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Thermostat with a local heat-bath coupling for exact energy conservation in dissipative particle dynamics

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We present a Markov process which models particle hydrodynamics with conservation of the first three momenta. This is achieved by extending the [Peters, Europhys. Lett. **66**, 311 (2004)] and [Lowe, Europhys. Lett. **47**, 145 (1999)] method to incorporate energy conservation. The equivalence of the energy conserving Peters method and dissipative particle dynamics with energy conservation (DPDE) in the limit of a vanishing time step is shown. Simple numerical experiments clearly demonstrate the applicability of the methods. This overcomes current limitations of DPDE in the study of complex fluids in the (N,V,E) ensemble.

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Dissipative particle dynamics (DPD) has attracted much attention over the past decade. Originally proposed to coarse grain the dynamics of fluids on a mesoscopic scale in the canonical ensemble [1], DPD can be considered as Brownian dynamics with additional momentum conservation. The dissipative and fluctuating forces act between pairs of particles, giving hydrodynamic behavior.

A generalization of DPD to nonisothermal systems by introducing a local equilibrium assumption has been developed independently by Avalos and Mackie [2] and Español [3]. The kinetic energy created or absorbed by the dissipative and fluctuating forces is balanced with each particle's local energy ε_i. A local entropy function $s(\varepsilon_i)$ is defined for each particle such that a definition of the particle's temperature is possible using the relation $1/T_i=\partial s/\partial\varepsilon_i$ if local equilibrium is assumed. This model is known as dissipative particle dynamics with energy conservation (DPDE).

DPDE becomes useful when applied to mesoscopic simulations of nonisothermal flow behavior. This may be of interest in microfluidic devices or biological applications where thermal fluctuations and viscous heating effects coexist. However, very few applications of DPDE have been published (see, e.g., [4]). We believe the reason for this is the fact that early versions of the discrete DPDE algorithm did conserve energy only in the mean and only in the limit of a vanishingly small time step [2,3]. The original idea behind DPD was, however, to be able to investigate systems at time scales longer than those possible using molecular dynamics. An approach to overcome this shortcoming was presented in [5]. This approach is an implicit scheme and does require a different interpretation of the stochastic differential equations of DPDE which is neither Itô nor Stratonovich. Our proposed method is a Markov process similar to existing thermostating schemes which gives an explicit algorithm. Energy conservation is imposed by inspecting the state of pairs of particles before and after the dissipative and random dynamics has been estimated. The essential result of this paper is the form of the fluctuation-dissipation theorem for the dissipative and random dynamics in the system. This is derived by comparing the limit of vanishing time step of our model to continuous DPDE.

The dissipative and random dynamics is estimated using the Peters thermostat [6]. Furthermore, a Lowe-Andersen thermostat [7] that is equivalent to DPDE with respect to its relaxation behavior in the temperature will be used. This procedure will, however, exhibit a different relaxation behavior in the higher order cumulants of the velocity distribution. Throughout this paper we will keep the term "thermostat" to outline the similarity between the traditional thermostat, which couples the system to one global and infinitely large heat bath, and our method, which couples the momentum relaxation process to each particle's local heat bath and then accounts for energy balance. By *local* heat bath, we refer to a system, which cannot be mechanistically controlled and whose heat capacity is finite but large. Thus, the energy conserving "thermostat" gives a prescription how to relax the system to its equilibrium *locally*.

The DPDE stochastic differential equations for a particle i are given by [2,3]

$$d\mathbf{r}_i = \mathbf{v}_i dt, \tag{1}$$

$$d\mathbf{v}_i = -\sum_{j\neq i} \gamma_{ij} w(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\mathbf{e}_{ij}dt + \sum_{j\neq i}\sigma_{ij}w^{1/2}(r_{ij})\mathbf{e}_{ij}dW_{ij}, \tag{2}$$

$$d\varepsilon_i = \frac{m}{2}\sum_{j\neq i}\gamma_{ij}w(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})^2dt - \frac{m}{2}\sum_{j\neq i}\sigma_{ij}^2 w(r_{ij})dt - \frac{m}{2}\sum_{j\neq i}\sigma_{ij}w^{1/2}(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})dW_{ij}, \tag{3}$$

where $\mathbf{r}_i$ is the position, $\mathbf{v}_i$ the velocity, and ε_i the internal energy of the ith particle. Furthermore, the two-particle quantities are defined as $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ and $\mathbf{v}_{ij}=\mathbf{v}_i-\mathbf{v}_j$, whereas $\mathbf{e}_{ij}$ denotes the unit vector pointing from particle j to particle i, i.e., $\mathbf{e}_{ij}=\mathbf{r}_{ij}/r_{ij}$. The symbol dW_{ij} denotes the Wiener increment [8]. Parameters of the DPDE model are the two-particle dissipation constant γ_{ij}, the two-particle noise amplitude σ_{ij}, which define the pace at which the system approaches equilibrium, and the weighting function $w(r)$, which defines

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the range of the forces. The corresponding fluctuation-dissipation theorem [2,3]

$$\gamma_{ij} = \frac{m}{4k_B}\sigma_{ij}^2\left(\frac{1}{T_i} + \frac{1}{T_j}\right) \tag{4}$$

ensures that the system relaxes to the equilibrium distribution

$$\rho^{\mathrm{eq}} = \frac{1}{Z}\exp\left(\sum_i s(\varepsilon_i)\right)\delta\left(\sum_i m\mathbf{v}_i - \mathbf{p}_0\right)$$

$$\delta\left(\sum_i (m\mathbf{v}_i^2 + \varepsilon_i) - E_0\right). \tag{5}$$

Here, E_0 and $\mathbf{p}_0$ are the total energy and the total momentum, respectively, which are conserved quantities. The kinetic theory of this model has been discussed in [9].

In the Peters thermostat for the (N,V,T) ensemble [6], the system under consideration is partially relaxed to the equilibrium situation which is known *a priori* from statistical mechanics. The thermostat considers pairs i-j of particles and modifies the relative velocity to ensure momentum conservation. The equilibrium relative velocity distribution between particles i and j is Gaussian with variance $2k_BT/m$ where T is the equilibrium temperature the system attains due to the coupling to an infinitely large heat bath. Effectively, the energy lost in the dissipative process is absorbed by the heat bath. All pairs are thermalized, but only to a fraction a, which depends on the relaxation constant γ that appears in the DPD equations of motion.

This procedure can be transfered to DPDE. In DPDE, each particle carries its own heat bath characterized by the internal energy ε_i. The kinetic energy lost in the dissipation process or gained due to fluctuations has to be balanced with the respective internal energies. Whenever a pair is thermalized the difference in kinetic energy E_{ij}^{kin} before and after the update process is split equally between the two participating particles. The equal splitting assures the system is modeled with equal *a priori* probabilities.

The variance of the local velocity distribution for a pair of particles i-j is not clear *a priori* and has to be determined by finding the limiting equation of motion for vanishing time steps Δt.

The update prescription for the Peters thermostat is

$$\mathbf{v}_i' = \mathbf{v}_i + \tfrac{1}{2}[-a_{ij}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij}) + b_{ij}W_{ij}]\mathbf{e}_{ij}, \tag{6}$$

$$\mathbf{v}_j' = \mathbf{v}_j - \tfrac{1}{2}[-a_{ij}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij}) + b_{ij}W_{ij}]\mathbf{e}_{ij}, \tag{7}$$

$$\varepsilon_i' = \varepsilon_i + \tfrac{1}{2}[(E_i^{\mathrm{kin}} + E_j^{\mathrm{kin}}) - (E_i^{\mathrm{kin}\prime} + E_j^{\mathrm{kin}\prime})], \tag{8}$$

$$\varepsilon_j' = \varepsilon_j + \tfrac{1}{2}[(E_i^{\mathrm{kin}} + E_j^{\mathrm{kin}}) - (E_i^{\mathrm{kin}\prime} + E_j^{\mathrm{kin}\prime})], \tag{9}$$

where the primed quantities denote the state after the update process and W_{ij} is a Gaussian noise term with unit variance. Note that this construction allows for *numerically exact* energy conservation. Inserting $E_i^{\mathrm{kin}}=m\mathbf{v}_i^2/2$ and using Eqs. (6) and (7), the energy update equation becomes

$$\varepsilon_i' = \varepsilon_i - \frac{m}{4}[-a_{ij}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij}) + b_{ij}W_{ij}](\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})$$

$$- \frac{m}{8}[-a_{ij}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij}) + b_{ij}W_{ij}]^2.$$

The terms quadratic in W_{ij} are also considered explicitly in the algorithm given in [5].

A compact way to express this update process is by considering the total state of the system $\mathbf{x}=\{\mathbf{r}_i,\mathbf{v}_i,\varepsilon_i, i=1,\ldots,N\}$, where N is the number of particles. Let $\mathcal{T}_{ij}$ be the operator acting on the state $\mathbf{x}$ and giving the update steps Eqs. (6)–(9) for the pair of particles i-j. Then the total operator for the thermostat is $\mathcal{T}=\Pi_{\alpha_k}\mathcal{T}_{\alpha_k}$. Here, α_k gives the order of the pairs i-j.

The update operator can be further split according to

$$\mathcal{T}_{ij} = \mathbb{1} + \mathcal{T}_{ij}^D + \mathcal{T}_{ji}^D + \mathcal{T}_{ij}^R + \mathcal{T}_{ji}^R + \mathcal{T}_{ij}^E + \mathcal{T}_{ji}^E,$$

where $\mathcal{T}_{ij}^D$ and $\mathcal{T}_{ij}^R$ give the dissipation and the random contribution to the velocity update, respectively. Update of the energy is given by $\mathcal{T}_{ij}^E$. The operators replace the specific state variable, i.e., $\mathbf{v}$ or ε, with their value after the update process, i.e., the primed quantities. These operators have the properties $\mathcal{T}_{ij}^{\mu}\mathcal{T}_{i'j'}^{R}=0$ and $\mathcal{T}_{ij}^{E}\mathcal{T}_{i'j'}^{\mu}=0$ with $\mu\in\{D,R,E\}$. Because other combinations do not necessarily give zero, the outcome of the thermalization does depend on the order of the α_k. In fact, during simulation one has to choose random permutations of all pairs for α_k in order to avoid biasing.

In equilibrium the variance of the distribution of the relative velocities must not be changed locally by the update process, i.e., $\langle\mathcal{T}_{ij}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})^2\rangle=\langle(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})^2\rangle\equiv\theta_{ij}^2$. This leads to the condition $b_{ij}=\theta_{ij}(2a_{ij}-a_{ij}^2)^{1/2}$.

By considering the update equations in the limit of vanishing time step Δt it is possible to identify a_{ij} and θ_{ij} from the DPDE equations of motion. The only quantity left that is allowed to depend on the time step is a_{ij}. Expanding to first order gives

$$a_{ij} = a_{ij}^{(1)}\Delta t + O(\Delta t^2),$$

$$b_{ij}^2 = 2\theta_{ij}^2 a_{ij}^{(1)}\Delta t + O(\Delta t^2),$$

where $a_{ij}^{(0)}=0$ must be presumed. This assures no unphysical jumps occur due to the dissipative part of the update equations for $\Delta t\to 0$. Inserting into (6)–(9) gives the vanishing time step expression for the update equations for the particle pair i-j,

$$\tilde{\mathcal{T}}_{ij}\mathbf{v}_i = -\tfrac{1}{2}a_{ij}^{(1)}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})\mathbf{e}_{ij}\Delta t + \tfrac{1}{2}(2a_{ij}^{(1)})^{1/2}\theta_{ij}W_{ij}\mathbf{e}_{ij}\Delta t^{1/2},$$

and

$$\tilde{\mathcal{T}}_{ij}\varepsilon_i = +\frac{m}{4}a_{ij}^{(1)}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})^2\Delta t - \frac{m}{4}(2a_{ij}^{(1)})^{1/2}(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})\theta_{ij}W_{ij}\Delta t^{1/2}$$

$$- \frac{m}{4}a_{ij}^{(1)}(\theta_{ij}W_{ij}\Delta t^{1/2})^2,$$

where $\tilde{\mathcal{T}}$ denotes a vanishing time step operator.

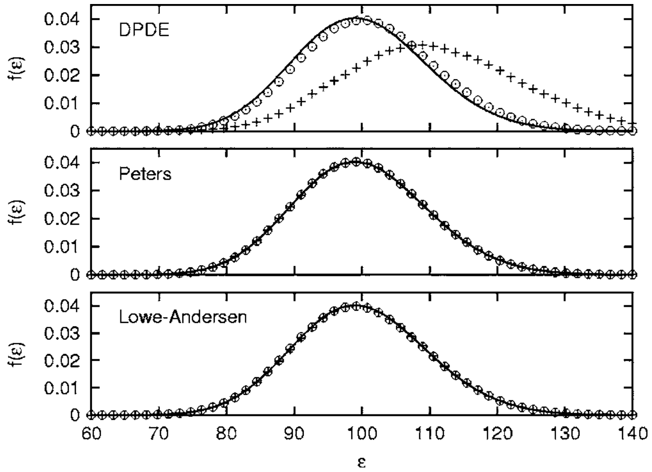

FIG. 1. Distribution of the internal energy ε in equilibrium. Figures show the results for the DPDE (top), Peters (middle), and Lowe-Andersen (bottom) integration scheme. The solid line gives the theoretical results, whereas simulation results are given for a time step of $\Delta t=0.01$ (+) and $\Delta t=0.001$ (○). For the simulation, $N=5000$ particles where observed over a total time of $t=200$.

In the limit of $\Delta t \rightarrow 0$, when only retaining terms of the order of $\Delta t^{1/2}$ and Δt, we can define the limiting operators $\tilde{\mathcal{T}}^{x}_{ij}$. These operators exhibit the properties

$$\tilde{\mathcal{T}}^{D}_{i'j'}\tilde{\mathcal{T}}^{E}_{ij}\varepsilon_i \sim (\delta_{ii'}\delta_{jj'} - \delta_{ji'}\delta_{ij'})\Delta t,$$

$$\tilde{\mathcal{T}}^{R}_{i'j'}\tilde{\mathcal{T}}^{E}_{ij}\varepsilon_i \sim (\delta_{ii'}\delta_{jj'} - \delta_{ji'}\delta_{ij'})\Delta t,$$

$$\tilde{\mathcal{T}}^{R}_{i'j'}\tilde{\mathcal{T}}^{D}_{ij}\varepsilon_i = 0.$$

Because a thermalizing operator is never applied twice, the case $i=i'$ and $j=j'$ or $i=j'$ and $j=i'$ does not occur. Thus, the total thermalization process is

$$\tilde{\mathcal{T}} = \mathbb{1} + \sum_{i\neq j} (\tilde{\mathcal{T}}^{D}_{ij} + \tilde{\mathcal{T}}^{R}_{ij} + \tilde{\mathcal{T}}^{E}_{ij}),$$

giving exactly the equations of motion for DPDE. Note that for $\Delta t \rightarrow 0$ one can identify $W_{ij}\Delta t^{1/2} = dW_{ij}$ [8].

The update equations thus reduce to the stochastic differential equations for DPDE. This allows us to make the identifications

$$a^{(1)}_{ij} = -2\gamma_{ij} w(r_{ij}),$$

$$b^2_{ij} = \frac{4k_B}{m}\left(\frac{1}{T_i} + \frac{1}{T_j}\right)^{-1}(2a_{ij} - a^2_{ij}), \tag{10}$$

with (10) being the manifestation of the fluctuation-dissipation theorem for DPDE (4). Note that (10) is the main result of this report, defining the correct equilibrium distribution in the nonisothermal case. In analogy to continuous-time DPDE a_{ij} can be called the dissipation variable and b_{ij} the noise amplitude. Note that (10) is always stable because $0 < a_{ij} < 1$. For $a_{ij}=1$ the system relaxes to its local equilibrium instantaneously.

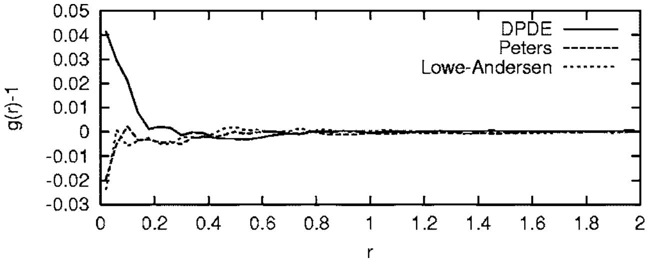

FIG. 2. Pair distribution function $g(r)-1$ for the different integration methods. The deviation from $g(r)-1=0$ for small r is due to poor statistics in this region. Time step and number of particles are chosen to be $\Delta t=0.001$ and $N=50\,000$, respectively, while averaging over $n=50\,000$ simulation steps.

There is obviously more than one choice for a_{ij}. The specific choice of a_{ij} crucially defines the deviation of the particles' trajectories from continuous DPDE. In this paper, we will use the value for a_{ij} obtained when solving the dissipative dynamics of two particles exactly, i.e.

$$a_{ij} = 1 - \exp[-2\gamma_{ij} w(r_{ij})\Delta t], \tag{11}$$

which has been proposed by Peters [6].

The Lowe-Andersen thermostat [7] is the predecessor to the Peters thermostat, and similar in the respect that pairs of particles are thermalized. However, not all pairs are thermalized, rather each pair with a probability of $\Gamma\Delta t$. The pairs are equilibrated completely, i.e., $a=1$ for the Peters thermostat. Here, Γ is the relaxation constant of the Lowe-Andersen thermostat.

Instead of using the Peters update Eqs. (6)–(9), it is also possible to use the Lowe-Andersen update equations. However, as the equations of the Lowe-Andersen thermostat do not reduce to DPD in the limit of vanishing time step, it is unclear how to choose the variance θ_{ij}. Because of the similarity between the Peters and the Lowe-Andersen method we will choose the variance θ_{ij} identically to Eq. (10). Furthermore, we will choose the relaxation constant Γ to depend on the relative position of two particles. Specifically it will be set to

$$\Gamma_{ij}\Delta t = 1 - \exp[-2\gamma_{ij} w(r_{ij})\Delta t].$$

In analogy to (11) this gives the same relaxation rate in the temperature as the corresponding Peters thermostat.

In all simulations the units are fixed to $m=1$ and $r_c=1$ using the weighting function $w(r)=15/(2\pi r_c^3)(1-r/r_c)^2$. The dissipation constant is chosen to be $\gamma=1$. Furthermore, the local entropy function is chosen to be $s(\varepsilon)=C_p \ln \varepsilon$, where $C_p=100$ is the local per-particle heat capacity. The derived quantities displayed in Figs. 1–3 are thus dimensionless, but units can be readily reintroduced. For the standard DPDE equations of motion from [2,3], a Velocity-Verlet algorithm is used for the integration of the positions and velocities as presented in [10]. An Euler algorithm is used for the integration of the energies.

The velocity and energy distribution in the equilibrium case are exactly reproduced for the Peters and Lowe-

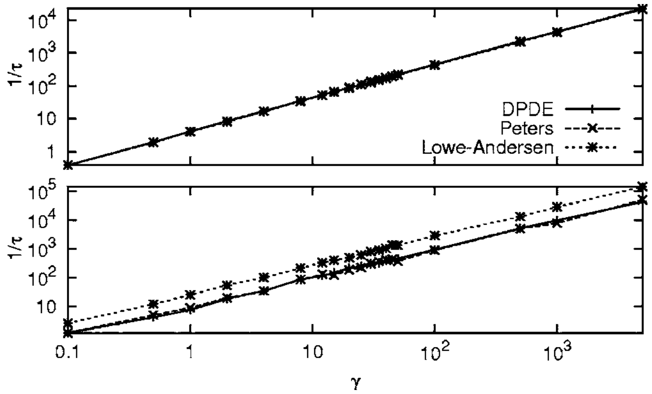

FIG. 3. Inverse relaxation time $1/\tau$ of the second cumulant (top) and the fourth cumulant (bottom) of the relative velocity distribution in dependence on the model relaxation constant γ. The time step is chosen to be $\Delta t = 2\times 10^{-5}/\gamma$ for $N=100\,000$ particles and a total of $n=10\,000$ simulation steps.

Andersen method, but not for DPDE. A Maxwell-Boltzmann distribution is obtained for velocities and the energies are distributed according to [11]

$$f(\varepsilon) = \frac{1}{M}\frac{1}{E_0}\left(\frac{\varepsilon}{E_0}\right)^{C_p/k_B}\left(1-\frac{\varepsilon}{E_0}\right)^{(N-1)(C_p/k_B+1)-1}, \qquad (12)$$

with E_0 being the total energy and M a normalization constant. This energy distribution is shown in Fig. 1. In the case of DPDE, the average energy of a particle is shifted to higher values. This corresponds to a larger total energy E_0, i.e., energy is not conserved.

The fact that both thermostating procedures do not induce structure into the system can be seen from the pair correlation function $g(r)-1$. It shows a deviation from the theoretical curve $g(r)-1=0$ that is virtually nonexisting. This is shown in Fig. 2. Note that the deviation for $r\to 0$ is due to poor statistics in that region. This is consistent with the isothermal results presented in [12].

In order to study the dynamical relaxation behavior of the thermostating schemes the system is set to nonequipartition initially. Specifically the initial velocity and energy distributions were chosen to be $f(v)=[\delta(v-(k_BT_v/m)^{1/2}]/2$ and $f(\varepsilon)=\delta(\varepsilon - C_pT_\varepsilon)$, respectively. Here T_v and T_ε correspond to two different temperatures giving nonequipartition. The relaxation of the second and fourth cumulant of the relative velocity distribution, i.e., $\langle\langle(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})^2\rangle\rangle$ and $\langle\langle(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})^4\rangle\rangle$, respectively, is observed over time, showing an exponential decay. This decay can be quantified by the inverse relaxation time $1/\tau$ and compared to the relaxation constant γ of the thermostats. Figure 3 shows that the relaxation time of the second cumulant is identical for the three methods presented. However, the Lowe-Andersen thermostat does show a faster relaxation of the fourth cumulant of the relative velocity distribution. This effect has been first predicted by Peters [6].

We presented a Markov process for particle hydrodynamics equivalent to dissipative particle dynamics with energy conservation. Outstanding results are the conservation of energy and the reduction to the DPDE equation of motion in the limit of vanishing time step. The equivalence of DPDE and the Peters scheme has been also verified numerically. This model can be regarded as a prototypical example for Markov processes that possess hydrodynamic behavior.

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