Nosé-Hoover chain method for nonequilibrium molecular dynamics simulation

A. C. Brańka

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland
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It is demonstrated that the Nosé-Hoover chain (NHC) thermostat method influences the properties of a system out of equilibrium. A simple modification of the NHC equations is proposed which enables both steady-state averages and time correlation functions to be obtained correctly for nonequilibrium states, and consistent with those computed using Gaussian isokinetic and Nosé-Hoover dynamics.

I. INTRODUCTION

The Nosé-Hoover chain (NHC) method proposed by Martyna, Klein, and Tuckerman [1] has been considered a primary tool for thermostatting small or stiff systems where other approaches are less efficient or even fail. The method is based on a hierarchy of thermostats, which are themselves thermostatted. It is a generalization of the original Nosé-Hoover (NH) dynamics [2] and is designed to produce isothermal time reversible dynamics and a canonical distribution for both positions and momenta of many-particle systems.

The NHC method has been applied to a large number of complex problems such as protein dynamics [3], quantum studies of metal-ammonia solutions [4], and the integration of the *ab initio* Car-Parrinello equations [5]. The NHC scheme and its isothermal-isobaric version have been implemented in path integral simulations [6]. For very stiff systems a generalization of the NHC thermostat, called the massive Nosé-Hoover chain dynamics (MNHC), has been introduced [1,7]. It consists of attaching an independent Nosé-Hoover chain to each degree of freedom of the system. The MNHC method has been used for calculating the free-energy of solids from first-principles [8] and in the adiabatic switching procedure for an Einstein crystal [9]. Also, the NHC and its isothermal-isobaric version have been used to study molecular fluids under shear [10].

Although the NHC approach is valid at equilibrium its utility for nonequilibrium problems is not so obvious [11,12]. Recently, Holian, Voter, and Ravelo [13] pointed out that the desired kinetic temperature of the studied system can no longer be guaranteed away from equilibrium if the NHC dynamics is used. This undesirable feature of the NHC thermostat clearly casts some doubt concerning its general applicability. In this paper we shall study this problem in more detail and propose a simple modification of the NHC equations which ensures correct temperature control away from equilibrium.

II. NH AND NHC THERMOSTATS

In order to analyze the behavior of the NHC thermostats in the nonequilibrium nonlinear regime, we consider the specific system of a WCA fluid subjected to a Couette shear strain rate field, which are the same system and conditions as used by Evans and Sarman [14] in their investigations of the equivalence between the Gaussian and Nosé-Hoover thermostatted nonlinear responses. The WCA fluid used in the simulations consisted of systems of $N = 108$, 512, and 2048 particles interacting via a pairwise Lennard-Jones potential $u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, truncated and shifted at its minimum $r/\sigma = 2^{1/6}$. The equations of motion were the thermostatting SLLOD equations [15]

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{x}\gamma y_i, \tag{1}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{x}\gamma p_{yi} - \zeta\mathbf{p}_i. \tag{2}$$

In these equations $\mathbf{q}_i$ and $\mathbf{p}_i$ are the position and peculiar momenta of particle i, respectively, and $\mathbf{F}_i$ is the net force on particle i due to the other particles in the system, m is the mass of the particle, $\mathbf{x}$ is the unit vector in the x direction, and γ is the imposed strain rate. ζ represents the thermostatting mechanism and the expression for it depends on the particular choice of the thermostat.

In the case of the NH thermostat the ζ is governed by the following equation:

$$\dot{\zeta} = \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} - gk_BT \right) \bigg/ Q, \tag{3}$$

where T denotes the temperature, k_B is the Boltzmann constant, g is the number of degrees of freedom of the system, and Q is a parameter that describes the coupling between the particles and the thermal bath.

For the NHC method [1], in the general case, the thermostat is represented by M thermostatting variables $\{\zeta, \zeta_2, \ldots, \zeta_M\}$ and M associated parameters $\{Q, Q_2, \ldots, Q_M\}$. The thermostatting variable ζ, which is the only one coupled directly to the system of particles, is governed by the following chain of the equations:

$$\dot{\zeta} = \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} - gk_BT \right) \bigg/ Q - \zeta\zeta_2, \tag{4}$$

$$\dot{\zeta}_2 = (Q\zeta^2 - k_BT)/Q_2 - \zeta_2\zeta_3, \tag{5}$$

$$\dot{\zeta}_{M-1} = (Q_{M-2}\zeta_{M-2}^2 - k_BT)/Q_{M-1} - \zeta_{M-1}\zeta_M, \tag{6}$$

$$\dot{\zeta}_M = (Q_{M-1}\zeta_{M-1}^2 - k_BT)/Q_M. \tag{7}$$

The results quoted in this work are in conventional reduced units: the length in σ, the energy in ε, the temperature in ε/k_B, and the time unit is $\sigma\sqrt{m/\varepsilon}$. The Q parameters are in Lennard-Jones units ε. The state point simulated was at the reduced temperature $T=0.722$, and a reduced density $\varrho=0.8442$. Most calculations were performed at the reduced shear rate $\gamma=1$. The equations of motion were solved using a fourth-order Runge-Kutta method with a time step of $\Delta t=0.001$. For the 108 and 512 particle systems the simulations were carried out for 5×10^6 and 1×10^6 time steps, respectively. For a 2048-particle system several calculations for 5×10^5 time steps were performed.

The optimum choice for the parameter Q in the NH dynamics has been the subject of several previous investigations [16,13]. It has been established that the optimal choice for Q is the value that reproduces correctly not only the average value of the kinetic energy but, importantly, also its fluctuations. Q is proportional to the number of particles and can be approximately estimated from the expression

$$Q^c \approx \frac{Nk_BT}{\omega^2}, \tag{8}$$

where ω is a characteristic frequency of the system.

For $Q\ll Q^c$ there is a strong coupling between the system of particles and the thermal bath, manifest in a persistent underestimation of the fluctuations of the kinetic energy. (In the limit, $Q\to 0$, the dynamics tend to produce an instantaneous control of the temperature and thus the canonical dynamics are no longer followed.)

In the weak coupling limit, $Q\gg Q^c$, the evolution of the variable ζ is too slow to produce efficient feedback of the temperature and consequently a slow convergence to the correct results is observed. It has also been observed that for, $Q\approx Q^c$, the autocorrelation functions (ACF) of dynamical quantities such as the kinetic energy or the thermostat variable itself, vanishes rapidly. However, for Q different from Q^c, the ACF decay slowly with long-lived oscillations.

In the case of the NHC method it has been argued that the additional $M-1$ parameters can be estimated quite well from the relation $Q_j=Q^c/N$ [1]. It has also been argued that the choice of the Q-parameter values are less critical in the NHC approach than in NH dynamics.

In order to establish the optimum value of the Q parameter for our system, we have performed some preliminary simulations with the unsheared (i.e., $\gamma=0$) WCA fluid. Using several values of Q in the range $0.01-100$ it was observed that, in the 108-particle system governed by NH dynamics, the temperature variance was close to the canonical expectation for $0.1<Q<10$ and the best estimate was obtained for $Q^c(108)\approx 0.5$. Similar calculations with the 512-particle system led to the optimal value $Q^c(512)\approx 2$. Calculations performed with the same conditions using the NHC dynamics (M=2, $Q_2=Q/N$) gave similar values for the optimal Q for 108- and 512-particle system. In both dynamics, the autocorrelation functions of the kinetic energy and $\langle\zeta(t)\zeta(0)\rangle$, vanished rapidly when the Q^c was used and displayed a very long oscillatory decay when $Q<0.1$ or $Q>10$ was used. Similar behavior was observed when the shear rate ($\gamma=1$) was applied to the $N=108$ particle system and the NH thermostat was used. Furthermore, in this case,
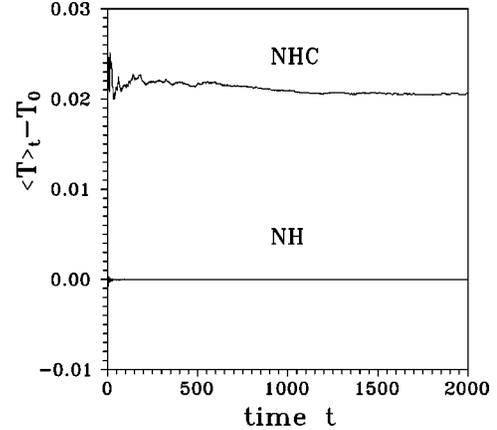

FIG. 1. Deviations of the average kinetic temperature from the target temperature $T_0=0.722$, as a function of accumulated simulation time in the WCA fluid of $N=108$ particles under shear $\gamma=1$ with the NHC (upper curve) and the NH (bottom curve) dynamics ($Q=Q^c$).

as long as $0.1<Q<10$, the calculated quantities were insensitive to its exact value. The above results allow us to consider the values close to 0.5 (2.0) as suitable values of Q for the studied WCA fluid of $N=108$ ($N=512$) particles both at equilibrium and steady-states under applied shear. For the 2048-particle system, exploiting the relation (8) we estimate the Q^c to be $Q^c(2048)\approx 2048Q^c(108)/108\approx 10$.

We mention that a steady-state at the desired temperature was reached quickly if the NH thermostat was used (e.g., in the case of $N=108$, usually fewer than 2×10^4 time steps were required to achieve the target kinetic temperature T_0 of 0.722). As may be seen in Fig. 1, the steady state was also readily produced by the NHC dynamics. However, with these dynamics the average temperature was significantly higher than the required one. Consequently other quantities such as the internal energy and the components of the pressure tensor were different from the values obtained using the NH dynamics. We have checked, by performing simulations two and five times longer, that the simulation length does not change the values of the averages and the temperature does not converge to the required value as simulation time increases.

Unlike the sllod (so named because of its close relationship to the Dolls tensor algorithm) equations with the NH dynamics, the sllod equations with the NHC thermostat produced a steady state with a ''temperature'' that strongly depends on the particular value of the Q parameter. This undesirable behavior is demonstrated in Fig. 2. The temperature deviation increases monotonically with increasing Q. It may seem that at small values of Q, the NHC dynamics are able to produce the correct value for the temperature. However, even at quite small values of the Q the deviations are still noticeable (e.g., for 108-particle system and $Q=0.05$ we obtained $\langle T\rangle=0.7226$). Furthermore, applying small values of Q compared to the Q^c, one shifts the dynamics towards the strong coupling limit (discussed above) in which a very long oscillatory decay of the kinetic energy ACF is observed.

As may be seen in Fig. 2 the Q dependence of the ''temperature'' for the 512-particle system is very similar to that of the (small) 108-particle system. The ''temperature'' deviation at Q^c in the larger system is substantially larger than
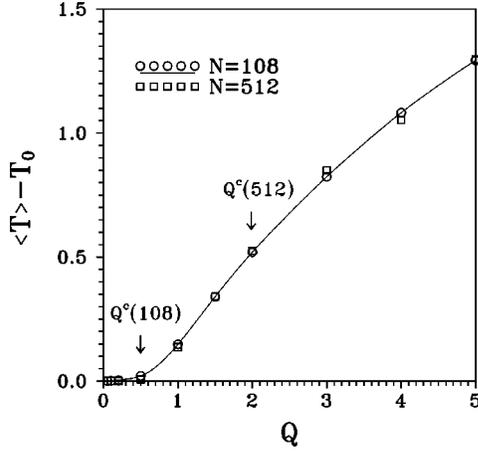
FIG. 2. Temperature deviations from the target temperature T_0 produced by the NHC thermostat [Eqs. (4)–(7)] as a function of the parameter Q. The solid line is meant to guide the eye.

that in the small system. Thus, as Q^c is proportional to N, the deviation from the target temperature produced by the NHC dynamics with Q^c *increases* with the number of particles in the system.

The influence of the value of the Q_2 parameter is less critical on the calculated temperature, and as long as Q_2 is not substantially different from Q^c/N, the result is relatively insensitive to its precise value.

As one can see in Fig. 3, the ''temperature'' in the NHC dynamics is also a function of the strain rate. The dependence is roughly exponential: $\langle T \rangle = T_0 + A \exp(a\gamma)$, where A and a are constants which in general depend on Q and N. In the particular state studied ($N = 108$, $Q = Q^c$) we found that $A = 2.06 \times 10^{-5}$ and $a = 6.86$. As a is fairly large and A is small the deviations from the desired temperature increase markedly for shear strain rates greater than 0.5 but are practically indetectable for the strain rates less than 0.2.

Also the number of thermostat variables used in the NHC scheme does influence the resulting ''temperature.'' The most significant improvment is achieved when $M = 3$ is used instead of $M = 2$. For $M > 3$ the improvment, if any, is mar-
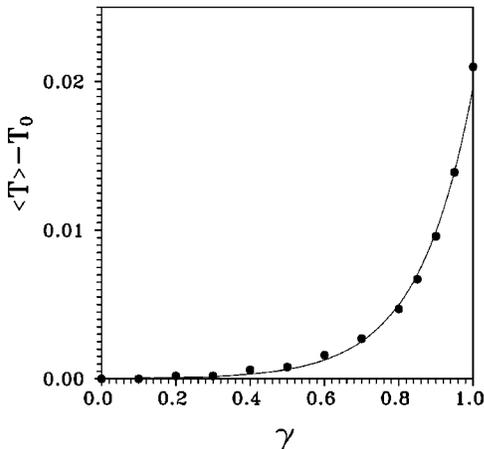

FIG. 3. Temperature deviations from the target temperature T_0 for 108 WCA fluid ($T_0 = 0.722$, $\varrho = 0.8442$, $Q = Q^c$) as a function of the strain rate (dots). The solid line is the exponential fit.
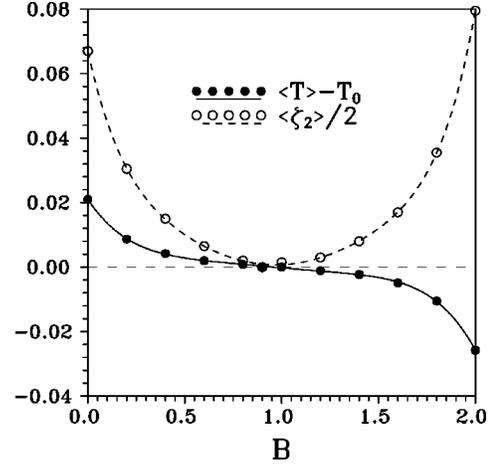

FIG. 4. Temperature deviations and the average of the chain variable ζ_2 obtained under the modified NHC thermostat [Eqs. (9)–(12)] at several different values of the parameter B (the WCA fluid, $N = 108$, $T_0 = 0.722$, $\varrho = 0.8442$, $\gamma = 1$, $Q = Q^c$). The dashed and solid lines are 6th and 5th order polynomial fits to the simulation data, respectively.

ginal and thus, a further increase of M does not help in achieving the desired temperature T_0.

The above results clearly demonstrate that for a system out of equilbrium the NHC approach is not able to provide dynamics consistent with the desired temperature. We should add, however, that in calculations with $Q \approx Q^c$ and $M \geqslant 3$ the deviations from the correct results become practically undetectable if γ is less than 0.2. Thus, at small shear rates not too far from equilibrium, the drawbacks of the NHC scheme are not so serious, even for systems with a fairly large number of particles.

Some explanation of the inability of the NHC approach to produce the correct steady-state averages in the nonlinear regime can be deduced from the equivalence theory of the thermostatted nonlinear responses derived by Evans and Sarman [14]. As has been demonstrated [17,14], both theoretically and by the MD simulations, the different thermostatting approaches yield essentially the same time correlation functions and steady-state averages even in the far-from-equilibrium nonlinear regime. In particular, it has been shown that (in the large system limit) the Gaussian and Nosé-Hoover isothermal thermostats produce the same steady-state averages.

In the theory the same steady-state average value of the phase-space compression factor [15] Λ are assumed for the Gaussian and Nosé-Hoover thermostatted systems. This assumption apparently is not fulfilled in the case of the NHC thermostat. For $M = 2$, for example, the phase-space compression factor $\Lambda_{NHC} = -3N\zeta_{NHC} - \zeta_2$, differs from the appropriate Nosé-Hoover compression factor $\Lambda_{NH} = -3N\zeta_{NH}$, by ζ_2. As it is reasonable to assume $\langle \zeta_{NHC} \rangle - \langle \zeta_{NH} \rangle = 0$ the average compression factors differ by $\langle \zeta_2 \rangle$. Thus, as far as $\langle \zeta_2 \rangle \neq 0$ one may expect that the NHC dynamics will produce different results to the NH dynamics. (Note that at equilibrium, $\langle \zeta_2 \rangle$ is equal to zero and the NH and NHC schemes produce the same, correct, result.)

The above considerations suggest that if the NHC equations could be modified in a way to produce $\langle \zeta_2 \rangle = 0$, they

TABLE I. Comparison between the three thermostats for 108 WCA particles under shear $\gamma = 1$, at $T_0 = 0.722$ and $\varrho = 0.8442$.

Property	Gaussian[a] const T	NH const T	NHC M=2 B=0.983	NHC M=5 B=0.983	NHC M=2 B=0
$\langle \zeta \rangle$	0.989(2)	0.984(2)	0.981(2)	0.983(2)	0.943(4)
$\langle T \rangle$	0.722	0.7220	0.7220	0.7220(1)	0.743(1)
U		0.837(1)	0.836(1)	0.837(1)	0.854(1)
P_{xy}	1.786(3)	1.782(2)	1.779(2)	1.781(3)	1.784(3)
P_{xx}	7.182(5)	7.183(5)	7.181(7)	7.183(7)	7.297(6)
P_{yy}	7.207(2)	7.208(5)	7.204(5)	7.204(4)	7.311(7)
P_{zz}	6.832(5)	6.834(3)	6.832(3)	6.831(6)	6.946(8)
η_-	0.012(2)	0.013(4)	0.012(4)	0.011(4)	0.007(4)
η_0	0.180(1)	0.181(2)	0.180(3)	0.181(3)	0.179(3)

[a]From Ref. [14].

would also be expected to produce correct steady-state averages in the nonlinear regime at a given temperature. This is the subject of the next section.

III. MODIFIED NHC THERMOSTAT

We propose to consider the following modified NHC equations:

$$\dot{\zeta} = \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} - g k_B T \right) \bigg/ Q - (\zeta - B)\zeta_2, \qquad (9)$$

$$\dot{\zeta}_2 = [Q(\zeta - B)^2 - k_B T]/Q_2 - \zeta_2 \zeta_3, \qquad (10)$$

$$\dot{\zeta}_{M-1} = (Q_{M-2}\zeta_{M-2}^2 - k_B T)/Q_{M-1} - \zeta_{M-1}\zeta_M, \qquad (11)$$

$$\dot{\zeta}_M = (Q_{M-1}\zeta_{M-1}^2 - k_B T)/Q_M. \qquad (12)$$

The above equations differ from the original NHC equations only by the appearance of a constant B in Eqs. (9) and (10). The role of this constant is demonstrated in Fig. 4. As one can see, the calculations performed with different B lead to the different kinetic "temperatures" in a way well-described by a fifth order polynomial. An important fact is that at particular values of B close to $\langle \zeta \rangle$, the average of ζ_2 becomes practically zero and the target temperature is

achieved. Thus, using the modified NHC thermostat together with $B \approx \langle \zeta \rangle$ we are able to overcome the main problem with the NHC dynamics. Moreover, properties of the system calculated with this thermostat are totally consistent with the results produced by the NH and Gaussian dynamics. This is demonstrated in Tables I and II.

Table I presents some basic properties of the small system under shear obtained with the various thermostats. The η_0 and η_- denote the viscosity coefficients defined as $-[P_{zz} - (P_{xx} + P_{yy})/2]/2\gamma$ and $-(P_{xx} - P_{yy})/2\gamma$. $P_{\alpha\beta}$ are the components of the pressure tensor and U is the average potential energy per particle. All the properties produced by the NH and the modifed NHC dynamics agree very well within estimated statistical uncertainties. Apart from the average of the ζ, they also agree well with the results of the Gaussian thermostatted dynamics. The difference in the ζ is, however, less than $O(1/N) = 0.01$ which means the results agree according to predictions of the theory of equivalence of thermostatted responses. For comparison, the last column in the table shows apparently incorrect results produced by the original NHC equations [Eqs. (1), (2), (4)–(7)]. The results for the same properties obtained for larger 512- and 2048-particle systems are shown in Table II. Here all the properties, including $\langle \zeta \rangle$, agree within estimated statistical uncertainties. They also agree very well with the results of the Gaussian constant temperature dynamics. It is to be noticed

TABLE II. Comparison between the three thermostats for 512 and 2048 WCA particles under shear $\gamma = 1$, at $T_0 = 0.722$ and $\varrho = 0.8442$.

| Property	NH (N=512) const T	NHC (N=512) M=2, B=0.989	NH (N=2048) const T	NHC (N=2048) M=2, B=0.990	Gaussian[a] (N=2048)
$\langle \zeta \rangle$	0.991(3)	0.991(2)	0.989(2)	0.990(3)	0.990(2)
$\langle T \rangle$	0.7220	0.7220	0.7220	0.7220(1)	0.722
U	0.845(1)	0.845(1)	0.845(1)	0.846(1)	
P_{xy}	1.809(5)	1.809(2)	1.806(4)	1.809(5)	1.808(1)
P_{xx}	7.224(4)	7.224(3)	7.224(7)	7.229(8)	7.226(2)
P_{yy}	7.269(9)	7.269(4)	7.271(5)	7.270(9)	7.269(3)
P_{zz}	6.909(4)	6.909(4)	6.909(7)	6.913(4)	6.912(2)
η_-	0.023(5)	0.023(2)	0.024(4)	0.021(5)	0.021(2)
η_0	0.169(3)	0.169(3)	0.169(3)	0.168(5)	0.168(2)

[a]From Ref. [14].
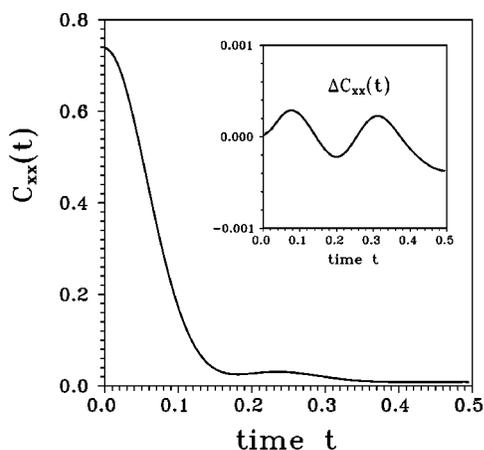
FIG. 5. The steady-state peculiar velocity autocorrelation function, $C_{xx}(t) = \langle p_x(t) p_x(0) \rangle / m^2$, computed for the 108-particle WCA fluid with the NH and modified NHC dynamics. On the scale of the graph both curves are the same. The differences between them ΔC_{xx} shown in the inset, are within the estimated statistical uncertanties of the ACF ± 0.001.

that there are no statistically significant differences between the results obtained for 512 and 2048 particle systems. Some statistically significant differences are, however, apparent between the properties of the small (Table I) and large (Table II) systems. The magnitudes of all properties (except η_0, η_-) increase slightly by a few percent with increasing N. This N dependence has also been reported by Evans and Sarman [14]. It should be stressed however that in spite of this N dependence, for a given N the estimates of the properties are thermostat independent.

Finally, an ability to reproduce properly the dynamic relaxation behavior was tested by the calculation of the steady-state peculiar velocity autocorrelation function $C_{xx}(t)$. The resulting functions computed with the modifed NHC and NH thermostats are plotted in Fig. 5. On the scale of the graph the curves are indistinguishable and the insert in the figure clearly shows that differences between both curves are statistically insignificant.

IV. CONCLUSIONS

In this work we have shown that the NHC thermostat does influence the values for the steady-state properties of a molecular system under shear. In particular, we have confirmed the observation made by Holian *et al.* [13] that the NHC thermostat does not guarantee that the target kinetic temperature is achieved in the system out of equilibrium. It has been demonstrated that the kinetic ''temperature'' produced by the NHC thermostat depends strongly on the Q parameter and the strain rate. It also depends on the number of thermostat variables used in the NHC scheme. The strong strain rate dependence (exponential-like growth) means that an influence of the NHC thermostat is hardly observed at small shear rates in small systems when more than two chain variables are used.

Our calculations and the theory of the thermostatted nonlinear responses [14] indicate that the failure of the NHC approach for nonequilibrium states is closely related to the production of nonzero values of the chain variable averages. It has been shown how a simple modification of the original NHC equations, which provides zero value chain variable averages, can lead to the correct thermostat-independent results for both the steady-state averages and steady-state time correlation functions.

The modified NHC equations contain only one extra parameter which basically is equal to the average of the first chain variable. In spite of its simplicity, the modification requires some additional computational effort to establish the appropriate value of this extra parameter at each state point. Consequently any application of the modified NHC thermostat away from equilibrium becomes considerably less routine and should only be used if other approaches such as the NH or Gaussian thermostats cannot be applied.

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