Generalised Energy-Conserving Dissipative Particle Dynamics with Mass Transfer. Part 1: Theoretical Foundation and Algorithm

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Abstract

An extension of the Generalised Energy-Conserving Dissipative Particle Dynamics method (GenDPDE) that allows mass transfer between mesoparticles via a diffusion process is presented. By considering the concept of the mesoparticles as *property carriers*, the complexity and flexibility of the GenDPDE framework was enhanced to allow for interparticle mass transfer under isoenergetic conditions, notated here as GenDPDE-M. In the formulation, the diffusion is described via the theory of mesoscale irreversible processes based on linear relationships between the fluxes and the thermodynamic forces, where their fluctuations are described by Langevin-like equations. The mass exchange between mesoparticles is such that the mass of the mesoparticle remains unchanged after the transfer process, and requires additional considerations regarding the coupling with other system properties such as the particle internal energy. The proof-of-concept work presented in this manuscript is the first part of a two-part manuscript series. In Part 1, the development of the GenDPDE-M theoretical framework and the derivation of the algorithm are presented in detail. Part 2 of this manuscript series is targeted for practitioners, where applications, demonstrations and practical considerations for implementing the GenDPDE-M method is presented and discussed.

1 INTRODUCTION

Micro- and mesoscale (below 1μm) phenomena play a dominant role in the resulting macroscopic properties for a wide variety of material types, e.g., soft matter, biological matter, complex fluids, composite materials, additively-manufactured materials, and many more. In many cases, the system can be divided into small domains with nearly homogeneous properties, whose behavior nevertheless dictates the long wavelength properties and response to stimuli such as mechanical, electrical, or thermal loading. Furthermore, the behavior of fluids and condensed matter systems, viewed from smaller scale dimensions, can differ significantly from their macroscale behavior, e.g., fluids in confinement. Both the spatial and temporal

breadth of the systems of such interest preclude the use of atomistic modelling. To bridge this gap, coarse-grain (CG) particle modelling and simulation is a valuable approach to study micro- and mesoscale phenomena because it overcomes these challenges that are encountered when applying atomistic and continuum approaches. A plethora of CG particle modelling studies of microscale phenomena can be found in the literature that exemplify the utility of CG approaches. Studies have been performed over an extensive scope of materials and applications, including, but not limited to, the life sciences (proteins, colloidal suspensions, bio-membranes, micelles), industrial applications (surfactants, asphaltenes, viscoelastic fluids), national defence applications (energetic material composites, liquid propellants), and novel materials (self-assembled block copolymers/nanoparticles).[1–17]

Presently, the most rigorous approaches for developing CG models occur in a bottom-up fashion, where groups of atoms are mapped onto a statistically-equivalent ensemble of structureless CG particles.[5,7,14,18–20] These bottom-up techniques target mapping to pairwise interactions, resulting in CG potentials that do not capture many-body interactions. However, it is now well recognised that these many-body interactions are critical for remediating the accuracy and transferability of the models for conditions beyond the parameterisation space.[5,12,14] As a means of addressing these deficiencies, a class of CG models that are both density- and temperature-dependent has recently emerged. These models have several key attributes, including robust transferability, scaling invariance, and the absence of unphysical ordered phases that can occur for pairwise-only CG models.[21] Such models may be built from higher resolution models,[12,22] or may be a many-body force field based on an equation-of-state (MB-FF-EoS).[21]

During this growing trend towards density- and temperature-dependent CG models, typically these models have been simulated at isothermal conditions, while non-isothermal simulations have been less common. However, non-isothermal conditions arise in many standard physical circumstances, e.g., under thermal, density, or concentration gradients, in response to mechanical and/or thermal loading, and from endo- and exothermic chemical reactivity.

For appropriately simulating any type of CG model at non-isothermal conditions, dissipative particle dynamics with energy conservation (DPDE)[23,24] is a CG methodology that has proven its applicability in a wide range of cases.[12,13,25–34] However, additional considerations arise when implementing a density- and temperature-dependent force field within the DPDE framework, since both the local particle density and particle temperature are fluctuating, and contribute to the interparticle forces and energies. As such, the simulation of density- and temperature-dependent CG models under non-isothermal conditions requires the recently developed *generalised* DPDE method (GenDPDE).[35,36] In addition to providing the appropriate simulation algorithm, the family of DPDE methods (DPDE,[23–25] DPDH[29] and GenDPDE) provides a mechanism to recover the unresolved (CG) degrees-of-freedom (DoF), which are a consequence of the CG mapping. Indeed, it is this mechanism that will allow us to address a key phenomenon lacking in CG particle modelling and simulation – mass transfer between CG particles.

Mass transfer via diffusion is the macroscopic manifestation of the distinctive motion of the species with respect to the mainstream velocity, typically represented by the so-called barycentric velocity $\mathbf{v}$, defined from the momentum density $\mathbf{j} = \sum_k \rho_k \mathbf{v}_k \equiv \rho\mathbf{v}$, where ρ is the total mass density, ρ_k is the mass density of species k, and $\mathbf{v}_k$ is its velocity. These diffusive fluxes are caused by chemical potential gradients occurring at the microscale, which are themselves dependent on pressure, temperature and concentration gradients. By construction,[37] the diffusive fluxes $\mathbf{J}_k$ are not all independent, as they are defined as deviations from the mainstream material flow, $\mathbf{J}_k \equiv \rho_k(\mathbf{v}_k - \mathbf{v})$, and hence $\sum_k \mathbf{J}_k = 0$.

Diffusion is a widely occurring phenomenon in many classes of materials and processes. Examples of diffusion-governed systems can be found in materials processing, extraction, and refining, which involve complex fluid mixtures that segregate or phase separate. The CG methodology presented in this series is targeted for such fluid mixtures, particularly those mixtures that contain inhomogeneity with respect to density, as the diffusive behavior will vary in the localized density regions. Some example systems include colloid structure

and transport in solution, and multi-phase fluid flow in confinement (e.g., channels) or near material interfaces. The archetypical system is a multicomponent multiphase fluid with or without thermal gradients; GenDPDE-M mesoparticles carrying composition can describe such a situation using EoS information, while any other CG method would require particles of different species and appropriate potentials between them to reproduce the observed phase diagram. Furthermore, chemically reacting systems can also be governed by diffusion, adding to the complexity required for predictive CG particle modelling and simulation. Examples include chemical separation in confinement or the reactive response of a material system (e.g., composite) under thermal or mechanical loading. In the latter case, as compressive or tensile waves move through the material, density localizations or gradients will arise. To accurately capture the reactive response of such systems, particularly those with a low Damköhler number, a CG methodology that can simulate inter-particle mass transfer is required. While it may be reasonable under some conditions to neglect mass transfer between particles (e.g., reacting systems with large Damköhler numbers), even in those circumstances, as the CG model resolution increases (i.e., less DoF are coarse grained into the model) this assumption becomes nebulous. Some specific potential applications include diffusion-governed mixing of reactive laminates,[?] and the reactive response of shocked materials.[10]

The development of a particle-based CG method that can simulate diffusion-governed behavior would address this computational gap in microscale modeling and simulation. As such, in this work, we present an extension of the GenDPDE method that allows mass transfer between CG particles via a diffusion process, termed Generalised Energy-Conserving Dissipative Particle Dynamics with Mass Transfer (GenDPDE-M). In the formulation, the diffusion is described via Onsager's theory of linear irreversible processes formulated at the mesoscale, based on relationships between the fluxes and the thermodynamic forces,[37] where their fluctuations are described by Langevin-like equations.[38] The basic ingredient of the GenDPDE method and the extension presented here, GenDPDE-M, is the definition of a particle mesoscopic thermodynamic description, which accounts for the physical behavior

of the CG DoF. While in the former such an internal state was characterized by the particle temperature, mass and local volume, in GenDPDE-M we add the particle composition, which can vary due to interparticle diffusive processes. Our formulation of these diffusive processes is analogous to the Maxwell-Stefan theory of multi-component diffusion,[39] where the material exchange between the CG particles is such that the mass of the mesoparticles remains unchanged after the mass-transfer process.[37,39] While this choice may appear restrictive, it is actually necessary, since some extensive property is required to be fixed to define the mesoparticle size, and thus provide a complete definition of the mesoparticle thermodynamic state. Without loss of physical consistency, other choices for defining the mesoparticle size are possible, such as fixing the mesoparticle volume, fixing the mass of a given species, or fixing the number of physically-embedded particles in the mesoparticle itself, i.e., fixing the molar content (see ref.,[37] Ch. XI, §. 2). However, such alternatives would influence the dynamics of the mesoparticle in the form of additional forces related to the mass variation, which would complicate the implementation and physical interpretation of the results. In summary, keeping the mesoparticle mass fixed during the material exchange is the only possible choice that complies with the classical non-equilibrium formulation of the balance equations, described in terms of the barycentric velocity, rendered in Lagrangian form.

The development of the GenDPDE-M method from the extension of the GenDPDE framework requires the formulation of the dynamic equation for the particle concentration change and the corresponding fluctuation-dissipation relation, along with the mechanical equations-of-motion (EoM). The isoenergetic interparticle mass transfer, considered here as a particular situation for proof-of-concept, demands additional considerations regarding the coupling with other system scalar properties, such as the particle internal energy. The general coupling between energy and material transport involves the explicit consideration of the Ludwig-Soret effect,[37] which will be addressed elsewhere.

The work presented in this manuscript is the first of a two-part manuscript series. In this work, Part 1, the development of the GenDPDE-M theoretical framework and the derivation

of the algorithm are presented. To allow us to investigate the subtleties of the method when both energy and mass exchange simultaneously occur, we employ a simple generic model for verification purposes. We explore various conceptual scenarios that enable us to establish an appropriate and consistent theoretical approach. Part 2 of this manuscript series is targeted for practitioners, where applications, demonstrations and practical considerations for implementing the GenDPDE-M method are presented and discussed, including a numerical discretisation algorithm, which is based upon a Shardlow-splitting algorithm.[29,35,40] In particular, in Part 2, demonstrations of the method are presented using the ideal gas and van der Waals equations-of-state as models for the particle internal thermodynamics, at both equilibrium and non-equilibrium conditions.

2 METHODOLOGY

Before proceeding with the description of the GenDPDE-M methodology, it may be helpful to place the method within the appropriate context of other DPD approaches. In the original DPD formulation,[? ?] and subsequent works to establish its physical connection,[41?] mesoparticles interact via pair-wise conservative short-range repulsion forces, and non-conservative dissipative and random forces; the latter acting as a thermostat set at some external reservoir temperature T. These mesoparticles are implicitly considered as fixed-volume systems that represent groups of atoms or molecules, molecular fragments, or "fluid packets", whose state is defined only by a position vector and its velocity. Using a top-down parameterization approach, the interaction parameters are usually related to the Flory-Huggins χ-parameters[41] or fit to experimental observables.[? ?] While using a bottom-up approach, these mesoparticle interactions can also be parameterized by deriving conservative interactions coarse-grained from structure matching,[18] force matching,[? ?] or relative entropy[? ?] approaches.

For modeling more complex behavior, such as vapor-liquid coexistence, as well as improving the overall transferability of the mesoparticle models, density-dependent potentials

were introduced.[42,43] For such models, the mesoparticles are considered to have a variable volume defined via the local particle density, giving rise to density-dependent conservative forces between the particles, and a local concept of "pressure". The local particle density can be introduced into the dynamics through a repulsion-amplitude parameter,[42] or alternatively using local density-dependent potentials defined through local EoS models,[43] or can be application-specific.[44? ?] Despite these improvements, these many-body models (MB-FF-EoS) can only describe isothermal conditions.

The development of the DPDE method was a step forward. DPDE extends the DPD method to non-isothermal conditions by including an internal energy variable associated with each mesoparticle.[23,24] This particle internal energy implicitly treats the states of the coarse-grain DoF embedded within each mesoparticle in a thermodynamic manner. Thus, the particle internal energy is associated with a particle temperature via an additional mesoscopic EoS; therefore, heat transport can be described at the mesoscopic level. While the conservative interactions in DPDE are analogous to those in the original formulation of DPD, density-dependent potentials were also introduced.[12,29] An interesting application has been utilized in the DPDE-RX method, where mesoparticles are conceptualised as CG reactors that mimic evolving species' chemistry.[16]

From a more general perspective, mesoparticle models can be considered as *property carriers*, which may include mass, energy and volume simultaneously. From this viewpoint, GenDPDE introduces a *particle thermodynamics* in a generalized way,[35,36] as the fundamental basis for consistently incorporating density- and temperature-dependent potentials. GenDPDE has been demonstrated for non-isothermal MB-FF-EoS,[35,36] as well as for mesoparticles treated as CG chemical reactors in the GenDPDE-RX method.[?] The inclusion of variable composition systems in the GenDPDE-M method is therefore a natural extension.

In more detail, the GenDPDE method[35] a mesoparticle represents a collection of physical entities such as molecules, atoms or ions, which are embedded within. Each mesoparticle encompasses a volume estimated as $\mathcal{V}_i = 1/n_i$, where n_i is the local particle (number)

density; both quantities depend on the local environment comprised of the neighboring mesoparticles. As a property carrier, its state is specified by the values of the properties that are transported with the mesoparticle, i.e., in addition to $\mathcal{V}_i$, the mass m_i, position $\mathbf{r}_i$, momentum $\mathbf{p}_i$, and internal energy u_i. In practice, the GenDPDE method performs isoenergetic simulations with particle interactions that are both density- and temperature-dependent, while the isothermal MB-FF-EoS methods performs isothermal simulations with particle interactions that are density-dependent only, or that parametrically depend on some external reservoir temperature T, kept constant.[42? –45]

Building further upon the property carrier concept within the GenDPDE framework, the mesoparticle composition is another property that can be transported and exchanged between mesoparticles. This extension of the GenDPDE method is the key element of the GenDPDE-M method introduced in this work. In addition to the properties m_i, $\mathbf{r}_i$, $\mathbf{p}_i$, u_i, and $\mathcal{V}_i$, the state of a mesoparticle in GenDPDE-M includes its chemical composition, which is specified by the set $\{m_i^\alpha\}_{\alpha=1}^{N_s}$, where N_s is the number of different types of chemical species α embedded in mesoparticle i, each with mass m_i^α. Similar to the Maxwell-Stefan theory of multi-component diffusion,[39] the extra condition, $m_i = \sum_{\alpha=1}^{N_s} m_i^\alpha = \text{constant}$, is imposed such that only the $N_s - 1$ embedded-species masses need to be specified. Maintaining the mesoparticle mass fixed during the material exchange ensures that the internal thermodynamic state of the mesoparticle is unambiguously defined, provides a means of appropriately defining the mesoparticle size, and complies with the classical non-equilibrium formulation of the balance equations in Lagrangian form.

In the following, we first review GenDPDE since it is the reference method from which the GenDPDE-M is constructed. We then define and describe the dynamics of the mesoparticle composition within the GenDPDE-M framework. For proof-of-concept purposes, we introduce simple generic models for the energy and mass exchange for the conditions of the mesoparticles fixed in space. These simple models allow for an unambiguous analysis of the simultaneous energy- and mass-exchange EoM under various physical conditions, which are

presented in the results section.

2.1 GenDPDE Equations-of-Motion

Since the mesoparticles have a constant mass, the GenDPDE-M method has the same EoM for the mechanical variables $\mathbf{r}_i$ and $\mathbf{p}_i$ as the GenDPDE method.[35] The starting point of the GenDPDE formulation is the generalized Hamiltonian for the system of N mesoparticles

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i(\mathbf{p}_i, s_i, \mathcal{V}_i) = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m_i} + u_i\left(s_i, \mathcal{V}_i\right) \right] \tag{1}$$

where s_i is the so-called *dressed* particle entropy (definition provided later), and the particle volume $\mathcal{V}_i = 1/n_i$ is related to the local particle density,

$$n_i = \sum_{j \neq i} w_{ij}, \tag{2}$$

where $w_{ij} \equiv w(r_{ij})$ is a smooth, monotonically decreasing ($dw_{ij}/dr_{ij} < 0$), non-negative, spherically symmetric weighting function, vanishing with the interparticle distance $r_{ij} \geq R_{cut}$; R_{cut} is the cut-off range, and w_{ij} is normalised so that $4\pi \int_0^{R_{cut}} w(r)\, r^2\, dr = 1$ (cf. footnote* regarding a notation change from the original work).

The equilibrium distribution for the system of N mesoparticles in the canonical ensemble is

$$P_{eq}(\Gamma)\, d\Gamma \propto e^{\sum_i [T s_i - \mathcal{H}_i(\mathbf{p}_i, s_i, \mathcal{V}_i)]/(k_B T)}\, d\Gamma \tag{3}$$

where $\Gamma = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N, \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, s_1, s_2, \ldots, s_N)$, T is the system (reservoir) temperature, and k_B is the Boltzmann constant. The set of variables Γ is referred to as *control variables*, which play a central role in the mesoscopic thermodynamic framework developed

*In the original formulation of the GenDPDE method,[35] a non-normalised w_{ij} was used, where the normalising factor explicitly appeared in the definition of the local particle density and the pairwise conservative force.

here. Further, it is convenient to introduce the functional

$$\mathcal{F}(\Gamma) = \sum_i [\mathcal{H}_i(\mathbf{p}_i, s_i, \mathcal{V}_i) - T s_i] \tag{4}$$

which is defined from Eq. (3) as $P(\Gamma) \propto e^{-\mathcal{F}(\Gamma)/(k_B T)}$. The equilibrium distribution of Eq. (3) is derived from classical statistical mechanics and represents the link between the equilibrium properties of the mesoscopic system and the underlying physical system. To make this link more evident, consider a transformation to a different set of control variables, where the entropy s_i is replaced by the internal energy u_i, i.e., $\tilde{\Gamma} = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N, \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, u_1, u_2, \ldots, u_N)$. Hence, Eq. (3) can be rewritten as

$$P_{eq}(\tilde{\Gamma})\, d\tilde{\Gamma} \propto e^{\sum_i [T\tilde{s}_i(u_i, \mathcal{V}_i) - \mathcal{H}_i(\mathbf{p}_i, u_i, \mathcal{V}_i)]/(k_B T)}\, d\tilde{\Gamma} \tag{5}$$

where the *bare* particle entropy $\tilde{s}_i$ has been introduced as

$$\begin{aligned} \tilde{s}_i &= s_i(u_i, n_i) + k_B \ln \left| \frac{\partial \Gamma}{\partial \tilde{\Gamma}} \right| && (6) \\ &= s_i(u_i, n_i) + k_B \ln \left. \frac{\partial s_i}{\partial u_i} \right|_{\mathcal{V}_i} && (7) \end{aligned}$$

The bare entropy $\tilde{s}_i$ is directly related to the density of states $g(u_i, \mathcal{V}_i)$ of the unresolved (CG) DoF of the mesoparticle, i.e.,[36,46]

$$\tilde{s}_i = k_B \ln g(u_i, \mathcal{V}_i) \tag{8}$$

Note that Eq. (6) is in fact a differential equation that yields the functional form of the dressed entropy s_i in terms of the resolved variables u_i and $\mathcal{V}_i$. We further require that any specified measure obtained from Eq. (5) remain invariant for the distribution in Eqs. (3), as well as for any other distribution that results from a control variable transformation. For

the set of control variables in Eq. (5), we can define an analogous functional to $\mathcal{F}$, i.e.,

$$\tilde{\mathcal{F}}(\tilde{\Gamma}) = \sum_i [\mathcal{H}_i(\mathbf{p}_i, u_i, \mathcal{V}_i) - T\tilde{s}_i(u_i, \mathcal{V}_i)] \tag{9}$$

Analogous to the macroscopic system, the existence of the function $u_i(s_i, \mathcal{V}_i)$ allows the (inherently fluctuating) mesoparticle intensive properties to be defined, i.e.,

$$\begin{aligned} du_i &= \left.\frac{\partial u_i}{\partial s_i}\right|_{\mathcal{V}_i} ds_i + \left.\frac{\partial u_i}{\partial \mathcal{V}_i}\right|_{s_i} d\mathcal{V}_i \\ &= \theta_i ds_i - \pi_i d\mathcal{V}_i \end{aligned} \tag{10}$$

where θ_i is the particle temperature and π_i is the particle pressure, by analogy with macroscopic systems. Eq. (10) is used to identify the form of the reversible work in terms of the mesoparticle variables, where the last term is the reversible work done on the mesoparticle, $dW_i^C = -\pi_i d\mathcal{V}_i$. The particle temperature plays the role of an *estimator* of the system (reservoir) temperature T, since its ensemble average satisfies[35,36]

$$T = \frac{1}{Z_i} \int ds_i \left.\frac{\partial u_i}{\partial s_i}\right|_{\mathcal{V}_i} e^{[Ts_i - u(s_i,\mathcal{V}_i)]/(k_B T)} = \langle \theta_i \rangle \tag{11}$$

where Z_i is the partition function of the mesoparticle, which is considered at rest, for simplicity. Similarly, the particle pressure is an estimator of the excess system pressure, since the motion of the mesoparticles adds an ideal gas contribution to the system (macroscopic) pressure. To illustrate this, we consider the variation of the Helmholtz free energy F of a mesoparticle under a volume change, which corresponds to the excess system pressure, P^{ex}, i.e.,

$$P^{ex} = -\left.\frac{\partial F(T, m_i)}{\partial \mathcal{V}_i}\right|_T = \frac{k_B T}{Z_i} \int ds_i \left.\frac{\partial}{\partial \mathcal{V}_i}\right|_{s_i} e^{[Ts_i - u_i(s_i,\mathcal{V}_i)]/(k_B T)} = \langle \pi_i, \rangle \tag{12}$$

where the implicit definition of π_i in Eq. (10) has been used (see refs.[35,36] for a detailed analysis of Eq. (12)). Furthermore, the conservative force between a pair of mesoparticles, $\mathbf{f}_{ij}^C$, can be given by a MB-FF-EoS, and depends on local particle densities, n_i and n_j,

particle pressures, π_i and π_j, and particle temperatures, θ_i and θ_j,[43,47] and results from the generalized Hamiltonian of Eq. (1) as

$$\mathbf{f}_i^C = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\sum_j \frac{\partial u_j}{\partial \mathbf{r}_i} = -\sum_{j\neq i} \left(\frac{\partial u_j}{\partial \mathbf{r}_i} - \frac{\partial u_i}{\partial \mathbf{r}_j} \right) \equiv \sum_{j\neq i} \mathbf{f}_{ij}^C \tag{13}$$

where we have used $\partial u_i/\partial \mathbf{r}_i = -\sum_{j\neq i} \partial u_i/\partial \mathbf{r}_j$ due to translational invariance of $\mathcal{H}$. Then, using Eq. (2),[35,36]

$$\mathbf{f}_{ij}^C = -\left(\pi_j \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} - \pi_i \frac{\partial \mathcal{V}_i}{\partial \mathbf{r}_j} \right) = -\left(\frac{\pi_i}{n_i^2} + \frac{\pi_j}{n_j^2} \right) \frac{dw_{ij}}{dr_{ij}} \, \mathbf{e}_{ij} \tag{14}$$

In Eq. (14), $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the separation-distance unit vector, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and $r_{ij} = |\mathbf{r}_{ij}|$. Note that $dw_{ij}/dr_{ij} < 0$; thus, the interparticle force is repulsive for positive pressures, as expected. Within this framework, complex interparticle potentials depending on the internal state of the mesoparticles can be introduced.

The EoM for the reversible part of the dynamics follow from classical mechanics with the generalized Hamiltonian of Eq. (1) and need to be supplemented by an expression for the additional variable describing the internal state of the mesoparticle, $\dot{s}_i = 0$:

$$\dot{s}_i = 0 \tag{15}$$

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \tag{16}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = \mathbf{f}_i^C = \sum_{j\neq i} \mathbf{f}_{ij}^C \tag{17}$$

The additional expression, $\dot{s}_i = 0$, imposes the condition that the reversible processes are *adiabatic*, i.e., no heat transport between particles is permitted. Note that we implicitly assume that the unresolved (CG) DoF are instantaneously at thermal equilibrium. Following the derivation in Ref.,[36] the irreversible processes are added in accordance with the physical nature of the underlying system. Specifically, the irreversible processes are both the dissipative work due to pairwise friction forces, $\mathbf{f}_{ij}^D$, and the heat exchanged between mesoparticles,

$\dot{q}_{ij}$. In addition, we require that $\mathbf{f}_{ij}^D = -\mathbf{f}_{ji}^D$ and $\dot{q}_{ij} = -\dot{q}_{ji}$ to maintain both momentum and energy conservation. From Eqs. (15) and (17), we then can write

$$\begin{aligned} \dot{\mathbf{p}}_i &= \mathbf{f}_i^C + \mathbf{f}_i^D & (18) \\ \theta_i \dot{s}_i &= \dot{q}_i + \dot{W}_i - \dot{W}_i^C & (19) \\ &= \dot{q}_i + \dot{W}_i^{irrev} \end{aligned}$$

where $\mathbf{f}_i^D = \sum_{j \neq i} \mathbf{f}_{ij}^D$ and $q_i = \sum_{j \neq i} q_{ij}$, while the total, the reversible and irreversible (dissipative) works done on the mesoparticle are W_i, W_i^C, and W_i^{irrev}, respectively. Eq. (19) follows from the First Law of Thermodynamics

$$\begin{aligned} du_i &= dq_i + dW_i \\ &= \theta_i ds_i + dW_i^C \end{aligned}$$

The functional form of W_i^{irrev} depends on the underlying physical model, but its overall contribution can be determined from the requirement that the total (system) energy is conserved, even in the presence of dissipative interactions. This is the key element related to the particle internal energy u_i introduced in the DPDE method.[23] Hence, in an isolated system of interacting mesoparticles, energy conservation implies that $\dot{\mathcal{H}} = 0$. Differentiating Eq. (1), and using Eqs. (18) and (19), we can write

$$\begin{aligned} \dot{\mathcal{H}} &= \sum_i \left(\frac{\mathbf{p}_i}{m_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial u_i}{\partial s_i} \dot{s}_i + \sum_{j \neq i} \frac{\partial u_j}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{p}_i}{m_i} \right) & (20) \\ &= \frac{1}{2} \sum_i \sum_{j \neq i} \mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \right) + \sum_i \dot{W}_i^{irrev} = 0 \end{aligned}$$

where we used $\sum_i \mathbf{f}_i^D = 0$ because $\mathbf{f}_{ij}^D = -\mathbf{f}_{ji}^D$, and $\sum_i \dot{q}_i = 0$ because $\dot{q}_{ij} = -\dot{q}_{ji}$. The energy balance of Eq. (20) should be satisfied by any number of particles,[36] and therefore the balance should be independently satisfied by each pair, i.e., $\dot{W}_{ij}^{irrev} + \dot{W}_{ji}^{irrev} = -\mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \right)$. How-

ever, additional information is required to elucidate the actual form of $\dot{W}_{ij}^{irrev}$, specifically, the proportion and distribution of the irreversible work among the interacting mesoparticles, where such information is outside of the mesoscopic framework. For the present model, we consider that the irreversible work is evenly distributed between pairs of mesoparticles, i.e.,

$$\dot{W}_i^{irrev} = -\frac{1}{2}\sum_{j\neq i}\mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right) \tag{21}$$

Furthermore, the consistency of the model with respect to its irreversible behavior requires that, in the absence of fluctuations and taking into account the interaction with the reservoir,

$$\dot{\mathcal{F}} < 0 \tag{22}$$

is satisfied, where $\mathcal{F}$ is given by Eq. (4). By assuming that the condition in Eq. (22) is satisfied again for an arbitrary number of mesoparticles, it is then satisfied independently for each pairwise interaction. Further, it can be shown that the *entropy production* for the exchange of the momentum and heat between a pair of mesoparticles i and j satisfies $\dot{s}_i + \dot{s}_j > 0$, which, using Eq. (19), is given by

$$\dot{s}_i + \dot{s}_j = \mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\left(\frac{1}{\theta_i} + \frac{1}{\theta_j}\right) + \dot{q}_{ij}\left(\frac{1}{\theta_i} - \frac{1}{\theta_j}\right) > 0 \tag{23}$$

As discussed in Ref.,[36] Eq. (23) is reminiscent of Onsager's formulation of irreversible processes at the macroscale, but used here at the mesoscopic level. In Eq. (23), the pairwise friction force $\mathbf{f}_{ij}^D$ and the interparticle heat flux $\dot{q}_{ij}$ are phenomenological, but the positiveness of Eq. (23) suggests that at least near equilibrium, $\mathbf{f}_{ij}^D$ and $\dot{q}_{ij}$ are proportional to their conjugated *thermodynamic forces*

$$\mathbf{X} = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \tag{24}$$

$$X_u = \frac{1}{\theta_i} - \frac{1}{\theta_j} \tag{25}$$

For the construction of the GenDPDE framework and also following Onsager's viewpoint, we chose a linear relationship between a flux and a thermodynamic force, which is valid over a wide range of conditions, including rather far from equilibrium.[37] Following Ref.,[36] we thus consider

$$\mathbf{f}_{ij}^{D} = -\gamma_{ij}\left(\frac{\mathbf{p}_i}{m_i}-\frac{\mathbf{p}_j}{m_j}\right)\cdot\mathbf{e}_{ij}\;\mathbf{e}_{ij} \tag{26}$$

$$\dot{q}_{ij} = -\kappa_{ij}(\theta_i-\theta_j) \tag{27}$$

where $\gamma_{ij}=\gamma\,\omega(r_{ij})$ and $\kappa_{ij}=\kappa\,\bar{\omega}(r_{ij})$, γ and κ are mesoscopic analogues of the friction coefficient and the thermal conductivity, respectively, and ω_{ij} and $\bar{\omega}_{ij}$ are weighting functions depending on the distance between the mesoparticles that become zero for r_{ij} larger than cut-off ranges R_{cut}^{D} and $\bar{R}_{cut}$, respectively. While we have chosen linear relationships between the fluxes and the thermodynamic forces, non-linear relationships satisfying Eq. (23) can also be considered for the dissipative interactions. Moreover, the advantage of Eq. (27) with respect to e.g. $\dot{q}_{ij}\propto(1/\theta_i-1/\theta_j)$ is that $\langle\dot{q}_{ij}\rangle=0$ straightforwardly follows from Eq. (27). Similarly, $\langle\mathbf{f}_{ij}^{D}\rangle=0$ straightforwardly follows from Eq. (26). The two irreversible processes given by Eqs. (26) and (27) are not coupled since they differ in tensorial nature (Curie's principle).[37]

Finally, the GenDPDE framework is completed by adding random terms associated with the irreversible processes. As in the classical Langevin equations, the random contributions are considered additive along with the conservative and dissipative interactions. The properties of the random contributions must generate dynamics such that the equilibrium probability of Eq. (3) is correctly sampled, which is guaranteed by the Fluctuation-Dissipation Theorems (FDTs). Following Ref.,[36] we have

$$\delta\mathbf{p}_{ij}^{R} = \sqrt{\gamma_{ij}k_B(\theta_i+\theta_j)}\;\mathbf{e}_{ij}\;\xi_{ij}\delta t^{1/2} \tag{28}$$

$$\delta u_{ij}^{R} = \sqrt{2\kappa_{ij}k_B\theta_i\theta_j}\;\bar{\xi}_{ij}\delta t^{1/2} \tag{29}$$

where δt is the timestep since the dynamics is formulated using a discrete algorithm. The derivation of the random terms is outlined in Appendix A. The normalized Gaussian random number ξ_{ij} (and analogously $\bar{\xi}_{ij}$) satisfies

$$\langle \xi_{ij} \rangle = 0 \tag{30}$$

$$\langle \xi_{ij}(t)\xi_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\,\delta_{tt'} \tag{31}$$

where δ_{ij} is the Kronecker delta, and $\delta_{tt'}$ indicates that the random numbers are not correlated if they belong to different time intervals, spanning δt each.

The EoM for the GenDPDE method are derived in Refs.[35,36] and they refer to the internal energy dynamics rather than the entropy dynamics, which allowed us to introduce the appropriate forms of the irreversible system processes. For completeness, the GenDPDE EoM are provided here:

$$\mathbf{r}_i' = \mathbf{r}_i + \frac{\mathbf{p}_i}{m_i}\delta t \tag{32}$$

$$\mathbf{p}_i' = \mathbf{p}_i + \sum_{j\neq i} \mathbf{f}_{ij}^C \delta t + \sum_{j\neq i} \mathbf{f}_{ij}^D \delta t + \sum_{j\neq i} \delta \mathbf{p}_{ij}^R \tag{33}$$

$$\begin{aligned} u_i' = {} & u_i - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot \mathbf{f}_{ij}^C\,\delta t \\ & - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot \mathbf{f}_{ij}^D\,\delta t - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot \delta\mathbf{p}_{ij}^R - \frac{1}{2m_i}\sum_{j\neq i}\sum_{l\neq i}\delta\mathbf{p}_{ij}^R\cdot\delta\mathbf{p}_{il}^R \\ & + \sum_{j\neq i}\dot{q}_{ij}\delta t + \sum_{j\neq i}\delta u_{ij}^R \end{aligned} \tag{34}$$

where primed variables refer to the final state at time $t+\delta t$, and non-primed variables refer to the initial state at time t. For momentum and energy conservation, the random terms must satisfy $\delta\mathbf{p}_{ij}^R = -\delta\mathbf{p}_{ji}^R$ and $\delta u_{ij}^R = -\delta u_{ji}^R$.

On the right-hand-side of Eq. (33), the second term corresponds to the conservative interactions, while the third and fourth terms represent, respectively, the dissipative and random interactions. These latter two terms account for the unresolved (CG) DoF dynamics, which

can be adjusted to reproduce the higher resolution model dynamics that the mesoparticle is intended to mimic. On the right-hand-side of Eq. (34), the second to fifth terms represent the mechanical work done on the system by the conservative, dissipative and random forces, while the last two terms correspond to the heat conduction exchange between mesoparticles. The GenDPDE method preserves Galilean invariance, conserves the total system energy, $\mathcal{H} = E = \sum_i (\frac{p_i^2}{2m_i} + u_i)$, and conserves total linear and angular momenta.

2.2 GenDPDE-M Framework

In this section, the GenDPDE-M method is formulated as an extension of the GenDPDE method. Analogous to the GenDPDE method, within each GenDPDE-M mesoparticle is an N_s-component mixture of physical particles referred to as *embedded particles*, which correspond to different chemical species. The number of embedded particles of species α in mesoparticle i is $\mathcal{N}_i^\alpha$, and the total number of embedded particles in mesoparticle i is $\mathcal{N}_i = \sum_{\alpha=1}^{N_s} \mathcal{N}_i^\alpha$. Further, $\bar{m}_\alpha$ and C_V^α are the mass and constant-volume heat capacity per embedded particle of species α, respectively, which are analogues of the molar mass and molar heat capacity. The mass of embedded particles of species α in mesoparticle i is $m_i^\alpha = \bar{m}_\alpha \mathcal{N}_i^\alpha$, and the total mass of mesoparticle i is $m_i = \sum_{\alpha=1}^{N_s} m_i^\alpha$. Analogously, the constant-volume heat capacity of mesoparticle i is $C_{V,i} = \sum_{\alpha=1}^{N_s} C_V^\alpha \mathcal{N}_i^\alpha$. Since m_i is kept constant during the diffusion process, the interparticle mass exchange only allows the $N_s - 1$ embedded-particle masses to vary independently.

In summary, in a GenDPDE-M simulation, the total mass embedded in each mesoparticle is transported by the motion of the mesoparticles governed by the GenDPDE EoM, Eqs. (32) to (34), while via interparticle mass exchange at fixed m_i, neighboring mesoparticles i and j can exchange amounts of each species, $\{\mathcal{N}_i^\alpha\}_{\alpha=1}^{N_s}$ and $\{\mathcal{N}_j^\alpha\}_{\alpha=1}^{N_s}$. The new element of GenDPDE-M is the interparticle mass exchange, which is formulated next.

In the GenDPDE-M method, we consider an extended set of control variables, $(s_i, \mathcal{V}_i, \{m_i^\alpha\}_{\alpha=1}^{N_s-1})$,

for $i = 1 \ldots N$, along with the generalized Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m_i} + u_i \left(s_i, \mathcal{V}_i, \{m_i^\alpha\}_{\alpha=1}^{N_s-1} \right) \right] \tag{35}$$

Eq. (35) leads to the equivalent reversible system dynamics as in GenDPDE, given by the EoM, Eqs. (15) to (17), together with the additional condition, required for the new DoF,

$$\dot{m}_i^\alpha = 0 \tag{36}$$

for all independent embedded particles $\alpha = 1, \ldots, N_s - 1$. Eqs. (15) and (36) indicate that there are no reversible processes associated with the internal variables s_i and m_i^α. If the reversible processes exist, then it would be necessary to include the conjugated momenta of s_i and m_i^α into the Hamiltonian of Eq. (35), together with their relevant dynamics, which is outside of the classical non-equilibrium thermodynamics formulation[37] considered in this work. Since Eq. (17) also holds for the GenDPDE-M method, the conservative force $\mathbf{f}_{ij}^C$ is given by Eq. (14) as in GenDPDE.

Similarly as in GenDPDE, we introduce the irreversible interactions $\dot{q}_i$ and $\mathbf{f}_i^D$ together with the mass dissipative fluxes J_i^α to the right-hand-side of Eqs. (15), (17) and (36), i.e.,

$$\theta_i \dot{s}_i = \dot{q}_i + \dot{W}_i^{irrev} = \sum_{j \neq i} \dot{q}_{ij} + \dot{W}_i^{irrev} \tag{37}$$

$$\dot{\mathbf{p}}_i = \mathbf{f}_i^C + \mathbf{f}_i^D = \sum_{j \neq i} \mathbf{f}_{ij}^C + \sum_{j \neq i} \mathbf{f}_{ij}^D \tag{38}$$

$$\dot{m}_i^\alpha = J_i^\alpha = \sum_{j \neq i} J_{ij}^\alpha \tag{39}$$

Note that the system mass conservation imposes $\sum_i J_i^\alpha = 0$, i.e., $J_{ij}^\alpha = -J_{ji}^\alpha$. Analogous to the introduction of Eq. (10), the existence of the function $u_i(s_i, \mathcal{V}_i, m_i^\alpha)$ allows the mesopar-

ticle intensive properties to be defined

$$
\begin{aligned}
du_i &= \left.\frac{\partial u_i}{\partial s_i}\right|_{\mathcal{V}_i,\{m_i^\beta\}} ds_i + \left.\frac{\partial u_i}{\partial \mathcal{V}_i}\right|_{s_i,\{m_i^\beta\}} d\mathcal{V}_i + \sum_{\alpha=1}^{N_s} \left.\frac{\partial u_i}{\partial m_i^\alpha}\right|_{s_i,\mathcal{V}_i,\{m_i^{\beta\neq\alpha}\}} dm_i^\alpha \qquad (40)\\
&= \theta_i ds_i + \frac{\pi_i}{n_i^2}\sum_{j\neq i}\frac{dw_{ij}}{dr_{ij}}\,\mathbf{e}_{ij}\cdot d\mathbf{r}_{ij} + \sum_{\alpha=1}^{N_s-1}\left(\mu_i^\alpha - \mu_i^{N_s}\right) dm_i^\alpha
\end{aligned}
$$

where

$$
\mu_i^\alpha = \left.\frac{\partial u_i}{\partial m_i^\alpha}\right|_{s_i,\mathcal{V}_i,m_i^{\beta\neq\alpha}}
$$

is the chemical potential of species α within mesoparticle i. For the purpose of eliminating the mass of the embedded particle of the ultimate-numbered species N_s as an independent variable, in Eq. (40) we employed the constraint that the total mass of mesoparticle i is conserved, Eq. (36), i.e., $\sum_{\alpha=1}^{N_s} dm_i^\alpha = 0$. To further simplify notation, we define the exchange chemical potential $\bar{\mu}_i^\alpha = \mu_i^\alpha - \mu_i^{N_s}$. By evaluating the time-derivative of the Hamiltonian $\mathcal{H}$, given by Eq. (35), similar to the formulation of GenDPDE, see Eq. (20) and text below, we identify the system irreversible work by imposing $\dot{\mathcal{H}} = 0$ after the irreversible fluxes are included. Further following the GenDPDE formulation, we assume that the energy balance holds for each pair of mesoparticles,

$$
\dot{W}_{ij}^{irrev} + \dot{W}_{ji}^{irrev} = -\mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right) - \sum_{\alpha=1}^{N_s-1} J_{ij}^\alpha \left(\bar{\mu}_i^\alpha - \bar{\mu}_j^\alpha\right) \qquad (41)
$$

Before proceeding further, the form of the coupling between the particle internal energy, u_i, and the embedded-particle masses, $\{m_i^\alpha\}_{\alpha=1}^{N_s-1}$, during the interparticle energy and mass transfer must be defined. In the following, for simplicity, we consider no coupling between the energy and mass transfer, i.e., the embedded-particle masses of each mesoparticle remain constant during the energy transfer and the internal energy of each mesoparticle is also kept fixed during the mass transfer. For this simple case, the irreversible work exerted on mesoparticle i is equal to the variation of its internal energy due to the mass transfer to

neighboring mesoparticle j. As such, in analogy with Eq. (21), we can write

$$\dot{W}_i^{irrev} = -\frac{1}{2}\sum_{j\neq i} \mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right) - \sum_{j\neq i}\sum_{\alpha=1}^{N_s-1} J_{ij}^{\alpha}\, \bar{\mu}_i^{\alpha} \tag{42}$$

In Eq. (42), we also considered the irreversible work to be evenly distributed between pairs of mesoparticles since u_i and $\{m_i^\alpha\}_{\alpha=1}^{N_s-1}$ are scalar properties, and thus are not coupled with the distribution of the irreversible work. In contrast to Eq. (21), which refers to the GenDPDE method, Eq. (42) contains an additional irreversible term corresponding to the mass exchange, while analogous to GenDPDE, the total energy of an isolated system of mesoparticles is conserved by construction; cf. Eq. (20).

A brief aside is worthwhile here. In formulating the GenDPDE-M method, the addition of the variable m_i^α introduces a degree of complexity that is not present in the GenDPDE method, namely, the possible coupling between the scalar quantities u_i and m_i^α. In the simplest case considered here, we have assumed that the energy transfer and the mass transfer are effectively decoupled, as well as that the different material fluxes are also decoupled from each other. Other scenarios that allow coupling between u_i and $\{m_i^\alpha\}_{\alpha=1}^{N_s-1}$ during the interparticle energy and mass exchange deserve separate treatment and will be published elsewhere.

Up to this point in the manuscript, the GenDPDE-M framework has been formulated using the control variables (s, m). For further development of GenDPDE-M, it is convenient to change the set of control variables from (s, m) to (u, m), such that we can determine the appropriate independent thermodynamic forces for the mass transfer. (Note that a corresponding change in the heat flow model that is used follows this change in the control variables.[36]) Hence, equivalent to Eq. (22), for the control parameters (u, m) one has

$$\dot{\tilde{\mathcal{F}}} < 0 \tag{43}$$

with $\tilde{\mathcal{F}}$ given by Eq. (9) using the new Hamiltonian of Eq. (35). Hence, the entropy produc-

tion for the GenDPDE-M method is

$$\dot{\tilde{s}}_i + \dot{\tilde{s}}_j = \mathbf{f}_{ij}^D \cdot \left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j} \right) \left(\frac{1}{\tilde{\theta}_i} + \frac{1}{\tilde{\theta}_j} \right) + \dot{q}_{ij} \left(\frac{1}{\tilde{\theta}_i} - \frac{1}{\tilde{\theta}_j} \right) + \sum_{\alpha=1}^{N_s-1} J_{ij}^{\alpha} \left(\frac{\bar{\tilde{\mu}}_i^{\alpha}}{\tilde{\theta}_i} - \frac{\bar{\tilde{\mu}}_j^{\alpha}}{\tilde{\theta}_j} \right) > 0 \quad (44)$$

From Eq. (44), we can identify the new thermodynamic force for the mass transfer as

$$X_m^{\alpha} = \frac{\bar{\tilde{\mu}}_i^{\alpha}}{\tilde{\theta}_i} - \frac{\bar{\tilde{\mu}}_j^{\alpha}}{\tilde{\theta}_j} \quad (\alpha = 1, \ldots, N_s - 1) \quad (45)$$

where

$$\frac{\tilde{\mu}_i^{\alpha}}{\tilde{\theta}_i} = - \left. \frac{\partial \tilde{s}_i}{\partial m_i^{\alpha}} \right|_{u_i, \mathcal{V}_i, m_i^{\beta \neq \alpha}} \quad (46)$$

and

$$\frac{1}{\tilde{\theta}_i} = \left. \frac{\partial \tilde{s}_i}{\partial u_i} \right|_{\mathcal{V}_i, m_i^{\beta}} \quad (47)$$

Using the fact that from Eq. (6) we can write $\tilde{s}_i = s_i - k_B \ln \theta_i$, the bare variables can be directly related to the dressed ones, as we will explicitly show below. In Eqs. (44) and (45), $\bar{\tilde{\mu}}_i^{\alpha} = \tilde{\mu}_i^{\alpha} - \tilde{\mu}_i^{N_s}$ is the exchange bare chemical potential, $\tilde{\mu}_i^{\alpha}$ is the bare chemical potential of species α, and $\tilde{\theta}_i$ is the bare particle temperature. Note that the equilibrium average of the thermodynamic force vanishes due to the fact that this quantity is an estimator of the macroscopic chemical potential of the system μ^{α}, i.e.,

$$\mu^{\alpha} = \left. \frac{\partial F(T, \{m_i^{\beta}\})}{\partial m_i^{\alpha}} \right|_T = - \frac{k_B T}{Z_i} \int du_i \left. \frac{\partial}{\partial m_i^{\alpha}} \right|_{u_i} e^{[T\tilde{s}(u_i, m_i^{\alpha}) - u_i]/(k_B T)} = T \left\langle \frac{\tilde{\mu}_i^{\alpha}}{\tilde{\theta}_i} \right\rangle \quad (48)$$

according to the equivalence of the probability distributions Eqs. (3) and (5). From Eq. (44), the thermodynamic force for the heat transfer is

$$X_u = \frac{1}{\tilde{\theta}_i} - \frac{1}{\tilde{\theta}_j} \quad (49)$$

With this set of control parameters, we previously demonstrated that $\langle 1/\tilde{\theta}_i \rangle = 1/T$.[35,36]

Hence, the equilibrium average of X_u is therefore also zero. Eqs. (24), (45), and (49) thus represent the complete set of thermodynamic forces for the GenDPDE-M method. Along with Eq. (26), which is still valid for GenDPDE-M, we establish a linear relationship between the energy and mass fluxes and their corresponding conjugate thermodynamic forces as

$$\dot{q}_{ij} = -\kappa_{ij}\left(\frac{1}{\bar{\tilde{\theta}}_j} - \frac{1}{\bar{\tilde{\theta}}_i}\right) \tag{50}$$

$$J^{\alpha}_{ij} = -\text{Đ}^{\alpha}_{ij}\left(\frac{\bar{\tilde{\mu}}^{\alpha}_i}{\tilde{\theta}_i} - \frac{\bar{\tilde{\mu}}^{\alpha}_j}{\tilde{\theta}_j}\right) \tag{51}$$

where $\text{Đ}^{\alpha}_{ij} = \text{Đ}^{\alpha}\tilde{\omega}(r_{ij})$, Đ^{α} is analogous to a Maxwell-Stefan diffusion coefficient for species α, and $\tilde{\omega}_{ij}$ is a weighting function that becomes zero for r_{ij} larger than the cut-off range $\tilde{R}_{cut}$. Note that the expression of X_u for the GenDPDE-M method necessarily differs from Eq. (25) for GenDPDE, otherwise the energy and mass fluxes would still be coupled. This point is not demonstrated here, but will be addressed later when formulating the framework for the coupling of the scalar properties exchanged between mesoparticles.

Analogous to the formulation of the GenDPDE method, the final step is adding the random terms to the EoM, which then become

$$\mathbf{r}'_i = \mathbf{r}_i + \frac{\mathbf{p}_i}{m_i}\delta t \tag{52}$$

$$\mathbf{p}'_i = \mathbf{p}_i + \sum_{j\neq i}\mathbf{f}^C_{ij}\delta t + \sum_{j\neq i}\mathbf{f}^D_{ij}\delta t + \sum_{j\neq i}\delta\mathbf{p}^R_{ij} \tag{53}$$

$$\begin{aligned} u'_i &= u_i - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot\mathbf{f}^C_{ij}\,\delta t \\ &- \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot\mathbf{f}^D_{ij}\,\delta t - \frac{1}{2}\sum_{j\neq i}\left(\frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_j}{m_j}\right)\cdot\delta\mathbf{p}^R_{ij} - \frac{1}{2m_i}\sum_{j\neq i}\sum_{l\neq i}\delta\mathbf{p}^R_{ij}\cdot\delta\mathbf{p}^R_{il} \\ &+ \sum_{j\neq i}\dot{q}_{ij}\delta t + \sum_{j\neq i}\delta u^R_{ij} \end{aligned} \tag{54}$$

$$m^{\alpha\,\prime}_i = m^{\alpha}_i - \sum_{j\neq i}\text{Đ}^{\alpha}_{ij}\left(\frac{\bar{\tilde{\mu}}^{\alpha}_i}{\tilde{\theta}_i} - \frac{\bar{\tilde{\mu}}^{\alpha}_j}{\tilde{\theta}_j}\right)\delta t + \sum_{j\neq i}\delta m^{\alpha\,R}_{ij} \quad (\alpha = 1,\ldots,N_s-1) \tag{55}$$

The choice of the irreversible work given by Eq. (42) leads to decoupling between the energy

and mass transfer, therefore, the dynamics of the GenDPDE-M method are analogous to the GenDPDE dynamics with the addition of Eq. (55) that accounts for the interparticle mass exchange.

The random term for the mesoparticle momenta satisfies the FDT given by Eq. (28), while the random term for the energy transfer satisfies the FDT consistent here with Eq. (50), and given by

$$\delta u_{ij}^{R} = \sqrt{2\kappa_{ij}k_B}\,\bar{\xi}\delta t^{1/2} \tag{56}$$

The FDT for the random term associated with the mass transfer is

$$\delta m_{ij}^{\alpha\,R} = \sqrt{2\text{Đ}_{ij}^{\alpha}k_B}\,\tilde{\xi}_{ij}^{\alpha}\,\delta t^{1/2} \tag{57}$$

Both of the FDTs, Eqs. (56) and (57), are derived in Appendix A. The normalized Gaussian random numbers $\tilde{\xi}_{ij}^{\alpha}$ satisfy properties analogous to the random numbers ξ_{ij} and $\bar{\xi}_{ij}$ (cf. Eqs. (30) and (31)), and $\tilde{\xi}_{ij}^{\alpha}$ are decoupled from ξ_{ij} and $\bar{\xi}_{ij}$.

Next, as a proof-of-concept of the internal consistency and robustness of the energy- and mass-exchange dynamics, we analyze different energy- and mass-transfer dynamics using mesoparticles kept at rest. The analysis of various mass-transfer dynamics of practical interest is provided in Part 2 of this manuscript series.

2.3 GenDPDE-M Energy- and Mass-Transfer Dynamics

To illustrate the subtleties of fluctuating interparticle mass exchange within GenDPDE-M, we consider a simplified model system of mesoparticles that: (1) are kept at rest; (2) can only exchange internal energy via heat conduction; and (3) can exchange interparticle mass via diffusive fluxes. For this model system, we consider that each mesoparticle contains only a single type of embedded particle, i.e., only a single chemical species will be exchanged with neighboring mesoparticles. Consequently, the masses of the mesoparticles can vary, however, the mass variation is irrelevant for the simplified model system since the mechanical

motion of the mesoparticles is restricted and a single component system is considered. This model system allow us to investigate the energy- and mass-transfer processes in the GenD-PDE framework under different conceptual scenarios, which are compared against numerical simulations as further consistency verification.

In the model system, we consider N mesoparticles fixed in space and randomly distributed in a volume V, with a time-dependent particle internal energy u_i and particle mass m_i. Pairs of mesoparticles can exchange energy and mass such that both the total energy and the total mass of the isolated system remain constant. Starting from Eqs. (54) and (55), the EoM for this test model system can be derived by eliminating the mechanical contribution, i.e., momenta, and relaxing the constant mass constraint, Eq. (36), for each particle, while maintaining system energy and mass conservation. Hence, the simplified EoM become

$$u_i' = u_i - \sum_{j\neq i} \kappa_{ij} \left(\frac{1}{\tilde{\theta}_j} - \frac{1}{\tilde{\theta}_i} \right) \delta t + \sum_{j\neq i} \delta u_{ij}^R \tag{58}$$

$$m_i' = m_i - \sum_{j\neq i} \text{Đ}_{ij} \left(\frac{\tilde{\mu}_i}{\tilde{\theta}_i} - \frac{\tilde{\mu}_j}{\tilde{\theta}_j} \right) \delta t + \sum_{j\neq i} \delta m_{ij}^R \tag{59}$$

with the random terms δu_{ij}^R and δm_{ij}^R given by Eqs. (56) and (57), respectively. The corresponding functional is then

$$\tilde{\mathcal{F}}(\tilde{\Gamma}) = \sum_i [u_i - T\tilde{s}_i(u_i, m_i)] \tag{60}$$

3 RESULTS

Since the complete thermodynamic information regarding the underlying physical system is contained within the probability distributions, the energy- and mass-exchange dynamics is validated by sampling the corresponding probability distributions. Correct sampling is determined by comparing the particle distributions from the energy- and mass-transfer EoM with those obtained by Monte Carlo (MC) sampling; specifically, the EoM Eqs. (58) and

(59). Furthermore, the equilibrium properties should be independent of the transport coefficients. Thus, as an additional consistency check, we compared the equilibrium distributions obtained with two different sets of transport coefficients. Note that reproducing the MC probability distributions provides a rigorous validation that goes beyond merely establishing the correctness of the first and second moments of the probability distributions.

3.1 Mesoparticle Thermodynamic Model

For performing the validation simulations described above, we need to introduce a model for the mesoparticle thermodynamics. Analogous to macroscopic thermodynamics, the mesoparticle thermodynamic functions are also subject to Legendre transformations despite the fluctuating nature of the variables. Hence, the mesoscopic equivalent of the Helmholtz free energy has the general form

$$f(\theta, m) = u - \theta s \tag{61}$$

which allows us to consider the particle temperature θ as an independent variable rather than the entropy s, whereby θ fluctuates in a manner analogous to other mesoparticle properties. The use of θ in the Legendre transform allows us to define f locally for each mesoparticle. On one hand, it is important to realize that such a change of the independent variables in the mathematical description is not accompanied with a change in the control variables of the thermodynamic description, therefore, it is a necessary change considering that the control variables remain (s, m). On the other hand, note that f, given by Eq. (61), is not an estimator of the system Helmholtz free energy. Throughout this section due to the factorization of the functional, Eqs. (60), we do not include the subindex i in the mesoparticle variable notation, unless necessary to avoid confusion.

Based on the general expression introduced in Eq. (61), the particular form of the mesoparticle Helmholtz free energy used here is

$$f(\theta, m) = -C_V m\, \theta \ln(\theta + 1) + \beta\, (m - m_0)^2 \tag{62}$$

where the first term is inspired by the ideal gas model, while the second term corresponds to an "elastic spring" for the particle mass with a spring constant β and equilibrium mass m_0. Note that f in Eq. (62) is not an extensive function of m, which poses no conceptual issues in the following analysis. However, thermodynamic relations based on the first-order homogeneity of the thermodynamic potentials such as the Gibbs-Duhem equation or the Euler form cannot be invoked here.[48]

Related properties such as the entropy, the internal energy, and the chemical potential follow from f in Eq. (62) as,

$$\begin{aligned} s &= -\left.\frac{\partial f}{\partial \theta}\right|_m \\ &= C_V\, m \left[\ln(\theta+1) + \frac{\theta}{\theta+1}\right] \end{aligned} \tag{63}$$

$$\begin{aligned} u &= f + \theta s \\ &= C_V\, m\, \frac{\theta^2}{\theta+1} + \beta\,(m-m_0)^2 \end{aligned} \tag{64}$$

and

$$\begin{aligned} \mu &= \left.\frac{\partial f}{\partial m}\right|_\theta \\ &= -C_V\,\theta \ln(\theta+1) + 2\,\beta\,(m-m_0) \end{aligned} \tag{65}$$

respectively. It is worth mentioning that the form of the intensive quantities such as μ is independent of the particle thermodynamic potential, where this independence is utilized

throughout this work. For example,

$$\begin{aligned} \mu\left(\theta, m\right) &= \left.\frac{\partial f}{\partial m}\right|_{\theta} \\ &= \mu\left(\theta(s,m), m\right) = \left.\frac{\partial u}{\partial m}\right|_{s} \\ &= \mu\left(s, m\right) \end{aligned} \tag{66}$$

or

$$\begin{aligned} \mu\left(\theta, m\right) &= \left.\frac{\partial f}{\partial m}\right|_{\theta} \\ &= \mu\left(\theta(u,m), m\right) = -\theta \left.\frac{\partial s}{\partial m}\right|_{u} \\ &= \mu\left(u, m\right) \end{aligned} \tag{67}$$

The equalities of μ in Eqs. (66) and (67) need to be interpreted within the context of the control variables (s, m) because they are different from the analogous quantities of other sets of control parameters, $\tilde{\mu}$. The relevant quantity is the associated probability distribution, depending on a given set of control variables.

The implication of the change in the control variables can be illustrated from the following analysis. Effectively, the EoM Eqs. (58) and (59) require a change in the control variables from (s, m) to (u, m), which is accompanied with the Jacobian of the transformation

$$\begin{aligned} J(u,m) = \left|\frac{\partial(s,m)}{\partial(u,m)}\right| &= \begin{vmatrix} \frac{\partial s}{\partial u} & \frac{\partial s}{\partial m} \\ \frac{\partial m}{\partial u} & 1 \end{vmatrix} \\ &= \frac{1}{\theta} \end{aligned} \tag{68}$$

Therefore, given the mesoscopic thermodynamic model of Eq. (62), the relevant quantity is

$$\begin{aligned}
\frac{\tilde{\mu}}{\tilde{\theta}} = -\left.\frac{\partial \tilde{s}}{\partial m}\right|_u &= -\left.\frac{\partial}{\partial m}\right|_u [s(u,m) + k_B \ln J(u,m)] \\
&= \frac{\mu}{\theta} - \frac{k_B}{J}\left.\frac{\partial J}{\partial m}\right|_u \\
&= \frac{\mu}{\theta} - \frac{k_B}{C\theta}\left.\frac{\partial u}{\partial m}\right|_\theta \\
&= \frac{\mu}{\theta}\left(1 - \frac{k_B}{C}\right) - \frac{k_B}{C}\left.\frac{\partial \mu}{\partial \theta}\right|_m
\end{aligned} \tag{69}$$

where C is the heat capacity given by

$$\begin{aligned}
C(\theta, m) &= \left.\frac{\partial u}{\partial \theta}\right|_m \\
&= C_V\, m\, \frac{\theta(\theta+2)}{(\theta+1)^2}
\end{aligned} \tag{70}$$

Hence, we arrive at

$$\frac{\tilde{\mu}}{\tilde{\theta}} = -C_V \ln(\theta+1) + \frac{2\beta}{\theta}(m - m_0) - \frac{k_B}{C(\theta,m)}\left[\frac{C_V \theta}{\theta+1} + \frac{2\beta}{\theta}(m - m_0)\right] \tag{71}$$

In addition to the bare chemical potential $\tilde{\mu}$, we need the bare particle temperature, which is given by[35,36]

$$\begin{aligned}
\frac{1}{\tilde{\theta}} &= \left.\frac{\partial \tilde{s}}{\partial u}\right|_m = \left.\frac{\partial}{\partial u}\right|_m [s(u,m) + k_B \ln J(u,m)] \\
&= \frac{1}{\theta}\left[1 - k_B \left.\frac{\partial \theta}{\partial u}\right|_m\right] \\
&= \frac{1}{\theta}\left[1 - \frac{k_B}{C(\theta,m)}\right]
\end{aligned} \tag{72}$$

Analogous to the GenDPDE method, Eqs. (71) and (72) allow us to relate the bare thermodynamic variables to the dressed thermodynamic variables. Note that the differences between the corresponding bare and dressed thermodynamic variables within different sets

of control variables is of the order of the size of the fluctuations, which is proportional to k_B/C_V.

3.2 Numerical verification

For simulating the dynamics and the corresponding MC sampling, we used $N = 20$ mesoparticles fixed in space, $T = 1$, $C_V = 5k_B$, $\beta = 1$, and $m_0 = 8$ with initial particle masses $m = 10$. We employed either $\kappa = 0.05$ and $Đ = 0.01$ with $\delta t = 0.01$, or $\kappa = 0.5$ and $Đ = 0.1$ with $\delta t = 0.001$. A comparison of two simulations with different transport coefficients κ and $Đ$ verifies the independence of the equilibrium properties on the transport coefficients, and the correctness of the FDTs. The EoM were solved using the Shardlow splitting algorithm,[29,40] where all details regarding the numerical integration can be found in Part 2 of this manuscript series.[?]

In Fig. 1 we compare the MC particle distributions with those obtained from simulation, where the dynamics are given by the EoM of Eqs. (58) and (59). We consider distributions for the particle mass, particle internal energy, and particle temperature. For a single particle variable, the MC sampling is carried out by attempting energy and mass exchanges between randomly chosen pairs of mesoparticles such that the total energy and mass of the system remain constant. The MC energy- and mass-exchange moves are accepted/rejected according to the Metropolis algorithm based on the probability distribution

$$P(u, m)\, du\, dm \propto e^{-\tilde{\mathcal{F}}(u,m)/(k_B T)}\, du\, dm \tag{73}$$

which follows from Eq. (60). The particle temperature distribution is then determined by the values of u and m for the mesoparticles, which are independently fluctuating quantities in the MC sampling. Fig. 1 shows excellent agreement between the simulated and MC particle distributions, verifying the thermodynamic consistency of the energy- and mass-exchange dynamics. Note also the ability of the simulations to sample non-Gaussian particle internal

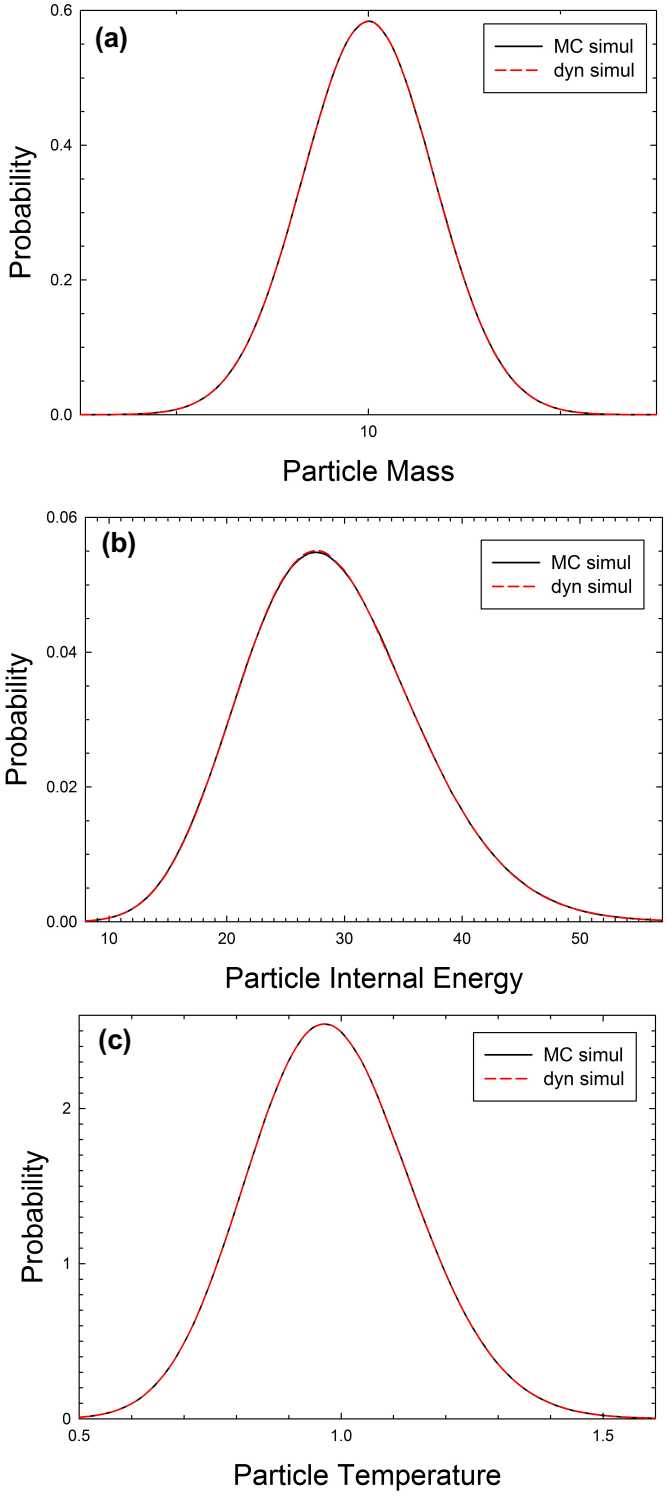

Figure 1: (a) Particle mass, (b) particle internal energy, and (c) particle temperature distributions from Monte Carlo (MC) and interparticle simulation (dyn) for isoenergetic mass exchange.

energy distributions in Fig. 1b, which is rather skewed due to the small value of C_V used.

Finally, the particle distributions determined from the simulations should be independent of the values of the transport coefficients, κ and Đ. Therefore, as a final assessment of the energy- and mass-exchange dynamics, the particle distributions using two different sets of κ and Đ values are presented in Fig. 2. From Fig. 2, it is evident that the energy- and mass-exchange algorithms are independent of the values of the transport coefficients, indicating the correctness of the FDTs for the random terms, thus providing further evidence of the consistency of the thermodynamic framework for the interparticle energy and mass exchanges.

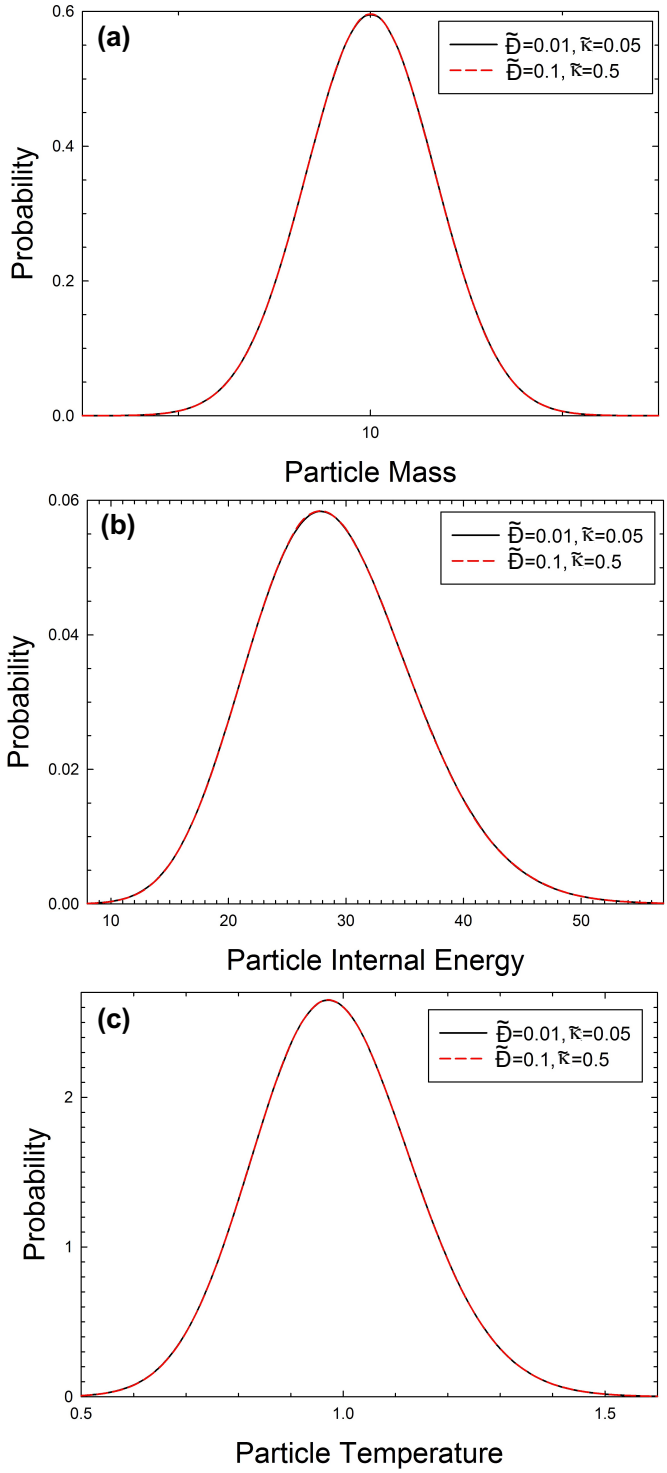

Figure 2: (a) Particle mass, (b) particle internal energy, and (c) particle temperature distributions from interparticle simulation with different values of the diffusion coefficient Đ and heat conductivity coefficient κ for isoenergetic mass exchange.

4 CONCLUSIONS

In summary, the GenDPDE method[35,36] was developed by generalizing the original DPDE method[23] to allow for the transfer of properties other than solely the particle momentum and particle internal energy. In this work, we advanced the complexity and flexibility of the GenDPDE framework by further considering the concept of the mesoparticles as *property carriers*. For the method introduced here, GenDPDE-M, mass can be exchanged between mesoparticles, which can be a key mechanism in modelling systems with chemical reactions and/or phase changes.[49] In this first part of the two-part paper series, we described the formulation of the theoretical framework, where the target audience are those interested in the internal consistency of the GenDPDE-M method. For the sake of clarity in the demonstration and validation of the method, we employed a simple thermodynamic model and simplified dynamics, where the mesoparticles were kept at rest and were only allowed to exchange energy and mass. Nonetheless, the model system has sufficiently complex temperature and mass dependencies in the mesoparticle thermodynamic function, cf. Eq. (62), which allows for the investigation of the subtleties of the GenDPDE-M method when the transfer of the particle internal energy u_i, and particle mass m_i occurs simultaneously under different conditions.

For further simplicity, we have studied only the situation in which energy and mass exchanges are decoupled. However, by considering frictional forces between the fluxes, the theory of irreversible processes[37,38] also allows for the introduction of the couplings through the transport of properties of the same tensorial nature, such as the internal energy u_i or any of the different constituents of the mesoparticle composition, namely, m_i^α. Some examples include the Ludwig-Soret process between species, or the Maxwell-Stefan theory of mass transfer. Nonetheless, the treatment of a general coupling between energy and mass transfers is beyond the scope of this work and will be addressed elsewhere.

Part 2 of this series follows and is targeted for practitioners. Applications, demonstrations, and practical considerations for implementing the GenDPDE-M method are presented

and discussed, including a numerical discretization algorithm. In Part 2, demonstrations are presented using the ideal gas and van der Waals equations-of-state at both equilibrium and non-equilibrium conditions.

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Disclaimer

APPENDIX A

For determining the Fluctuation-Dissipation Theorem (FDTs), we consider that the equations-of-motion (EoM) represent a transformation from an initial phase-space point Γ to a final phase-space point Γ' that is reached within the timestep δt. Thus, in general, the EoM can be expressed as

$$\Gamma' = \hat{\Gamma}[\Gamma, \xi; \delta t] \tag{A1}$$

where $\hat{\Gamma}$ is the functional form of the EoM, and ξ represents random numbers transitioning the EoM and parametrically determining new values of the state variables. Then, the transition probability between the initial and final states is given by

$$W(\Gamma \to \Gamma') = \left\langle \delta(\Gamma' - \hat{\Gamma}[\Gamma, \xi; \delta t]) \right\rangle_{\xi} \tag{A2}$$

where the average $\langle . \rangle$ in Eq. (A2) is performed over the random numbers ξ. The particular FDTs are thus obtained from the requirement that the system dynamics satisfies Detailed Balance

$$P_{eq}(\Gamma) W(\Gamma \to \Gamma') = P_{eq}(\Gamma^*) W(\Gamma^* \to \Gamma^{*'}) \tag{A3}$$

where $\Gamma^* = \varepsilon \Gamma'$ and $\Gamma^{*'} = \varepsilon \Gamma$; ε assigns a positive or a negative sign to variables depending on whether the variables are, respectively, even or odd under time reversal (see ref.[35] for details). For the first moment, in general, we get

$$\int d\Gamma d\Gamma' \, P_{eq}(\Gamma) \, \Gamma' \left\langle \delta(\Gamma' - \hat{\Gamma}[\Gamma, \xi; \delta t]) \right\rangle_{\xi} = \int d\Gamma^* d\Gamma^{*'} \, P_{eq}(\Gamma^*) \, \Gamma' \left\langle \delta(\Gamma^{*'} - \hat{\Gamma}[\Gamma^*, \xi^*; \delta t]) \right\rangle_{\xi^*} \tag{A4}$$

The right-hand-side of Eq. (A4) can be readily evaluated using the time-reversal operator, leading to

$$\int d\Gamma \, P_{eq}(\Gamma) \left\langle \hat{\Gamma}[\Gamma, \xi; \delta t] \right\rangle_{\xi} = \langle \varepsilon \Gamma \rangle \tag{A5}$$

Similarly, for the second moment, we obtain

$$\int d\Gamma\, P_{eq}(\Gamma)\, \left\langle \hat{\Gamma}[\Gamma,\xi;\delta t]\, \hat{\Gamma}[\Gamma,\xi;\delta t] \right\rangle_{\xi} = \langle \varepsilon\Gamma\varepsilon\Gamma \rangle \tag{A6}$$

For the isoenergetic mass exchange, we changed the control variables from (s,m) to (u,m), which does not affect the physics of the system. The functional of Eq. (60) for a mesoparticle pair in the framework of the control variables (u,m) is

$$\tilde{\mathcal{F}}(u_i,m_i;u_j,m_j) = \{T\,[\tilde{s}(u_i,m_i)+\tilde{s}(u_j,m_j)] - u_i - u_j\} \tag{A7}$$

The EoM, Eqs. (58) and (59), in terms of Δu_{ij} and Δm_{ij} become

$$\Delta u'_{ij} = \Delta u_{ij} - 2\kappa_{ij}\left(\frac{1}{\tilde{\theta}_j} - \frac{1}{\tilde{\theta}_i}\right)\delta t + 2\tilde{\Gamma}^u_{ij}\,\bar{\xi}_{ij}\delta t^{1/2} \tag{A8}$$

$$\Delta m'_{ij} = \Delta m_{ij} - 2\text{Đ}_{ij}\left(\frac{\tilde{\mu}_i}{\tilde{\theta}_i} - \frac{\tilde{\mu}_j}{\tilde{\theta}_j}\right)\delta t + 2\tilde{\Gamma}^m_{ij}\,\tilde{\xi}_{ij}\delta t^{1/2} \tag{A9}$$

The thermodynamic forces are derivatives of the functional Eq. (A7), i.e.,

$$\begin{aligned} X_u &= \frac{1}{T}\left(\left.\frac{\partial\tilde{\mathcal{F}}(u_i,m_i;u_j,m_j)}{\partial u_i}\right|_m - \left.\frac{\partial\tilde{\mathcal{F}}(u_i,m_i;u_j,m_j)}{\partial u_j}\right|_m\right) \qquad \text{(A10)}\\ &= \frac{1}{\tilde{\theta}_i} - \frac{1}{\tilde{\theta}_j} \\ X_m &= \frac{1}{T}\left(\left.\frac{\partial\tilde{\mathcal{F}}(u_i,m_i;u_j,m_j)}{\partial m_i}\right|_u - \left.\frac{\partial\tilde{\mathcal{F}}(u_i,m_i;u_j,m_j)}{\partial m_j}\right|_u\right) \qquad \text{(A11)}\\ &= \frac{\tilde{\mu}_i}{\tilde{\theta}_i} - \frac{\tilde{\mu}_j}{\tilde{\theta}_j} \end{aligned}$$

If for an arbitrary function $h(u_i,m_i;u_j,m_j)$

$$\int du_i dm_i du_j dm_j\, P_{eq}\, h\frac{\partial\mathcal{F}}{\partial u_i} = k_B\int du_i dm_i du_j dm_j\, P_{eq}\frac{\partial h}{\partial u_i} \tag{A12}$$

then we obtain $\langle X_u \rangle = \langle 1/\tilde{\theta}_i - 1/\tilde{\theta}_j \rangle = 0$ and $\langle X_m \rangle = \langle \tilde{\mu}_i/\tilde{\theta}_i - \tilde{\mu}_j/\tilde{\theta}_j \rangle = 0$.

The second moment of the dynamic equation Eq. (A8) is given by

$$\begin{aligned} &\int du_i dm_i du_j dm_j \, P_{eq} \left[-4\Delta u_{ij} \kappa_{ij} \left(\frac{1}{\tilde{\theta}_j} - \frac{1}{\tilde{\theta}_j} \right) + 4\tilde{\Gamma}_{ij}^{u\,2} \langle \bar{\xi}_{ij}^2 \rangle \right] \\ &= \int du_i dm_i du_j dm_j \, P_{eq} \left[-4\kappa_{ij} k_B \left(\frac{\partial}{\partial u_i} - \frac{\partial}{\partial u_i} \right) \Delta u_{ij} + 4\tilde{\Gamma}_{ij}^{u\,2} \right] \\ &= 0 \end{aligned} \tag{A13}$$

Note that $\partial \mathcal{F}/\partial u|_m = T/\theta - 1$, and we then arrive at the FDT for the energy transfer

$$\tilde{\Gamma}_{ij}^{u\,2} = 2\kappa_{ij} k_B \tag{A14}$$

cf. Eq. (56). Proceeding similarly with the second moment of the dynamic equation, Eq. (A9), we arrive at the FDT for the mass transfer

$$\tilde{\Gamma}_{ij}^{m\,2} = 2Đ_{ij} k_B \tag{A15}$$

cf. Eq. (57).

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