Maintaining the equipartition theorem in small heterogeneous molecular dynamics ensembles

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It has been reported recently that the equipartition theorem is violated in molecular dynamics simulations with periodic boundary condition [Shirts et al., J. Chem. Phys. 125 164102 (2006)]. This effect is associated with the conservation of the center of mass momentum. Here, we propose a fluctuating center of mass molecular dynamics approach (FCMMD) to solve this problem. Using the analogy to a system exchanging momentum with its surroundings, we work out—an validate via simulations—an expression for the rate at which fluctuations shall be added to the system. The restoration of equipartition within the FCMMD is then shown both at equilibrium as well as beyond equilibrium in the linear response regime.

I. INTRODUCTION

The equipartition theorem states that the total kinetic energy of a classical system in canonical ensemble is equally distributed among all degrees of freedom and that the average kinetic energy associated with the translational motion of a particle is given by \( \langle p^2/(2m) \rangle = d k_B T/2 \). Here, \( p \) and \( m \) are the momentum and mass of the particle, \( k_B \) is the Boltzmann factor, \( T \) denotes the temperature and \( d \) is the spatial dimension. This relation serves to control the temperature in molecular dynamics (MD) simulations by adjusting the kinetic energy of the system [1].

It has been shown recently that in MD simulations with the periodic boundary condition (PBC) the equipartition theorem is violated [2]. This effect is attributed to the conservation of the center of mass (or, equivalently, total) momentum, \( P_{cen} \), due to the PBC. This additional constant of motion restricts the simulation trajectories to only a subset of the phase space and leads to a difference between the time- and ensemble-averages [3, 4]. It can be shown that, in canonical ensemble MD simulations with PBC, the average kinetic energy of a particle of mass \( m \) obeys \[ \langle E_{kin}^p \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{d k_B T}{2} \left( 1 - \frac{m}{M_{total}} \right), \]

where \( \langle \cdots \rangle \) stands for statistical average and \( M_{total} = \sum_{i=1}^{N} m_i \) is the total mass of the system (\( N \) is the total number of particles). Eq. 1 shows that the violation of the equipartition theorem can be safely ignored if the mass of a single particle is negligible compared to the total mass of the system. Also, if all the particles have the same mass, \( m/M_{total} = 1/N \) the effect is negligible for most simulation cases. This is also in line with the general observation that differences between molecular dynamics ensembles [5] and other thermodynamic ensembles become less significant as the system size grows and eventually vanishes in the thermodynamic limit (\( N \to \infty \)) [6].

However, beyond iso-particle systems, the same problem arises principally also in hetero-particle systems, where for instance a small number of massive particles are surrounded by a large number of light particles. This includes explicit solvent MD simulations of transport properties of colloids and nanoparticles in the dilute limit and generally all multi-component mixtures. In these cases, the violation of equipartitioning may not always be tolerable. For an estimate, let us consider a system consisting of \( N_l \) light particles of mass \( m_0 \) and \( N_h \) massive particles of mass \( \alpha m_0 \). This yields \( M_{total} = (N_l + \alpha N_h) m_0 \) and thus one obtains for the average kinetic energy of the heavy particle, \( \langle E_{kin}^{h} \rangle = \frac{1}{1 + \alpha N_h} d k_B T/2 \). Obviously, in the limit that the total mass of the heavy particles is large compared to the total mass of the light particles \( (\alpha \gg N_l/N_h) \), this reduces to \( \langle E_{kin}^{h} \rangle \approx (1 - 1/N_h) d k_B T/2 \). Thus, the average kinetic energy of a single heavy particle approaches zero with increasing mass.

The present paper addresses this point. We propose a method to restore the equipartition theorem in molecular dynamics ensembles containing components with different masses. For this purpose, we first use computer simulations of a massive tracer particle in an ambient liquid and provide evidence for the idea that, as noted in [2, 3], the main cause of the problem is the conservation of the center of mass momentum. Based on this understanding, we propose a molecular dynamics method which allows for the fluctuations of the center of mass momentum, \( P_{cen} \) (note that, in equilibrium, \( \delta P_{cen} = P_{cen} \), since \( \langle P_{cen} \rangle = 0 \)). For a reliable implementation of the method, we also determine the rate at which fluctuations shall be added to the system, Eq. 3. The validity of this expression is confirmed via computer sim-
ulations of systems with rigid walls, which do not have the artificial constant motion, \( P_{\text{cm}} = 0 \). Finally, we test the method showing that it does restore equipartitioning both in equilibrium and beyond equilibrium in the linear response regime.

II. VIOLATION OF EQUIPARTITION FOR A MASSIVE TRACER

As mentioned above, a strong violation of the equipartition theorem is expected for the case of a massive tracer particle in a liquid environment. In order to demonstrate this property, we perform MD simulations of a generic 80:20 binary mixture of Lennard-Jones particles (types A and B) \( \text{[8, 9]} \). A and B particles interact via \( U_{\text{LJ}}(r) = 4\epsilon_{\alpha\beta}[(d_{\alpha\beta}/r)^{12} - (d_{\alpha\beta}/r)^{6}] \), with \( \alpha, \beta = A, B \), \( \epsilon_{\alpha\beta} = 1.5\epsilon_{AA} \), \( \epsilon_{BB} = 0.5\epsilon_{AA} \), \( d_{AB} = 0.8d_{AA} \), \( d_{BB} = 0.88d_{AA} \), and \( m_A = m_B \). The potential is truncated at twice the minimum position of the LJ potential, \( r_{c,\alpha\beta} = 2.245d_{\alpha\beta} \). The parameters \( \epsilon_{\alpha\beta} \), \( d_{\alpha\beta} \) and \( m_A \) define the units of energy, length and mass. The unit of time is kept constant at the value of 1.2 and temperature at \( T = 1 \) for all simulations whose results are reported here. Depending on the case studied, linear dimension and total particle number are in the range of \( L \in [4.7, 203] \) and \( N \in [125, 10684] \). Equations of motion are integrated using the velocity-Verlet algorithm with a discrete time step of \( dt = 0.005 \).

The results presented here are expected to be largely model independent and hence general. The choice of the above model is purely historical and is motivated by the fact that we have been using it to study a number of problems in the context of the physics of glasses \( \text{[12, 13]} \). We indeed encountered the present problem of the violation of the equipartition theorem as we inserted massive tracer particles into our model to study the concept of effective temperature \( \text{[14, 15]} \).

With the exception of one, the mass of all particles is set to unity. One of the particles (of type B) is taken to be the massive tracer. The mass of this particle is then varied and its kinetic energy is monitored. Simulation results are averaged over 40 independent runs. In order to investigate the possible role of the thermostat, all the simulations are performed both for the Nosé-Hoover (N-H) \( \text{[16, 17]} \) and the Andersen \( \text{[18]} \) thermostats. In equilibrium simulations, all components of particle velocities are coupled to the thermostat. We also extend the present analysis to a non-equilibrium steady state situation by imposing a linear shear flow via the SLLOD-algorithm combined with the Lees-Edwards boundary condition (LEBC) \( \text{[19]} \). In this case, coupling to the thermostat is done only for the velocity component in the direction perpendicular to the shear plane (vorticity direction). By doing so, we avoid problems related to the flow-induced bias on the kinetic energy, when regulating the system temperature \( \text{[20]} \).

Results obtained via these simulations are depicted in Fig. (1). As seen in this plot, the violation of the equipartition theorem occurs in perfect agreement with the theoretical predictions of Eq. (1), independent of the specific thermostat.

Next we provide evidence from simulation that the deep reason for the violation of the equipartition theorem is indeed the conservation of the total momentum \( \text{[2, 3]} \). For this purpose, we have designed a simulation setup where \( P_{\text{cm}} \) is not conserved. This is achieved by introducing two planar walls separated by a distance \( L_z \) along the \( z \)-direction, while PBC is used along the \( x \) and \( y \) directions. The walls are made of particles with the same size and structure as the liquid particles so that liquid-wall interactions induce fluctuations of \( P_{\text{cm}} \) along all spatial directions. Results of these simulations are also shown in Fig. (1), demonstrating that, as expected, the equipartition theorem is valid in systems with walls.

III. FLUCTUATING CENTER OF MASS MD (FCMMD)

The above results suggest that a possibility to restore the equipartition theorem is to introduce walls with roughness on the particle scale. However, in studies focusing on bulk properties, walls are undesired since they in general influence the system properties unless very large wall-to-wall separations are used (see, e.g., \( \text{[21, 22]} \) and references therein). Thus, it is desirable to introduce a method which uses PBC, while at the same time allowing for fluctuations of the total momentum. Such a method is proposed here. Our approach is quite simple...
and is motivated by the fact that, in a system exchanging momentum with its environment, the center of mass momentum is a fluctuating quantity.

Motivated by this idea, we perform the following two steps: (i) Draw a value for \( P_{\text{cn}} \) and (ii) distribute it among particles. These steps are carried over, repeatedly, during the simulation. In order to have the canonical sampling of the phase space, the total momentum assigned in step (i) should assume a distribution probability coinciding with the canonical distribution function for \( P_{\text{cn}}'s \):

\[
\bar{f}(P_{\text{cn}}) = \int f(\chi)\delta(\sum_{i=1}^{N} p_i - P_{\text{cn}}) d\chi = \sqrt{\frac{1}{2\pi k_B T M_{\text{total}}}} \exp \left[-\frac{P_{\text{cn}}^2}{2k_B T M_{\text{total}}} \right],
\]

where \( f(\chi) \) is the probability of the micro-state \( \chi \), and \( \delta \) is the Dirac delta-function. Similar to the discussion in Ref. [1] for choosing kinetic energy from the canonical distribution, one has a certain flexibility in choosing the sampling rate. Here, we provide a physical criterion to estimate the time scale of the \( P_{\text{cn}} \)-fluctuations. We build our analysis upon the fact that fluctuations of \( P_{\text{cn}} \) are caused by the exchange of momentum with the surrounding medium.

For a system with \( P_{\text{cn}}(t = 0) = 0 \), it follows from the above considerations that, due to interactions with the surrounding medium, \( P_{\text{cn}} \) will not remain zero but increases with time. On the other hand, too large a value of \( P_{\text{cn}} \) will decay due to the same interactions. Collisions with the surrounding medium thus provide a source of stochastic noise and, at the same time, give rise to viscous friction. This is very similar to the fluctuations of the velocity of a Brownian particle in a fluid. The probability distribution of these fluctuations is obtained as the solution of a Fokker-Planck equation subjected to the potential \( \phi \) [24],

\[
\frac{\partial f(P_{\text{cn}}, t)}{\partial t} = \mu \nabla |P_{\text{cn}}| \cdot (\nabla |P_{\text{cn}}| \phi) + D (\nabla |P_{\text{cn}}|)^2 \bar{f},
\]

where \( \phi(P_{\text{cn}}) = -P_{\text{cn}}^2/(2M_{\text{total}}) \) and \( \nabla |P_{\text{cn}}| = (\partial/\partial P_{\text{cn},x}, \partial/\partial P_{\text{cn},y}, \partial/\partial P_{\text{cn},z}) \). The mobility, \( \mu \), and diffusion constant, \( D \), obey the Einstein relation, \( \mu = D/(k_B T) \). Given \( P_{\text{cn}} \) at time \( t' \), the conditional probability distribution at a time \( t > t' \) is [24],

\[
\bar{f}(P_{\text{cn}}, t | P_{\text{cn}}', t') = \sqrt{\frac{1}{2\pi \sigma^2(t, t')}} \exp \left\{ -\frac{(P_{\text{cn}} - P_{\text{cn}}')^2}{2\sigma^2(t, t')} \right\},
\]

where \( \gamma = \mu M_{\text{total}} \) and \( \sigma^2(t, t') = dk_B T M_{\text{total}}[1 - \exp(-2\gamma(t - t'))] \). It is seen from Eq. [4] that \( \rho \) reaches the expected Maxwell distribution, Eq. [2], in the limit of long times, \( t - t' \gg 1/\gamma \). The characteristic time for reaching the equilibrium distribution of center of mass fluctuations is thus obtained from \( \tau = 1/\gamma \),

\[
\tau = \frac{M_{\text{total}} k_B T}{D}.
\]

This expression is not fully satisfactory as it contains an important unknown parameter, \( D \). We therefore attempt at an estimate of \( \tau \) from a microscopic consideration. For this purpose, we again recall that, starting with \( P_{\text{cn}}(t = 0) = 0 \) collisions with the surrounding medium will lead to \( \langle P_{\text{cn}}^2 \rangle = dM_{\text{total}} k_B T \) within a time of the order of \( \tau \). For simplicity, we assume here that \( P_{\text{cn}} \) is the sum of \( N_s \) statistically independent elementary momentum fluctuations, \( \delta p_i \), resulting from the collisions between fluid particles with the system’s boundary, \( P_{\text{cn}} = \sum_i N_s \delta p_i \). This yields \( \langle P_{\text{cn}}^2 \rangle = N_s \langle \delta p^2 \rangle \) and thus \( N_s \langle \delta p^2 \rangle = dM_{\text{total}} k_B T \). The time scale \( \tau \) is encoded in the number of elementary collisions \( N_s \). To see this, we first note that momentum exchange occurs within a “skin” – which runs parallel to the boundary – of thickness equal to mean free path, \( l_{\text{free}} \). On average, \( 1/6 \)th of these particles in the skin layer move along the perpendicular direction toward the boundary and will undergo a collision within a time of \( \delta t \sim l_{\text{free}}/(v_\perp) = 6 l_{\text{free}}/\sqrt{k_B T m} \) where \( \langle v_\perp \rangle \) is the average thermal velocity in the direction normal to the boundary. The total number of collisions within a time of \( \tau \) is thus obtained as \( N_s \sim \rho l_{\text{free}} A/6 \times \gamma /\delta t \sim \rho A \sqrt{k_B T/m}/6 \). To arrive at a closed expression for \( \tau \), the magnitude of the typical momentum exchange per collision is estimated: \( \delta \rho \sim 2 m \langle v_\perp \rangle = 2 \sqrt{m k_B T} \). Combining the above two expressions for \( N_s \) and using this last relation for \( \delta \rho \), one finally finds

\[
\tau = \frac{C}{\rho (mk_B T)^{1/2}} \frac{M_{\text{total}}}{A},
\]

where \( C \) is a constant prefactor. Equation [6] gives an estimate for the characteristic time of the \( P_{\text{cn}} \)-fluctuations in a system exchanging momentum with its surroundings through a boundary (interface) of surface area \( A \).

In order to test this result, we have performed a series of three dimensional MD simulations of the present binary LJ model confined between two parallel walls for different system sizes while keeping all other simulation parameters constant (e.g., \( T = 1 \), \( \rho = 1.2 \), \( m = 1 \)). The characteristic time is measured by the auto-correlation time of fluctuations of \( P_{\text{cn}} \). Note that, in these simulations, PBC is used along the \( x \) and \( y \) directions, so that no momentum fluctuations will originate from the corresponding boundaries. In other words, the relevant surface area, \( A \), appearing in Eq. [6] corresponds to the surface area of the walls. To better highlight the dependence of \( \tau \) on \( M_{\text{total}} \) and \( A \), we studied two different geometries leading to qualitatively different results for \( \tau \) in terms of the total mass. In the first series of simulations, the system was a cube with length \( L \) so that \( M_{\text{total}} = \rho L^3 \) and
The time scale, $\tau$, for $P_{\text{cm}}$-fluctuations versus total mass in a system confined by two planar walls. $\tau$ is determined from the decay of the autocorrelation function, $\langle P_{\text{cm}}(t)P_{\text{cm}}(0) \rangle$. Results are shown for two different geometries. In case I, the simulation box is a cube and the variation of $M_{\text{total}}$ is accompanied by a corresponding change of the surface area of the walls. In case II, the surface area of the walls is kept constant but only the distance of the walls is varied. Using Eq. (6), one thus expects $\tau \propto M_{\text{total}}^{1/3}$ in case I but $\tau \propto M_{\text{total}}$ in case II (solid lines).

In our scheme, we update $P_{\text{cm}}$ using a random walk sampling $f(P_{\text{cm}})$ with time scale of order $\tau$, Eq. (2). The question arises now as how to distribute a given $P_{\text{cm}}$ among particles. In canonical ensemble, if the total momentum of the system is $P_{\text{cm}}$, the conditional average for the momentum of a particle is equal to $\langle p \rangle = mP_{\text{cm}}/M_{\text{total}}$. We, therefore, propose that the imposed momentum change be divided among particles proportional to their individual masses. In analogy to the system with walls, the momentum change is applied to each particle once at a time. The order of particles is chosen randomly. After adding momentum to each particle, relative velocities of all particles with respect to the center of mass are rescaled. This last operation does not modify the center of mass momentum but allows to restore the kinetic energy exactly to the value before updating $P_{\text{cm}}$.

Results obtained from these simulations are shown in Fig. 2. As shown in this figure, the proposed approach is able to restore the equipartition theorem both in equilibrium simulations as well as in a system beyond equilibrium in the linear response regime.

In this work, we propose a modification of the molecular dynamics method with periodic boundary condition to restore the equipartition theorem. The method is based on introducing fluctuations of the center of mass momentum. The issue of a proper rate at which $P_{\text{cm}}$ fluctuations are imposed to the system is also addressed and validated against simulations. It is shown that the method restores equipartition both at equilibrium and under steady shear in the linear response regime. This latter finding is of crucial importance for studies, which focus on a violation of the equipartition due to non-linear off-equilibrium effects [14, 15]. It is noteworthy that the violation of equipartition does not exclusively occur in MD simulations. As an example, it has also been observed in the fluctuating lattice Boltzmann method where equipartitioning is important at all length scales [22]. The relevance of the present work is thus not restricted to MD simulations but may also provide guidance for restoring equipartitioning and hence, a correct thermostat method, in other mesoscale simulations [26, 27].

IV. CONCLUSION

In this work, we propose a modification of the molecular dynamics method with periodic boundary condition to restore the equipartition theorem. The method is based on introducing fluctuations of the center of mass momentum. The issue of a proper rate at which $P_{\text{cm}}$ fluctuations are imposed to the system is also addressed and validated against simulations. It is shown that the method restores equipartition both at equilibrium and under steady shear in the linear response regime. This latter finding is of crucial importance for studies, which focus on a violation of the equipartition due to non-linear off-equilibrium effects [14, 15]. It is noteworthy that the violation of equipartition does not exclusively occur in MD simulations. As an example, it has also been observed in the fluctuating lattice Boltzmann method where equipartitioning is important at all length scales [22]. The relevance of the present work is thus not restricted to MD simulations but may also provide guidance for restoring equipartitioning and hence, a correct thermostat method, in other mesoscale simulations [26, 27].

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