mathbf{f}_{ij}^C = \left(\left.\frac{\partial u_i}{\partial \mathbf{r}_j}\right|_{s_i} - \left.\frac{\partial u_j}{\partial \mathbf{r}_i}\right|_{s_j}\right) = -\left(\frac{\pi_i}{n_i^2}+\frac{\pi_j}{n_j^2}\right)\frac{dw_{ij}}{dr_{ij}}\mathbf{e}_{ij}, \quad (34)$$

where $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the separation-distance unit vector with $r_{ij} \equiv |\mathbf{r}_{ij}|$.

Note that defining the force as an adiabatic transformation is convenient for devising a numerical integration splitting algorithm [1], where the mechanical motions are separated from the heat transfer. Moreover, it is important to realize we implicitly consider that the internal DoF of the mesoparticle relax much faster than the resolved DoF u and $\mathcal{V}$. As such, we implicitly assume that there is a clear separation of timescales between the resolved and unresolved DoF [12].

2. Irreversible, dissipative interactions

Next, we formulate the irreversible (dissipative) interactions. Analogous with macroscopic thermodynamics, for the dissipative interactions, we require an extremum principle to hold, i.e.,

(4) In the absence of fluctuations, the spontaneous dynamics of the system is such that

$$\dot{\mathcal{F}} < 0 \tag{35}$$

where $\mathcal{F}$ is the exponent of Eq. (26),

$$\mathcal{F}(\{\mathbf{p}_i\}, \{\mathbf{r}_i\}, \{s_i\}) = \sum_i \left[\frac{p_i^2}{2m_i} + u_i(s_i, n_i) - Ts_i\right]. \tag{36}$$

By adding the dissipative force on the right-hand side of Eq. (30), and by using Eq. (16), we obtain

$$\dot{\mathbf{p}}_i = \mathbf{f}_i^C + \mathbf{f}_i^D, \tag{37}$$

$$\theta_i \dot{s}_i = \dot{q}_i + \dot{W}_i^{\text{irrev}} = \dot{q}_i + \dot{W}_i - \frac{1}{2}\sum_{j\neq i} \mathbf{f}_{ij}^C \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right). \tag{38}$$

In Eq. (38), we define the *irreversible work*, $\dot{W}_i^{\text{irrev}}$, as the irreversible effect of the motion of the mechanical DoF converted into the heat. The overall dissipated work needs to be separated between the mesoscopic system and the environment. It is important to realize that in a general mesoscopic model, this splitting follows from knowledge of the underlying physical processes, which are outside of the thermodynamic framework. In our model, due to the fact that the particles are identical, it is reasonable to assume that the irreversible work done by the dissipative forces is shared in equal proportions by both interacting particles, i.e.,

$$\dot{W}_i^{\text{irrev}} = -\frac{1}{2}\sum_{j\neq i} \mathbf{f}_{ij}^D \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right). \tag{39}$$

Once we have defined the reversible work [Eq. (33)] and the irreversible work, $\dot{W}_i^{\text{irrev}}dt$, we can define the heat as the energy transferred by means other than those involving the mechanical DoF. As such, we next define the *irreversible heat exchange* between mesoparticles.

The heat flow on mesoparticle i, $\dot{q}_i$, can be separated into the heat exchanged with neighboring mesoparticles j, $\dot{q}_{ij}$, and the heat exchanged with the reservoir, $\dot{Q}_i$. Additionally, to enforce energy conservation, we require that $\dot{q}_{ij} = -\dot{q}_{ji}$. We can then express the irreversible heat flow on particle i as

$$\dot{q}_i = \sum_{j\neq i} \dot{q}_{ij} + \dot{Q}_i. \tag{40}$$

By inserting Eqs. (39) and (40) into Eq. (35), and by using Eqs. (37) and (38), we arrive at

$$\sum_i \dot{s}_i > \sum_i \frac{\dot{Q}_i}{T}, \tag{41}$$

where we have used the fact that the heat exchanged between mesoparticles satisfies $\sum_i \sum_{j\neq i} \dot{q}_{ij} = 0$. Further, by decomposing the left-hand side of the inequality in Eq. (41) into the internally produced entropy $\dot{s}_i^{(ij)}$, and the entropy due to the interaction with the reservoir $\dot{s}_i^{(\text{res})}$, the *entropy production* of the mesoparticle becomes

$$\dot{s}_i = \sum_{j\neq i} \dot{s}_i^{(ij)} + \dot{s}_i^{(\text{res})}. \tag{42}$$

As this property should be satisfied for an arbitrary number of particles, the more stringent condition on each interaction follows

$$\dot{s}_i^{(\text{res})} > \frac{\dot{Q}_i}{T}, \tag{43}$$

$$\dot{s}_i^{(ij)} + \dot{s}_j^{(ij)} > 0. \tag{44}$$

Interestingly, a statement equivalent to Eq. (44) can be found in the theory of nonequilibrium thermodynamics [15,24].

At this point in the formulation, we could proceed by considering either Eq. (43) or Eq. (44). However, the equations are analogous; therefore, for clarity and ease of presentation, let us proceed with Eq. (44). Substituting Eq. (38) into Eq. (44) for each particle, we have

$$\dot{s}_i^{(ij)} + \dot{s}_j^{(ij)} = \dot{q}_{ij}\left(\frac{1}{\theta_i} - \frac{1}{\theta_j}\right) + \mathbf{f}_{ij}^D\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\left(\frac{1}{\theta_i} + \frac{1}{\theta_j}\right) > 0. \tag{45}$$

In the absence of fluctuations, the positiveness of Eq. (45) allows us to identify the *thermodynamic forces* responsible for the dissipative processes, where specifically these forces are proportional to the factors multiplying $\mathbf{f}_{ij}^D$ and $\dot{q}_{ij}$, respectively, Eqs. (46) and (47) below.

A key ramification of identifying these forces is that

(5) The dynamic symmetries, namely Galilean invariance and invariance under solid-body rotations, can be applied to Eq. (45) to enforce the appropriate conservation laws for the dissipative interactions in a manner equivalent to those enforced for the conservative interactions [22].

We require that Eq. (45) is Galilean and solid-body rotation invariant, which ensures that the interactions conserve both linear and angular momenta.

3. Fluxes and thermodynamic forces

Next, we define the relationships between the fluxes and thermodynamic forces. We assume that these relationships are linear for both the dissipative interactions and the heat flow [15,24]:

$$\mathbf{f}_{ij}^D = -\gamma_{ij}\,\mathbf{e}_{ij}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\mathbf{e}_{ij}, \tag{46}$$

$$\dot{q}_{ij} = -\kappa_{ij}\,(\theta_i - \theta_j), \tag{47}$$

where $\gamma_{ij} = \gamma\omega_{ij}$, $\kappa_{ij} = \kappa\bar{\omega}_{ij}$, γ is the friction coefficient, κ is the heat conductivity parameter, and ω_{ij} and $\bar{\omega}_{ij}$ are weighting functions depending on the distance between the mesoparticles, which become zero for r_{ij} larger than the cutoff ranges R_{cut}^D and $\bar{R}_{\text{cut}}$, respectively. Note that Eqs. (46) and (47) comply with the requirements of dynamic symmetry mentioned above. The linearity between dissipative fluxes and thermodynamic forces implies that neither γ nor κ depend on $\mathbf{p}$ or θ (or u).

The dissipative forces of Eq. (46) have been defined in the standard form [15,24]. However, Eq. (47) is notably different from the form of $\dot{q}_{ij}$ in both the original GenDPDE [1] method and the DPDE [10] method itself. This alternative heat flow model is a key result of this work, where the characteristics are the following. The model: (i) satisfies Eq. (45); (ii) is expressed in terms of the proper estimators of the macroscopic temperature, i.e., in terms of the particle temperatures; and (iii) allows the GenDPDE method to be formulated in closed form using the perspective of the dressed entropy s in terms of the Γ variables only.

Key consequences of the formulation of both Eqs. (46) and (47), particularly Eq. (47) given in terms of the proper estimators of T, are that in equilibrium

$$\langle \mathbf{f}_{ij}^{D} \rangle = 0, \tag{48}$$

$$\langle \dot{q}_{ij} \rangle = 0. \tag{49}$$

Satisfying the conditions in Eqs. (48) and (49) allow some inconsistency issues to be avoided. For example, the use of the naive definition of $\dot{q}_{ij} = -\kappa_{ij}\,(1/\theta_j - 1/\theta_i)$, rather than Eq. (47), would lead to $\langle \dot{q}_{ij} \rangle \simeq \kappa_{ij}\, k_B (1/C_{V,i} - 1/C_{V,j}) \neq 0$, where $\langle \dot{q}_{ij} \rangle \neq 0$ is the so-called *spurious drift* [16] that would unwittingly be compensated for by the addition of *ad hoc* terms in the EoM. Moreover, at equilibrium, to satisfy the conditions in Eqs. (48) and (49), the system would move to a (steady-state) distribution different than those postulated in either Eq. (26) or Eq. (5). Note that the heat flow model $\dot{q}_{ij} = -\kappa_{ij}\,(1/\tilde{\theta}_j - 1/\tilde{\theta}_i)$, given in Eq. (70) of Ref. [1], uses the proper estimator of T, $1/\tilde{\theta}$, and avoids such issues. However, using the heat flow model of [1] requires a blending of the bare and dressed entropies. While this blending does not affect the GenDPDE framework, it causes the computation of the dissipative interactions in the original GenDPDE method to be rather complicated and cumbersome.

Last, consider the hypothetical heat flow model,

$$\dot{q}_{ij} = -\,\kappa_{ij}\,(\tilde{\theta}_i - \tilde{\theta}_j), \tag{50}$$

instead of the alternative heat flow model of Eq. (47). The difference between the models is a subtle change in the temperature estimators, which for the hypothetical heat flow model leads to

$$\begin{aligned}\langle \dot{q}_{ij} \rangle &= -\kappa_{ij}\,(\langle \tilde{\theta}_i \rangle - \langle \tilde{\theta}_j \rangle)\\ &\simeq -\kappa_{ij}\; k_B T \left(\frac{1}{C_{V,i}} - \frac{1}{C_{V,j}} \right) \neq 0.\end{aligned} \tag{51}$$

For a system of mesoparticles with different heat capacities, here again the system would produce a spurious drift. Therefore, if a heat flow model analogous to Fourier's law of heat conduction is desired within a linear Langevin equation, only the alternative heat flow model of Eq. (47) given in terms of the particle temperature is thermodynamically consistent with the postulated probability distribution functions given by Eqs. (26) and (28).

4. Random contributions

The final assumptions in the formulation concern the random contributions in the EoM.

(6) In equilibrium, the spontaneous transitions between states satisfy the detailed balance (DB) condition [16]:

$$P_{\text{eq}}(\Gamma)\bar{W}(\Gamma \to \Gamma') = P_{\text{eq}}(\Gamma^*)\bar{W}(\Gamma^* \to \Gamma^{*\prime}), \tag{52}$$

with $\Gamma^* = \varepsilon\Gamma'$ and $\Gamma^{*\prime} = \varepsilon\Gamma$, where ε assigns 1 to the even variables under time-reversibility, and -1 to the odd variables. The resulting dynamics leaves the measure in Eq. (26) invariant.

(7) The effect of the unresolved DoF in terms of the random contributions is additive, i.e., the dynamic equations are Langevin-like. The dynamics of the probability distribution can then be cast under a Fokker-Planck equation, where only the first and second moments of the distribution become relevant; see Ref. [16]. Furthermore, we consider Markovian processes only.

C. GenDPDE equations-of-motion

In this section, we present the complete set of EoM. For convenience, we use a discrete form of Eqs. (29) and (30), where primed variables refer to the final state at time $t + \delta t$ and nonprimed variables to the initial state at time t; δt is the time step. Note that in the discrete form, the interpretation of the random term is evident; thus, no Ito-Stratonovich dilemma exists. Considering terms up to the first order in δt:

$$\mathbf{r}_i' = \mathbf{r}_i + \frac{\mathbf{p}_i}{m_i}\delta t, \tag{53}$$

$$\mathbf{p}_i' = \mathbf{p}_i + \left(\mathbf{f}_i^C + \mathbf{f}_i^D\right)\delta t + \sum_{j\neq i} \delta\mathbf{p}_{ij}^R, \tag{54}$$

where $\mathbf{f}_i^C = \sum_{j\neq i} \mathbf{f}_{ij}^C$, $\mathbf{f}_i^D = \sum_{j\neq i} \mathbf{f}_{ij}^D$, and $\delta\mathbf{p}_{ij}^R$ is the random contribution to the momentum. In Ref. [1], we demonstrated that $\delta\mathbf{p}_{ij}^R$, consistent with the DB condition, is

$$\delta\mathbf{p}_{ij}^R = \sqrt{k_B \gamma_{ij}(\theta_i + \theta_j)}\, \xi_{ij}\, \mathbf{e}_{ij}\, \delta t^{1/2}, \tag{55}$$

where $\delta\mathbf{p}_{ij}^R = -\delta\mathbf{p}_{ji}^R$. The normalized Gaussian random numbers ξ_{ij} satisfy

$$\langle \xi_{ij} \rangle = 0, \tag{56}$$

$$\langle \xi_{ij}\xi_{kl} \rangle = (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\delta_{tt'}, \tag{57}$$

where the average is taken over the probability distribution of ξ_{ij}. Moreover, the random numbers are correlated only if they belong to the same time interval.

The EoM for the particle internal energy results from the energy balance (see Eq. (78) of Ref. [1]):

$$\begin{aligned}u_i' = u_i &- \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\mathbf{f}_{ij}^C\,\delta t\\ &- \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\mathbf{f}_{ij}^D\,\delta t - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\delta\mathbf{p}_{ij}^R\\ &- \frac{1}{2m_i}\sum_{j\neq i}\sum_{l\neq i}\delta\mathbf{p}_{ij}^R\delta\mathbf{p}_{il}^R + \dot{q}_i\delta t + \sum_{j\neq i}\delta u_{ij}^R,\end{aligned} \tag{58}$$

where $\dot{q}_i = \sum_{j\neq i}\dot{q}_{ij}$, and δu_{ij}^R is the random contribution to the heat associated with the alternative heat flow model $\dot{q}_{ij}$ of Eq. (47). The system dynamics, Eqs. (53), (54), and (58), is completed by specifying the properties of δu_{ij}^R.

However, before proceeding, let us finalize the complete forms of both the irreversible work done on the mesoparticle, and the heat exchanged between mesoparticles. By adding the random contributions to Eq. (39), the complete irreversible work becomes

$$\delta W_i^{\mathrm{irrev}} = -\frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i}-\frac{\mathbf{p}_j}{m_j}\right)\mathbf{f}_{ij}^D\,\delta t - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i}-\frac{\mathbf{p}_j}{m_j}\right)\delta\mathbf{p}_{ij}^R - \frac{1}{2m_i}\sum_{j\neq i}\sum_{l\neq i}\delta\mathbf{p}_{ij}^R\delta\mathbf{p}_{il}^R, \tag{59}$$

which by definition is identified from the (irreversible) action of the mechanical DoF of the system on the energy balance, Eq. (58). Note that the random contributions to the irreversible work in Eq. (59) also include a nonlinear quadratic term [the third term in Eq. (59)], which is of order $O(\delta t)$, and therefore cannot be neglected within the level of accuracy of our algorithm. Interestingly, when all the terms on the right-hand side of Eq. (59) are averaged with respect to both the equilibrium distribution and the random momenta, then $\langle \dot{W}_i^{\mathrm{irrev}}\rangle = 0$, which is the expected behavior for thermal equilibrium.

The remaining terms in the energy balance are associated with the heat, such that rewriting Eq. (58) as $u_i' = u_i + \delta W_i^C + \delta W_i^{\mathrm{irrev}} + \delta q_i$, gives

$$\delta q_i = \dot{q}_i\delta t + \sum_{j\neq i}\delta u_{ij}^R, \tag{60}$$

where δu_{ij}^R can be interpreted as the random heat exchanged between neighboring mesoparticles. With the form of the heat flow established in Eq. (47), the random energy contribution δu_{ij}^R is required to ensure that the particle internal energy properly samples the equilibrium probability distribution as the particle internal energy varies in time. This random energy transfer satisfies the core concept underlying the fluctuation-dissipation theorem (FDT).

Last, to finalize the complete set of EoM, we specify the properties of δu_{ij}^R. In Appendix A, by following Ref. [1], we derive δu_{ij}^R consistent with $\dot{q}_{ij}$ of Eq. (47) as

$$\delta u_{ij}^R = \sqrt{2k_B\kappa_{ij}\theta_i\theta_j}\;\bar{\xi}_{ij}\delta t^{1/2}, \tag{61}$$

where $\bar{\xi}_{ij}$ is the normalized Gaussian number with properties

$$\langle\bar{\xi}_{ij}\rangle = 0, \quad \langle\bar{\xi}_{ij}\bar{\xi}_{kl}\rangle = (\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk})\delta_{tt'}.$$

As before, $\bar{\xi}_{ij}(t)$ and $\bar{\xi}_{ij}(t')$ are uncorrelated if these do not belong to the same time interval.

Analogous to the heat flow between mesoparticles, Eqs. (47) and (61), the heat flow between mesoparticle i and the heat reservoir is $\dot{Q}_i = -\kappa_i(\theta_i - T) + \dot{Q}_i^R$, where the properties of the random heat flux $\dot{Q}_i^R$ are analogous to Eq. (61), and the reservoir temperature is set to T. For simplicity, if we ignore the interaction with the reservoir, then the heat exchange becomes analogous to Eq. (59), i.e.,

$$\delta q_i = -\sum_{j\neq i}\kappa_{ij}\,(\theta_i-\theta_j)\delta t + \sum_{j\neq i}\delta u_{ij}^R. \tag{62}$$

Equations (47) and (61) are the key results of this work since they cast the GenDPDE method [1] under a consistent framework, depending only on the particle variables connected with the dressed entropy. In comparison, the heat flow model presented in the original GenDPDE work [1] is

$$\delta q_i = -\sum_{j\neq i}\kappa_{ij}\left(\frac{1}{\tilde{\theta}_j}-\frac{1}{\tilde{\theta}_i}\right)\delta t + \sum_{j\neq i}\delta u_{ij}^R, \tag{63}$$

with

$$\delta u_{ij}^R = \sqrt{2k_B\,\kappa_{ij}}\;\bar{\xi}_{ij}\delta t^{1/2}, \tag{64}$$

where the temperature is defined via the entropic formulation instead, i.e., $1/\tilde{\theta} = \partial\tilde{s}/\partial u$. While Eq. (63) can be expressed in terms of θ via Eq. (17), we prefer to employ the direct link to the proper estimator of T, which is θ. Although Eqs. (62) and (63) are physically consistent and equivalent, as we will demonstrate below, they produce different forms of the macroscopic heat conductivity coefficient, particularly with respect to its temperature-dependence. An advantage of using Eq. (62) within the GenDPDE method is that the functional form is analogous to Fourier's law of heat conduction.

Last, in Appendix B, we present the numerical discretization of the EoM [Eqs. (53), (54), and (58)] with the alternative heat flow model, Eqs. (62) and (61), which was determined using the extended Shardlow splitting algorithm (eSSA) [1,25].

III. RESULTS

In this section, we provide further discussion and insight into the formulation presented. We begin by demonstrating the thermodynamic consistency of the alternative heat flow model, followed by a brief comparison to the heat flow model in the original GenDPDE work [1]. We finish with a discussion of other implications that arose from the analysis of the mesoparticle thermodynamic transformations.

A. Alternative heat flow model

1. Consistency of alternative heat flow model

The thermodynamic consistency of the alternative heat flow model introduced in this work was verified by analyzing the particle probability distributions for the van der Waals equation-of-state (EoS) at an initial system temperature $T = 1.5$ and system particle density $\rho = 0.5$ with $\rho = N/V$, where V is the system volume. The calculation of the probability distributions for the particle internal energy, particle temperature, particle momenta, and particle local density is detailed in the original GenDPDE work, see Secs. 4.3 and 5.1 in Ref. [1]. Figure 1 shows a comparison of the distributions determined from the GenDPDE simulation with the alternative heat flow model against the theoretical distributions obtained from the general probabilities. Consistent with the original GenDPDE work [1], excellent agreement between the simulated and theoretical distributions was found, indicating consistency of the alternative heat model and correct sampling of the equilibrium distributions by the integration algorithm. In addition, we also analyzed the energy conservation in the GenDPDE simulations with the alternative heat flow model using the eSSA. We observed excellent energy conservation with the magnitude of the energy drift consistent with the drift observed in the original GenDPDE work, see Sec. 5.2.2 in Ref. [1].

As a final verification of the alternative heat flow model, we determined the particle probability distributions from a simulation of mesoparticles fixed in space. Under these conditions,

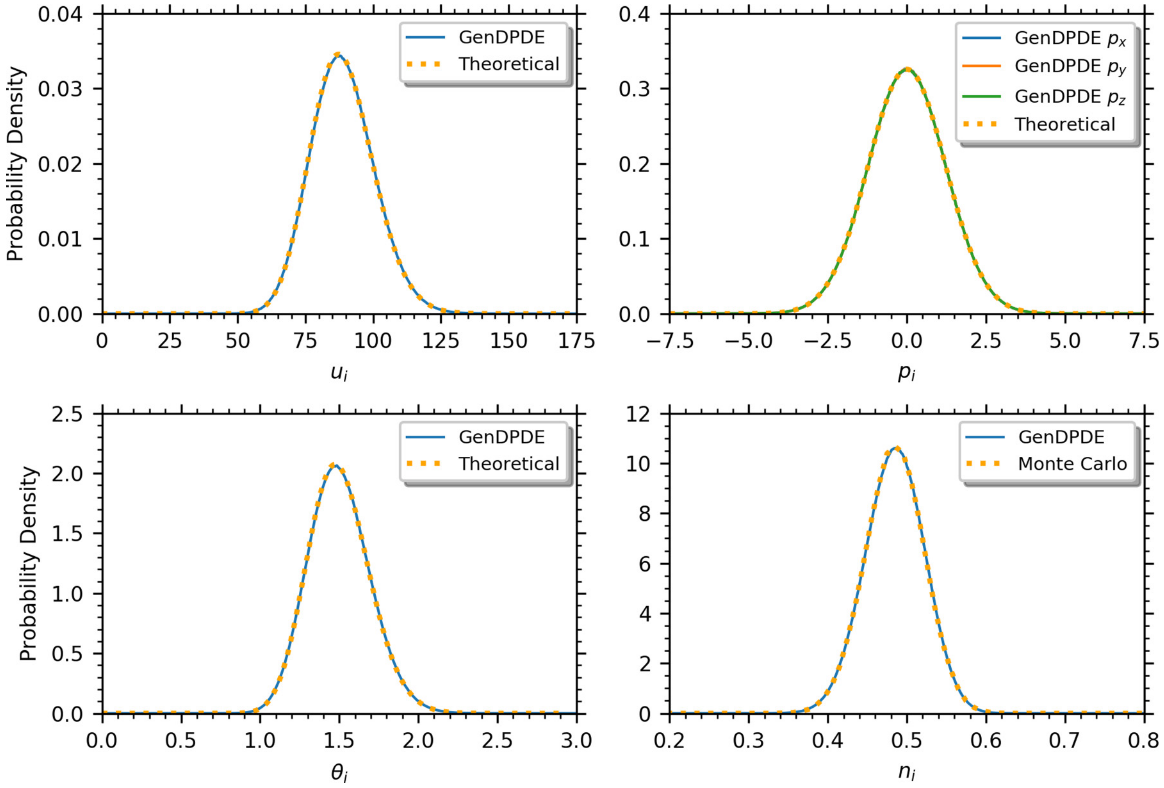

FIG. 1. Equilibrium probability distributions for the van der Waals equation-of-state at initial system temperature $T = 1.5$ and system particle density $\rho = 0.5$: (top left) particle internal energy; (bottom left) particle temperature; (top right) particle momentum; (bottom right) local particle density. Dashed lines are the probability distributions given by Eqs. (90), (91), (89), and (92) in Ref. [1], respectively, while solid lines are determined from a GenDPDE simulation with the alternative heat flow model. Due to each of the particle momenta being nearly identical, the plots for each component are indistinguishable.

the mesoparticles are subject only to heat exchange modeled by Eq. (62) supplemented with Eq. (61). A small constant-volume heat capacity value was used for the mesoparticle, $C_V = 5k_B$, which provides stringent heat exchange conditions due to the non-Gaussian energy probability distribution (see Fig. 2). In this case, the probability distribution for the particle internal energy fluctuations becomes

$$P(u) \propto e^{-u/(k_BT)} u^{C_V/k_B - 1}. \tag{65}$$

Note that the exponent of u is $C_V/k_B - 1$ and not $\tilde{C}_V/k_B$ as in Ref. [10], which is due to $\tilde{C}_V = \partial u/\partial\tilde{\theta}|_{\mathcal{V}} = C_V - k_B$, where $C_V = \partial u/\partial\theta|_{\mathcal{V}}$; see also Eq. (17). A comparison between the simulation and theoretical distributions is shown in Fig. 2, where again excellent agreement was observed, including for the skewness of the distribution.

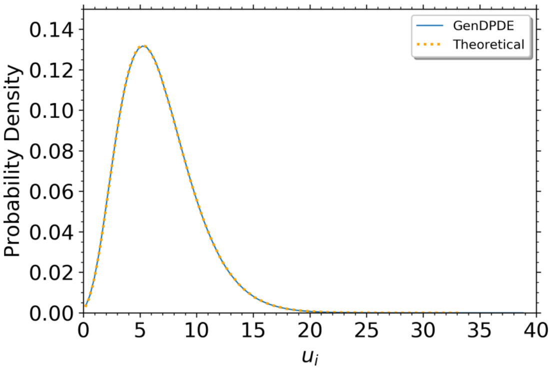

FIG. 2. Equilibrium particle internal energy probability distribution from a GenDPDE simulation of mesoparticles fixed in space using a small constant-volume heat capacity $C_V = 5k_B$, with initial system temperature $T = 1.5$, system particle density $\rho = 0.5$, and heat conductivity parameter $\kappa = 1$. The theoretical distribution was determined from Eq. (65).

2. A brief discussion comparing the original and alternative heat flow models

As mentioned previously, the alternative and original heat flow models are physically consistent and thermodynamically equivalent. However, some underlying differences exist between the models, some of which have already been mentioned as we proceeded with the formulation. For a particular application or future implementation of the GenDPDE framework, while these differences may appear subtle, one of the heat flow models may be better suited for a particular case. As such, the optimal choice of the model should be carefully assessed to determine its suitability in an application or implementation.

A key difference between the heat flow models worth highlighting is the choice of the proper estimators of the thermodynamic properties. While both models can be expressed in terms of the proper estimator of the macroscopic temperature, their respective forms differ. The alternative heat flow model of Eq. (47) allows the GenDPDE framework to be formulated in a closed form using the dressed entropy s in terms of the Γ variables only, while the original heat flow model requires a blending of the bare and dressed entropies [1]. While this blending does not alter the thermodynamics, the calculation of the dissipative interactions is more complex, and subsequently more computationally demanding.

Last, a possible consequence of proposing an alternative form for the mesoscopic heat exchange is a change in the functional form of the macroscopic heat conductivity coefficient, λ, with respect to the state variables of the ensemble, which are T and ρ in our case. Therefore, we compare the functional form of λ that results from both heat flow models. When deriving the expression for λ, we only consider the dissipative contribution, λ_D, and ignore the kinetic contribution, λ_K. This is a reasonable assumption because λ_K is independent of the heat flow model, and is primarily related to the interparticle friction model employed. Further, we consider the ideal DPD fluid, where conservative interactions are absent. Notably, if $\kappa\rho^3 \sim 1$, then both mechanical contributions leading to kinetic and potential energy transport scale as $k_BT \ll C_VT$, and are negligible when compared to the transport due to direct heat exchange between particles.

To begin, we consider the form of λ_D for the original heat flow model Eq. (63), and recall that this model is the same in both the original GenDPDE and DPDE frameworks. As such, the form of λ_D will be equivalent, which has been derived previously for the DPDE framework [26] as

$$\lambda_D = \frac{2\pi \bar{R}_{\mathrm{cut}}^5 \rho^2 \kappa}{3T^2}. \tag{66}$$

The derivation of λ_D for the alternative heat flow model is analogous to the derivation given in Ref. [26], where the resulting expression is

$$\lambda_D = \frac{2\pi \bar{R}_{\mathrm{cut}}^5 \rho^2 \kappa}{315}. \tag{67}$$

Comparing Eqs. (66) and (67), the units of κ differ, i.e., “energy×temperature” units versus “energy/temperature” units, respectively. Moreover, it is evident that the original and alternative heat flow models result in different functional forms for λ_D with respect to the state variables. The alternative heat flow model leads to a λ_D that is independent of the system temperature T, while $\lambda_D \propto 1/T^2$ for the original heat flow model. The strong temperature dependence exhibited by the original heat flow model may become a disadvantage in mesoscopic simulations of systems with a weak temperature dependence on λ, or for mesoscopic systems with large temperature gradients. A detailed study comparing the numerical behavior of the original and alternative heat flow models, including the general dependence of the heat conductivity coefficients on T will be addressed elsewhere.

B. Implications from the analysis of the mesoparticle thermodynamic transformations

In addition to the development of the alternative heat flow model, several consequences and ramifications from revisiting the formulation of the GenDPDE framework have emerged. Next, we summarize those already mentioned either here or in the previous work [1], along with some that were not previously mentioned.

(1) The choice of the dependent variable used to formulate the GenDPDE method alters the mesoparticle thermodynamic description. Thermodynamic relations, rather than being functions, are transformed into distributions when the choice of the independent variables is changed within the same ensemble. This fact also has an impact on the transport properties because the thermodynamic forces are defined using Onsager's perspective.

(2) A definitive path for deriving any dressed thermodynamic quantity from the corresponding bare thermodynamic quantity exists. Transformations to different ensembles and to different sets of independent particle variables can be consistently introduced, along with the transformations of the thermodynamic forces acting on the system.

(3) The mesoscopic thermodynamic transformations introduce additional terms of the order of the size of the local fluctuations, which prevent an unambiguous definition of both the heat and work. While there is a preferred choice of the physically meaningful definition of the heat and work for the mesoparticles, the choice becomes irrelevant in the thermodynamic limit.

(4) The thermodynamic framework presented here resembles *stochastic thermodynamics* (ST) [21,27], which was developed for small systems with significant fluctuations. As such, it is interesting to analyze the definitions of the mesoscopic work and heat, Eqs. (22) and (23), within the ST framework. A significant aspect of ST (as well as of Jarzinsky's and Crooks' theories of irreversible processes [28,29]) is that the control parameters drive a fluctuating system from one state to another, which involves heat and work transfer with the environment. In our framework, as well as in the canonical ensemble, the control parameters are T and $\mathcal{V}$. Hence, from Eq. (22), one can isothermally and reversibly vary the volume of the system, and measure the average work done. This result is given in Eq. (21), which can be related to an ensemble average over the property estimator π. The quasistatic nature of the volume variation guarantees that ensemble averages over π are the equilibrium averages. However, from Eq. (23), the analogy to the work is not obvious since s is neither an estimator of the entropy of the system, nor a control parameter. From the first law of thermodynamics, one can write

$$\langle dq \rangle = d\langle u \rangle - \langle dW^C \rangle = d\langle u \rangle + \langle \pi \rangle d\mathcal{V}. \tag{68}$$

The differential symbol d can be taken outside of the ensemble average for u because u is a state function, unlike q and W. Next, one can relate the heat in terms of averages over the estimators, i.e.,

$$d\langle u \rangle = \left.\frac{\partial \langle u \rangle}{\partial T}\right|_{\mathcal{V}} dT + \left.\frac{\partial \langle u \rangle}{\partial \mathcal{V}}\right|_{T} d\mathcal{V}, \tag{69}$$

where

$$\left.\frac{\partial \langle u \rangle}{\partial T}\right|_{\mathcal{V}} = \frac{1}{k_BT^2}\left[\langle u^2 \rangle - \langle u \rangle^2\right],$$

$$\left.\frac{\partial \langle u \rangle}{\partial \mathcal{V}}\right|_{T} = -\langle \pi \rangle + \frac{1}{k_BT}[\langle u\pi \rangle - \langle u \rangle\langle \pi \rangle],$$

and hence,

$$\langle dq\rangle = \frac{1}{k_B T^2}[\langle u^2\rangle - \langle u\rangle^2]dT + \frac{1}{k_B T}[\langle u\pi\rangle - \langle u\rangle\langle\pi\rangle]d\mathcal{V}, \tag{70}$$

which coincides with TdS. Moreover, for small fluctuations, $k_B/C_V \ll 1$, so the first term on the right-hand side of Eq. (70) gives the classical result $\langle dq\rangle_{\mathcal{V}} \simeq C_V(T,\mathcal{V})dT$, where $C_V = \partial u/\partial\theta|_{\mathcal{V}}$ is the constant-volume heat capacity calculated at the saddle point. In general, corrections of the order of k_B/C_V should be expected. Finally, it is important to realize that $S \neq \langle s\rangle$, since *s is not* an estimator of the entropy of the system.

Note that Eq. (70) is specific for the canonical ensemble. For example, for the Gibbs ensemble, one has

$$\langle dW^C\rangle = -Pd\langle\mathcal{V}\rangle = -\langle\pi\rangle\left(\left.\frac{\partial\langle\mathcal{V}\rangle}{\partial T}\right|_P dT + \left.\frac{\partial\langle\mathcal{V}\rangle}{\partial P}\right|_T dP\right), \tag{71}$$

from which an expression analogous to Eq. (21) can be derived. However, $\langle dq\rangle = TdS$. By expanding S in terms of dT and dP, one would determine an equation analogous, but not equal to Eq. (70), due to the change in the control parameters from T, $\mathcal{V}$ to T, P. Therefore, since there is no estimator of the entropy of the system, this leads to an expression for the average heat written in terms of other system estimators, and such a relationship becomes ensemble dependent.

(5) Furthermore, in the ST framework, $u(s,\mathcal{V})$ plays the role of a Hamiltonian of the potential of mean force [12], which can be defined if the dynamics of the unresolved DoF relax much faster than the dynamics of the resolved DoF. A system having both bare and dressed entropies requires that the internal variables, u and $\mathcal{V}$, are always in thermal equilibrium within the mesoparticle. However, such an assumption parallels the local equilibrium hypothesis, the basis of the classical theory of nonequilibrium thermodynamics [15]. Therefore, we implicitly consider the validity of internal thermal equilibrium within a GenDPDE application.

(6) The choice of the proper estimators of the thermodynamic properties that are embedded in the thermodynamic description must be considered to rigorously connect the particle thermodynamics to the corresponding macroscopic properties. This criteria is connected with the requirement that equilibrium averages of the linear thermodynamic forces are zero if expressed in terms of the proper estimators. These are necessary conditions to formulate Langevin-like equations for the dynamics with an additive random contribution with zero mean. Generally, nonlinear thermodynamic forces and spurious drifts can be compensated by additional contributions in the Langevin equations, resulting in random terms with a nonzero average. Although conceptually this can be done, we proceeded in such a way to completely avoid this complexity.

(7) The particle thermodynamics may be nonextensive with respect to the particle material content. For example, the interfacial contributions of the mesoscopic objects could represent a significant fraction of the internal energy content based on the particle size [30–32].

(8) The entanglement of the thermal and mechanical properties of the system into a state-dependent Hamiltonian introduces no-go theorems that restrict the suitable functional forms of the equations describing the reversible particle interactions. Effectively, the existence of the Hamiltonian Eq. (27) embeds the following necessary relation

$$\left.\frac{\partial\theta}{\partial n}\right|_s = \frac{1}{n^2}\left.\frac{\partial\pi}{\partial s}\right|_n, \tag{72}$$

which is analogous to the macroscopic Maxwell relation [19]. In the context of GenDPDE, Eq. (72) indicates that if the forces depend on the temperature θ (or more properly on s), then the EoS of the particle should have the appropriate volume-dependence through n. Hence, the thermal and mechanical components cannot be independently proposed, but instead must satisfy Eq. (72). Moreover, the existence of the Hamiltonian Eq. (27) also implies that the relation

$$\frac{\partial\mathbf{f}_i^C}{\partial\mathbf{r}_j} = \frac{\partial\mathbf{f}_j^C}{\partial\mathbf{r}_i}, \tag{73}$$

known as Warren's no-go theorem for density-dependent forces [33], is inherently satisfied.

IV. CONCLUSIONS

We revisited the formulation of the GenDPDE method, and rederived the particle thermodynamics to ensure consistency between the local thermodynamics in the mesoscopic systems and the corresponding macroscopic properties. We demonstrated this by introducing unambiguous, physically meaningful definitions of the heat and work, which lead to the formulation of an alternative heat flow model that is analogous to Fourier's law of heat conduction. We presented further analysis of the internal, unresolved DoF of the mesoparticles by considering the thermodynamics of an individual mesoparticle within the GenDPDE framework. Several key implications from the analysis were discovered and discussed, which are summarized as the following. The mesoscopic thermodynamic transformations: (1) are altered by the choice of the dependent variables; (2) introduce additional terms of the order of the size of the local fluctuations, where these fluctuations differentiate the mesoscopic and macroscopic descriptions; (3) require that the particle thermodynamics be considered as a distribution, rather than a thermodynamic potential; (4) allow for a definitive path to determine any dressed thermodynamic quantity from the corresponding bare thermodynamic quantity; and (5) require proper estimators of the macroscopic thermodynamic properties. These implications are critical when considering future extensions or implementations of the GenDPDE framework.

We also considered fundamental questions regarding the thermodynamic description of mesoparticles subject to significant system fluctuations in the context of ST [21,27]. Here the novelty with respect to ST is that the mesoscopic system of the GenDPDE approach is described via local thermodynamic functions related to its internal states, in addition to the mechanical DoF. Compared to the typical structureless systems addressed within the ST framework [21], our mesoscopic system can also store internal energy. The scenario is more varied because energy dissipated through irreversible work in GenDPDE can be shared between the system and the environment, while in structureless colloids it is completely absorbed by the environment. Another difference is that in GenDPDE, we allow direct heat exchange between the system and the environment, while there is no equivalent for the case of a structureless colloid embedded in a fluctuating fluid. This analogy will be further explored elsewhere.

For the alternative heat flow model introduced here, the analysis allowed us to distinguish between the bare and dressed entropies $\tilde{s}$ and s, respectively, from which two estimators of the macroscopic temperature T were derived. We found that compared to the original heat flow model [1], the alternative heat flow model leads to a change in the functional form of the macroscopic heat conductivity coefficient with respect to the state variables. Furthermore, it allowed us to demonstrate that it is essential to use these proper estimators of the system temperature to build the linear Langevin equations [16]. We have also shown that, with the alternative form of the heat flow model, the macroscopic heat conductivity coefficient is independent of the temperature. (Note that general Langevin equations with nonlinear heat flow models require a separate treatment, which is beyond the scope of this work.)

In summary, the GenDPDE framework developed here is capable of tackling the dynamics of complex systems subject to fluctuations within a consistent framework, which provides a direct connection with the underlying physics of the system. As such, other scenarios such as chemical reactions in multiphase systems can be addressed [34,35].

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APPENDIX A: FLUCTUATION-DISSIPATION THEOREM FOR THE ALTERNATIVE HEAT FLOW MODEL

The derivation of the FDT follows the derivation in Appendix B of Ref. [1], which uses the discrete form of the algorithm rather than the stochastic differential equations. Schematically, the numerical discretization algorithm provides a transition from a state point $\tilde{\Gamma} \equiv (\{\mathbf{p}_i\}, \{\mathbf{r}_i\}, \{u_i\})$ at t into a new state point $\tilde{\Gamma}' \equiv (\{\mathbf{p}'_i\}, \{\mathbf{r}'_i\}, \{u'_i\})$ at $t + \delta t$, where the transition is considered as a discrete stochastic process rather than a continuous process. The new state point is a function of the initial state point, system dynamic properties, and the value taken by the collection of random numbers Ω_{ij}. The algorithm can be written as

$$\tilde{\Gamma}' = \hat{\Gamma}[\tilde{\Gamma}, \Omega], \tag{A1}$$

where $\hat{\Gamma}$ is the generic function that specifies the dynamics, and its arguments represent the $\tilde{\Gamma}$-dependent variables. The transition also parametrically depends on δt. The transition probability thus becomes

$$\bar{W}(\tilde{\Gamma} \to \tilde{\Gamma}')\delta t = \langle \delta(\tilde{\Gamma}' - \hat{\Gamma}[\tilde{\Gamma}, \Omega]) \rangle_{\Omega}, \tag{A2}$$

where the subscript Ω indicates that the average is taken over all realizations of the random force pairs Ω_{ij}. From Eq. (A2) and the causal nature of the algorithm, it follows that

$$\int d\tilde{\Gamma}' \bar{W}(\tilde{\Gamma} \to \tilde{\Gamma}')\delta t = \int d\tilde{\Gamma}' \, \langle \delta(\tilde{\Gamma}' - \hat{\Gamma}[\tilde{\Gamma}, \Omega]) \rangle_{\Omega} = 1. \tag{A3}$$

The reverse trajectory is defined as $\tilde{\Gamma}^* \to \tilde{\Gamma}^{*\prime}$, where $\tilde{\Gamma}^* \equiv (\{-\mathbf{p}'_i\}, \{\mathbf{r}'_i\}, \{u'_i\})$ and $\tilde{\Gamma}^{*\prime} \equiv (\{-\mathbf{p}_i\}, \{\mathbf{r}_i\}, \{u_i\})$. The sign change depends on the parity under time reversal of the variable [16]. Note that the discrete nature of the algorithm requires that the initial and final state points also need to be exchanged in the time-reversibility operation.

The stochastic process described by the algorithm satisfies a master equation with the transition probabilities given by Eq. (A2). Under the condition of sufficiently small fluctuations, the master equation can be transformed into a Fokker-Plank equation, characterized only by the first and second moment of the transition probability $\bar{W}(\tilde{\Gamma} \to \tilde{\Gamma}')$ [16]. Therefore, to fix the form of the FDT at the level of the Fokker-Plank equation, we need to determine only the first and second moments of the variable in Eq. (52).

We start the evaluation of the first moment of the particle internal energy distribution by using Eq. (52). While for convenience we consider the dressed entropy s as the independent variable here, equivalently we may also use the particle internal energy u as the independent variable, since the distributions given in Eqs. (5) and (9) are themselves equivalent. Using the DB condition Eq. (52), we have

$$\begin{aligned} &\int d\tilde{\Gamma} d\tilde{\Gamma}' P_{\text{eq}}(\tilde{\Gamma})\, u'_i\, \bar{W}(\tilde{\Gamma} \to \tilde{\Gamma}') \\ &\quad = \int d\tilde{\Gamma} d\tilde{\Gamma}'\, P_{\text{eq}}(\tilde{\Gamma}^*)\, u'_i\, \bar{W}(\tilde{\Gamma}^* \to \tilde{\Gamma}^{*\prime}) \\ &\quad = \int d\tilde{\Gamma}^*\, P_{\text{eq}}(\tilde{\Gamma}^*)\, u^*_i = \langle u_i \rangle, \end{aligned} \tag{A4}$$

where Eq. (A3) was used for the last equality. The transition probability Eq. (A2) and the use of Eq. (58) in Eq. (A4) give

$$\begin{aligned} \int d\tilde{\Gamma}\, P_{\text{eq}}(\tilde{\Gamma}) \Bigg[&\frac{1}{2} \sum_{j \neq i} \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \right) \mathbf{e}_{ij}\, \gamma_{ij} \mathbf{e}_{ij} \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \right) \delta t \\ &- \frac{1}{2m_i} \sum_{j \neq i} \sum_{l \neq i} \left\langle \delta\mathbf{p}^R_{ij} \delta\mathbf{p}^R_{il} \right\rangle_{\xi} + \dot{q}_i \delta t + \sum_{j \neq i} \left\langle \delta u^R_{ij} \right\rangle_{\xi} \Bigg] = 0. \end{aligned} \tag{A5}$$

The contribution due to the conservative force is not included because it identically vanishes due to the positions and velocities being uncorrelated in equilibrium. Similarly, the $[1/2\sum_{j\neq i}(\mathbf{p}_i/m_i - \mathbf{p}_j/m_j)\delta\mathbf{p}_{ij}^R]$ term vanishes since causality indicates that the random momenta is not correlated with the actual value of the velocity. Moreover, the first and second terms identically cancel; see the derivation of the FDT in Ref. [23]. Therefore, Eq. (A5) simplifies to

$$\int d\tilde{\Gamma}\, P_{\mathrm{eq}}(\tilde{\Gamma})\left(\dot{q}_i\delta t + \sum_{j\neq i}\langle\delta u_{ij}^R\rangle_{\bar{\xi}}\right) = 0. \tag{A6}$$

We can now introduce the explicit expression for the alternative heat flow model, and changing the integration variables from $\tilde{\Gamma} \equiv (\mathbf{p}^N, \mathbf{r}^N, u^N)$ to $\Gamma \equiv (\mathbf{p}^N, \mathbf{r}^N, s^N)$, we arrive at

$$\int d\Gamma\, P_{\mathrm{eq}}(\Gamma)\left[-\sum_{j\neq i}\kappa_{ij}(\theta_i - \theta_j)\delta t + \sum_{j\neq i}\langle\delta u_{ij}^R\rangle_{\bar{\xi}}\right] = 0.$$

Since $\langle\theta_i\rangle = \langle\theta_j\rangle = T$, it follows that $\langle\delta u_{ij}^R\rangle_{\bar{\xi}} = 0$. Therefore, the alternative heat flow model introduces no spurious energy drift in the EOM that would need to be compensated by the numerical integration algorithm.

Next, we consider the second moment of the u distribution. Again, using the DB condition Eq. (52) together with Eq. (A3), we have

$$\begin{aligned}\int d\tilde{\Gamma} d\tilde{\Gamma}' P_{\mathrm{eq}}(\tilde{\Gamma})\, u_i' u_j'\, \bar{W}(\tilde{\Gamma} \to \tilde{\Gamma}') \\ = \int d\tilde{\Gamma} d\tilde{\Gamma}'\, P_{\mathrm{eq}}(\tilde{\Gamma}^*)\, u_i' u_j'\, \bar{W}(\tilde{\Gamma}^* \to \tilde{\Gamma}^{*\prime}) \\ = \int d\tilde{\Gamma}^*\, P_{\mathrm{eq}}(\tilde{\Gamma}^*)\, u_i^* u_j^* = \langle u_i u_j\rangle.\end{aligned} \tag{A7}$$

Then using the transition probability Eq. (A2), we obtain

$$\begin{aligned}\int d\tilde{\Gamma}\, P_{\mathrm{eq}}(\tilde{\Gamma})\Bigg(\Bigg\{u_i\Bigg[\frac{1}{2}\sum_{k\neq j}\left(\frac{\mathbf{p}_j}{m_j} - \frac{\mathbf{p}_k}{m_k}\right)\gamma_{jk}\left(\frac{\mathbf{p}_j}{m_j} - \frac{\mathbf{p}_k}{m_k}\right)\delta t - \frac{1}{2m_i}\sum_{k\neq j}\sum_{l\neq j}\langle\delta\mathbf{p}_{jk}^R\delta\mathbf{p}_{jl}^R\rangle_{\xi}\Bigg]\Bigg\} \\ + (i \leftrightarrow j) + (u_i\,\dot{q}_j + u_j\,\dot{q}_i)\delta t + \langle\delta u_i^R\delta u_j^R\rangle_{\bar{\xi}} + \frac{1}{4}\sum_{k\neq i}\sum_{l\neq j}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_k}{m_k}\right)\langle\delta\mathbf{p}_{ik}^R\delta\mathbf{p}_{jl}^R\rangle_{\xi}\left(\frac{\mathbf{p}_j}{m_j} - \frac{\mathbf{p}_l}{m_l}\right)\delta t\Bigg) = 0.\end{aligned} \tag{A8}$$

In Ref. [23], we have already shown that the sum of the terms involving momenta identically cancel; therefore, we are left with

$$\int d\tilde{\Gamma}\, P_{\mathrm{eq}}(\tilde{\Gamma})\big[(u_i\,\dot{q}_j + u_j\,\dot{q}_i)\delta t + \langle\delta u_i^R\delta u_j^R\rangle_{\bar{\xi}}\big] = 0. \tag{A9}$$

Analogous to the simplification of Eq. (A6) when evaluating the first moment, we can substitute the explicit expression for the alternative heat flow model, and change the integration variables from $\tilde{\Gamma} \equiv (\mathbf{p}^N, \mathbf{r}^N, u^N)$ to $\Gamma \equiv (\mathbf{p}^N, \mathbf{r}^N, s^N)$. After which, we arrive at

$$\int d\Gamma\, P_{\mathrm{eq}}(\Gamma)\left(-u_j\sum_k\kappa_{ik}\theta_k\,\delta t - u_i\sum_l\kappa_{jl}\theta_l\,\delta t + \langle\delta u_i^R\delta u_j^R\rangle_{\bar{\xi}}\right) = 0, \tag{A10}$$

where we introduced $\kappa_{ii} \equiv -\sum_{j\neq i}\kappa_{ij}$ and extended the summation to all the particles, for compactness of the notation. According to Eq. (61), the random energy correlation is

$$\langle\delta u_i^R\delta u_j^R\rangle_{\bar{\xi}} = \sum_{k\neq i}\sum_{l\neq j}\alpha_{ik}\alpha_{jl}\langle\bar{\xi}_{ik}\bar{\xi}_{jl}\rangle\delta t = \left[\sum_{k\neq i}\alpha_{ik}^2\delta_{ij} - \alpha_{ij}^2(1-\delta_{ij})\right]\delta t. \tag{A11}$$

Next, to determine the FDT expression for α_{ij}, we start with Eq. (A10), and first consider only the case of $j \neq i$. Since the integration with respect to momenta and positions can be straightforwardly performed at the end, we focus on the integration with respect to u, while keeping the mesoparticle positions fixed. Furthermore, because the system is in contact with a heat reservoir of temperature T, u_i of each mesoparticle can vary independently because the total energy is not fixed. Therefore, we can switch to s as the independent variable, and by using

$$\frac{\partial}{\partial s_k}e^{\sum_r[s_r/k_B - u_r/(k_BT)]} = \left(\frac{1}{k_B} - \frac{\theta_k}{k_BT}\right)e^{\sum_r[s_r/k_B - u_r/(k_BT)]},$$

the first term on the left-hand side of Eq. (A9) becomes

$$\begin{aligned}\int ds_1\ldots ds_N\, e^{\sum_r[s_r/k_B - u_r/(k_BT)]}\left(u_i\sum_k\kappa_{jk}\,\theta_k\right) \\ = \int ds_1\ldots ds_N\, e^{\sum_r[s_r/k_B - u_r/(k_BT)]}\left[\sum_k\kappa_{jk}\,T\left(1 + k_B\frac{\partial}{\partial s_k}\right)u_i\right] \\ = \int ds_1\ldots ds_N\, e^{\sum_r[s_r/k_B - u_r/(k_BT)]}\, k_BT\theta_i\,\kappa_{ji} \\ = \int ds_1\ldots ds_N\, e^{\sum_r[s_r/k_B - u_r/(k_BT)]}\, k_B\theta_j\theta_i\,\kappa_{ji}.\end{aligned} \tag{A12}$$

In Eq. (A12), we considered $j \neq i$ only, where the last equality follows from the independence of the integrations on each mesoparticle.

The case when $i = j$ is obtained using $\kappa_{ii} \equiv -\sum_{j \neq i} \kappa_{ij}$:

$$\begin{aligned} &\int ds_1 \dots ds_N \, e^{\sum_r [s_r/k_B - u_r/(k_B T)]} \, k_B T \theta_i \, \kappa_{ii} \\ &\quad = -\int ds_1 \dots ds_N \, e^{\sum_r [s_r/k_B - u_r/(k_B T)]} \, k_B T \theta_i \sum_{j \neq i} \kappa_{ji} \\ &\quad = \int ds_1 \dots ds_N \, e^{\sum_r [s_r/k_B - u_r/(k_B T)]} \left(-k_B \sum_{j \neq i} \theta_j \theta_i \, \kappa_{ji} \right). \end{aligned} \tag{A13}$$

By combining Eqs. (A11), (A12), and (A13) along with $\kappa_{ij} = \kappa_{ji}$, the FDT becomes

$$\alpha_{ij}^2 = 2 k_B \, \kappa_{ij} \, \theta_i \theta_j. \tag{A14}$$

Note that the replacement of T by θ in Eqs. (A11) and (A12) was possible because it did not change the values of the integrals. This replacement allows us to define the system dynamics in terms of the particle properties only; however, note that this would not be possible if κ_{ij} was a function of θ or u.

APPENDIX B: NUMERICAL DISCRETIZATION ALGORITHM

The integration of the EoM [Eqs. (53), (54), and (58)] with the alternative heat flow model, Eq. (62) supplemented with Eq. (61), was performed using the extended Shardlow splitting algorithm (eSSA) [1,25]. The eSSA separates the integration into reversible and irreversible terms with the overall solution operator [36], $\Phi_{\delta t}$, given as

$$\begin{aligned} \Phi_{\delta t} \simeq\ & \Phi^{\mathrm{irrev}}_{\delta t;1,2} \circ \Phi^{\mathrm{irrev}}_{\delta t;1,3} \circ \dots \circ \Phi^{\mathrm{irrev}}_{\delta t;i,j} \circ \dots \circ \Phi^{\mathrm{irrev}}_{\delta t;N-2,N} \\ & \times \circ \Phi^{\mathrm{irrev}}_{\delta t;N-1,N} \circ \Phi^{\mathrm{rev}}_{\delta t}. \end{aligned} \tag{B1}$$

The reversible term $\Phi^{\mathrm{rev}}_{\delta t}$ corresponds to

$$\begin{aligned} d\mathbf{r}_i &= \frac{\mathbf{p}_i}{m_i} \, \delta t \quad (i = 1, \dots, N), \\ d\mathbf{p}_i &= \mathbf{f}_i^C \, \delta t, \\ du_i &= -\frac{1}{2} \sum_{j \neq i} \mathbf{v}_{ij} \mathbf{f}_{ij}^C \, \delta t, \end{aligned} \tag{B2}$$

where $\mathbf{f}_i^C = \sum_{j \neq i} \mathbf{f}_{ij}^C$ and $\mathbf{v}_{ij} = \mathbf{p}_i/m_i - \mathbf{p}_j/m_j$.

The reversible term $\Phi^{\mathrm{rev}}_{\delta t}$ is discretized using the velocity-Verlet algorithm [37] as

$$\begin{aligned} \mathbf{p}_i\left(t + \frac{\delta t}{2}\right) &= \mathbf{p}_i(t) + \frac{\delta t}{2} \mathbf{f}_i^C(t) \quad (i = 1, \dots, N), \\ \mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \delta t \, \frac{\mathbf{p}_i\left(t + \frac{\delta t}{2}\right)}{m_i}, \\ u_i\left(t + \frac{\delta t}{2}\right) &= u_i(t) - \frac{\delta t}{4} \sum_{j \neq i} \mathbf{v}_{ij}(t) \mathbf{f}_{ij}^C(t), \\ & \mathrm{evaluate:} \left\{ \mathbf{f}_{\mathrm{i}}^{\mathrm{C}}(\mathrm{t} + \delta \mathrm{t}) \right\}_{\mathrm{i}=1}^{\mathrm{N}}, \\ \mathbf{p}_i(t + \delta t) &= \mathbf{p}_i\left(t + \frac{\delta t}{2}\right) + \frac{\delta t}{2} \mathbf{f}_i^C(t + \delta t) \quad (i = 1, \dots, N), \\ & \mathrm{evaluate:} \left\{ \sum_{\mathrm{j} \neq \mathrm{i}} \mathbf{v}_{\mathrm{ij}}(\mathrm{t} + \delta \mathrm{t}) \mathbf{f}_{\mathrm{ij}}^{\mathrm{C}}(\mathrm{t} + \delta \mathrm{t}) \right\}_{\mathrm{i}=1}^{\mathrm{N}}, \\ u_i(t + \delta t) &= u_i\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{4} \sum_{j \neq i} \mathbf{v}_{ij}(t + \delta t) \mathbf{f}_{ij}^C(t + \delta t) \quad (i = 1, \dots, N). \end{aligned} \tag{B3}$$

Each irreversible term $\Phi^{\mathrm{irrev}}_{\delta t;i,j}$ then corresponds to

$$\begin{aligned} d\mathbf{p}_i^{i-j} &= \mathbf{f}_{ij}^{D,i-j} \, \delta t + \delta \mathbf{p}_{ij}^{R,i-j}, \\ d\mathbf{p}_j^{i-j} &= -d\mathbf{p}_i^{i-j}, \end{aligned} \tag{B4}$$

$$\begin{aligned} du_i^{i-j} &= -\frac{1}{2} d\left(\frac{\mathbf{p}_i^{i-j} \mathbf{p}_i^{i-j}}{2m_i} + \frac{\mathbf{p}_j^{i-j} \mathbf{p}_j^{i-j}}{2m_j} \right) + q_{ij}^{i-j} \, \delta t + \delta u_{ij}^{R,i-j}, \\ du_j^{i-j} &= -\frac{1}{2} d\left(\frac{\mathbf{p}_i^{i-j} \mathbf{p}_i^{i-j}}{2m_i} + \frac{\mathbf{p}_j^{i-j} \mathbf{p}_j^{i-j}}{2m_j} \right) - q_{ij}^{i-j} \, \delta t - \delta u_{ij}^{R,i-j}, \end{aligned} \tag{B5}$$

where the superscript $i - j$ indicates that the variation of momenta and particle internal energy is considered for a pair of interacting particles i and j only.

Each irreversible term $\Phi^{\text{irrev}}_{\delta t;i,j}$ can also be discretized using the velocity-Verlet algorithm [1,25] as

$$\begin{aligned}
\mathbf{p}_i\left(t + \frac{\delta t}{2}\right) &= \mathbf{p}_i(t) - \frac{\delta t}{2}\gamma_{ij}\mathbf{v}_{ij}(t)\mathbf{e}_{ij}\mathbf{e}_{ij} + \frac{\delta t^{1/2}}{2}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij},\\
\mathbf{p}_j\left(t + \frac{\delta t}{2}\right) &= \mathbf{p}_j(t) + \frac{\delta t}{2}\gamma_{ij}\mathbf{v}_{ij}(t)\mathbf{e}_{ij}\mathbf{e}_{ij} - \frac{\delta t^{1/2}}{2}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij},\\
\mathbf{p}_i(t + \delta t) &= \mathbf{p}_i\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2}\frac{\gamma_{ij}}{1 + \frac{M_{ij}}{2}\gamma_{ij}\delta t}\left\{\mathbf{v}_{ij}\left(t + \frac{\delta t}{2}\right)\mathbf{e}_{ij}\mathbf{e}_{ij} + \frac{\delta t^{1/2}}{2}M_{ij}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij}\right\}\\
&\quad + \frac{\delta t^{1/2}}{2}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij},\\
\mathbf{p}_j(t + \delta t) &= \mathbf{p}_j\left(t + \frac{\delta t}{2}\right) + \frac{\delta t}{2}\frac{\gamma_{ij}}{1 + \frac{M_{ij}}{2}\gamma_{ij}\delta t}\left\{\mathbf{v}_{ij}\left(t + \frac{\delta t}{2}\right)\mathbf{e}_{ij}\mathbf{e}_{ij} + \frac{\delta t^{1/2}}{2}M_{ij}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij}\right\}\\
&\quad - \frac{\delta t^{1/2}}{2}\sqrt{k_B\gamma_{ij}(\theta_i + \theta_j)}\,\xi_{ij}\mathbf{e}_{ij},\\
u_i(t + \delta t) &= u_i(t) - \frac{1}{2}\left[\frac{\mathbf{p}_i(t + \delta t)\mathbf{p}_i(t + \delta t)}{2m_i} + \frac{\mathbf{p}_j(t + \delta t)\mathbf{p}_j(t + \delta t)}{2m_j} - \frac{\mathbf{p}_i(t)\mathbf{p}_i(t)}{2m_i} - \frac{\mathbf{p}_j(t)\mathbf{p}_j(t)}{2m_j}\right]\\
&\quad - \delta t\,\kappa_{ij}(\theta_i - \theta_j) + \delta t^{1/2}\sqrt{2k_B\kappa_{ij}\theta_i\theta_j}\,\bar{\xi}_{ij},\\
u_j(t + \delta t) &= u_j(t) - \frac{1}{2}\left[\frac{\mathbf{p}_i(t + \delta t)\mathbf{p}_i(t + \delta t)}{2m_i} + \frac{\mathbf{p}_j(t + \delta t)\mathbf{p}_j(t + \delta t)}{2m_j} - \frac{\mathbf{p}_i(t)\mathbf{p}_i(t)}{2m_i} - \frac{\mathbf{p}_j(t)\mathbf{p}_j(t)}{2m_j}\right]\\
&\quad + \delta t\,\kappa_{ij}(\theta_i - \theta_j) - \delta t^{1/2}\sqrt{2k_B\kappa_{ij}\theta_i\theta_j}\,\bar{\xi}_{ij},
\end{aligned}\tag{B6}$$

where $M_{ij} = 1/m_i + 1/m_j$, and the superscript $i - j$ has been omitted for notation simplicity. Before these equations are applied to a subsequent pair of particles, the particle temperatures θ_i and θ_j are updated through the mesoscopic EoS using the updated particle internal energies.

[1] J. B. Avalos, M. Lísal, J. P. Larentzos, A. D. Mackie, and J. K. Brennan, Phys. Chem. Chem. Phys. **21**, 24891 (2019).

[2] S. Y. Trofimov, E. L. F. Nies, and M. A. J. Michels, J. Chem. Phys. **117**, 9383 (2002).

[3] P. B. Warren, Phys. Rev. E **68**, 066702 (2003).

[4] J. D. Moore, B. C. Barnes, S. Izvekov, M. Lísal, M. S. Sellers, D. E. Taylor, and J. K. Brennan, J. Chem. Phys. **144**, 104501 (2016).

[5] J. P. Larentzos, J. M. Mansell, M. Lísal, and J. K. Brennan, Mol. Phys. **116**, 3271 (2018).

[6] P. Vanya, J. Sharman, and J. A. Elliot, J. Chem. Phys. **150**, 064101 (2019).

[7] K. M. Lebold and W. G. Noid, J. Chem. Phys. **150**, 014104 (2019).

[8] I. Pagonabarraga and D. Frenkel, J. Chem. Phys. **115**, 5015 (2001).

[9] P. B. Warren, Phys. Rev. Lett. **87**, 225702 (2001).

[10] J. B. Avalos and A. D. Mackie, Europhys. Lett. **40**, 141 (1997).

[11] P. Espanol, Europhys. Lett. **40**, 631 (1997).

[12] T. Herpich, K. Shayanfard, and M. Esposito, Phys. Rev. E **101**, 022116 (2020).

[13] C. Bustamante, Z. Bryant, and S. B. Smith, Nature (London) **421**, 423 (2003).

[14] C. Bustamante, J. Liphardt, and F. Ritort, Phys. Today **58**(7), 43 (2005).

[15] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover Publications, New York, NY, 1984).

[16] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North Holland, Amsterdam, 1992).

[17] P. Mazur and D. Bedeaux, Physica A **173**, 155 (1991).

[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.103.062128 for a list of symbols and notation used throughout the manuscript.

[19] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, New York, 1985).

[20] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005).

[21] K. Sekimoto, *Stochastic Energetics*, Lecture Notes in Physics (Springer, Berlin, 2010), Vol. 799.

[22] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing, MA, 1996).

[23] J. B. Avalos, M. Antuono, A. Colagrossi, and A. Souto-Iglesias, Phys. Rev. E **101**, 013302 (2020).

[24] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).

[25] M. Lísal, J. K. Brennan, and J. B. Avalos, J. Chem. Phys. **135**, 204105 (2011).

[26] J. B. Avalos and A. D. Mackie, J. Chem. Phys. **111**, 5267 (1999).

[27] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).

[28] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).

[29] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).

[30] T. L. Hill, J. Chem. Phys. **36**, 3182 (1962).

[31] S. Kjelstrup, S. K. Schnell, T. J. H. Vlugt, J.-M. Simon, A. Bardow, D. Bedeaux, and T. Trinh, Adv. Nat. Sci.-Nanosci. **5**, 023002 (2014).

[32] H. Qian, S. Kjelstrup, A. B. Kolomeisky, and D. Bedeaux, J. Phys.: Condens. Matter **28**, 153004 (2016).

[33] P. B. Warren, Phys. Rev. E **87**, 045303 (2013).

[34] M. Lísal, J. P. Larentzos, M. S. Sellers, I. V. Schweigert, and J. K. Brennan, J. Chem. Phys. **151**, 114112 (2019).

[35] M. Lísal, W. R. Smith, and I. Nezbeda, J. Chem. Phys. **113**, 4885 (2000).

[36] T. Shardlow, SIAM J. Sci. Comput. **24**, 1267 (2003).

[37] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Cambridge, UK, 2017).