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Kinetic Energy-Based Temperature Computation in Non-Equilibrium Molecular Dynamics Simulation

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A kinetic energy-based approach is developed to obtain the correct local temperature of non-equilibrium systems. We have demonstrated that as a temperature measure, the average disturbance kinetic energy of a sample is more applicable than its average total energy, and the latter has been widely used in most molecular dynamics software. However, it is proved and demonstrated by our simulation example that the average disturbance kinetic energy is sample-size dependent. By using a simple equilibrium system as a thermometer, we propose a calibration approach to eliminate this sample-size effect. A vibrating atomic bar is used as an example to test the validity and convergence of various temperature definitions.

Keywords: Temperature, Non-Equilibrium, Molecular Dynamics.

RESEARCH ARTICLE

1. INTRODUCTION

Temperature is one of the fundamental physics concepts independent of materials. It is used to quantitatively measure the extent of hotness or coldness, and represents the intensity of the thermal motion of molecules in microscopic theory. Recently, researchers have found that how to compute the temperature, or the definition of temperature, strongly influences molecular dynamics (MD) simulation, in which the velocities of atoms are continuously adjusted according to various temperature-control algorithms. For example, in modeling multi-walled carbon nanotubes as gigahertz oscillators, different oscillation properties, including quality factor Q, were obtained at the same reference temperature (e.g., Refs. [1–3]), which makes simulation results controversial. In equilibrium statistical mechanics, the absolute temperature is proportional to the average kinetic energy. Rugh[4,5] developed a method to determine temperature in Hamiltonian dynamical systems, which has been used and promoted by many researchers (e.g., Refs. [6–8]). Nevertheless, it has not yet been ascertained whether all components of kinetic energy contribute to temperature. Many researchers (e.g., Ref. [9]) omit the rigid translational kinetic energy from temperature calculation, while some (e.g., Ref. [10]) simply leave out translation of the mass center during simulation.

However, there are still some unanswered questions in computing kinetic energy-based temperature, which are addressed in this paper: Should rigid rotational and mechanical vibration kinetic energy also be excluded in temperature calculation? How to extract kinetic energy related to pure thermal motion? The answers to these questions are crucial for non-equilibrium MD simulations since many MD simulations aim to model dynamic processes and there is an urgent need to establish a definition of temperature for non-equilibrium states. Although many previous studies provide various definitions of temperature out of equilibrium (e.g., Refs. [8, 11–15]), there is no consensus as yet.

In this paper, we propose a simple temperature computation method for non-equilibrium MD simulations, which is kinetic energy-based and is easy to implement in MD. In order to investigate applicabilities of various temperature definitions, we first clarify four necessary conditions for a correct temperature definition:

Condition 1: If a system is in thermodynamic equilibrium, then the definition should yield the same value at different sample positions.

Condition 2: If a system is in thermodynamic equilibrium, the computed temperature should be almost independent of sample size when this size is sufficiently large.

Condition 3: The temperature based on this definition should be independent of the choice of reference frame.

Condition 4: The temperature definition should be reducible to the classical definition in the simple equilibrium situation.

The paper is organized as follows. Section 2 and Section 3 discuss the necessity and measures of filtering

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out the kinetic energy of the rigid-body motion and mechanical vibration, respectively, in temperature computation. The conclusions are summarized in Section 4.

2. WHY AND HOW TO FILTER OUT THE KINETIC ENERGY OF THE RIGID-BODY MOTION IN TEMPERATURE COMPUTATION

For an N-atom system, the Hamiltonian can be expressed with the square of momenta $\boldsymbol{p}_i$, and then the widely used temperature definition is

$$T = \frac{2}{3k_B}\left\langle \frac{1}{N}\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m_i}\right\rangle = \frac{2}{3k_B}\langle H\rangle \tag{1}$$

where $\langle \mathbf{p_i}\rangle$ denotes the temporal average, k_B is the Boltzmann constant, m_i is the mass of atom i, and H is the average kinetic energy for each atom.

To determine the temperature of a given point in a system, we need to compute the average kinetic energy of its local neighboring sample. A sample contains l atoms, $(l \le N)$, and their velocity can be decomposed into three parts as

$$\mathbf{v}_i = \mathbf{v}_\mathbf{C} + \boldsymbol{\omega}\times\hat{\mathbf{r}}^i + \mathbf{v}_\mathrm{i}^\mathrm{Dis} \tag{2}$$

where $\hat{\mathbf{r}}^i$ is the atom position vector relative to the mass center of the sample, $\mathbf{v}_\mathbf{C}$ is the translational velocity of the sample mass center, $\boldsymbol{\omega}$ is the average rotational velocity around the sample mass center, $\mathbf{v}_\mathbf{i}^\mathrm{Dis}$ is the disturbance velocity. These can be computed as

$$\mathbf{v}_C = \frac{1}{\sum_{i=1}^{l} m_i}\sum_{i=1}^{l} m_i\mathbf{v}_i \tag{3}$$

$$\sum_{i=1}^{l}\hat{\mathbf{r}}^i\times m_i\mathbf{v}_i = \sum_{i=1}^{l} m_i(\hat{r}_i^2\mathbf{I} - \hat{\mathbf{r}}^i\hat{\mathbf{r}}^i)\cdot\boldsymbol{\omega} \tag{4}$$

Correspondingly, there are three possible types of average kinetic energy:

$$\begin{aligned} H^{\mathrm{Total}} &= \frac{1}{l}\sum_{i=1}^{l}\frac{1}{2}m_i\mathbf{v}_i\cdot\mathbf{v}_i \\ &= \frac{1}{2l}\left(\sum_{i=1}^{l} m_i\mathbf{v}_i^{\mathrm{Dis}}\cdot\mathbf{v}_i^{\mathrm{Dis}} + \boldsymbol{\omega}\cdot\mathbf{J}_C\cdot\boldsymbol{\omega} + M\mathbf{v}_\mathbf{C}\cdot\mathbf{v}_\mathbf{C}\right) \end{aligned} \tag{5}$$

$$H^{\mathrm{Dis}+R} = \frac{1}{2l}\left(\sum_{i=1}^{l} m_i\mathbf{v}_i^{\mathrm{Dis}}\cdot\mathbf{v}_i^{\mathrm{Dis}} + \boldsymbol{\omega}\cdot\mathrm{J}_C\cdot\boldsymbol{\omega}\right) \tag{6}$$

and

$$H^{\mathrm{Dis}} = \frac{1}{2l}\sum_{i=1}^{l} m_i\mathbf{v}_i^{\mathrm{Dis}}\cdot\mathbf{v}_i^{\mathrm{Dis}} \tag{7}$$

where M is the total mass of the sample, and $\mathbf{J}_C = \sum_l m_i(\hat{r}_i^2\mathbf{I} - \hat{\mathbf{r}}^i\hat{\mathbf{r}}^i)$ is the rotational inertia. Obviously, H^{Total}, $H^{\mathrm{Dis}+R}$, and H^{Dis} are averages of the total kinetic energy, kinetic energy without the rigid body translation part, and disturbance kinetic energy excluding both the rigid body translation and rotation parts of the sample, respectively. In the following, we use a rotating atomic ball with 8630 atoms, as schematically shown in Figure 1(a), to test their applicabilities to serve as a temperature measure. The interatomic potential is the Lennard–Jones potential $V(\mathbf{r}) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6)$, where ε is the depth of the potential

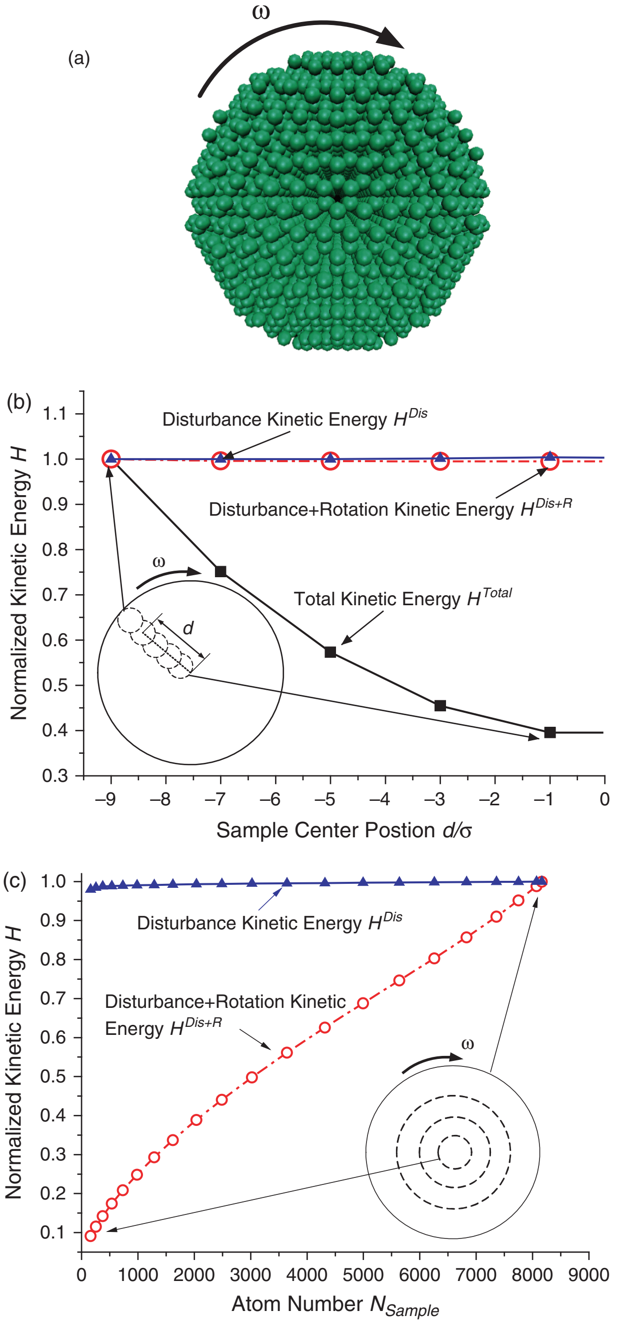

Fig. 1. (a) A snapshot of the isolated rotating atomic ball in thermodynamic equilibrium. The normalized average kinetic energy as a function of the sample position (b) and the sample size (c).

well, σ is the distance at which the interatomic potential is zero, and r is the distance between the atoms. The ball is simulated as an isolated system. Initially, each atom has a random thermal velocity and the system has a rotational velocity. After a sufficient amount of time has passed, this isolated system finally reaches a state of thermodynamic equilibrium, in which all physical state variables remain statistically unchanged over time but the rotational momentum is non-zero and conserved. For this system in thermodynamic equilibrium, the temperature should be uniform, as stated earlier in *Condition 1*.

Normalized by the value of the whole system, the three types of average kinetic energy from different sample positions of the rotating ball are shown in Figure 1(a); each sample consists of 860 neighbor atoms. It is found that the average total kinetic energy of samples H^{Total} has significantly different values for different sample positions, which indicates that the average total kinetic energy should not be used as the measurement of temperature in some cases. Then we study the effect of sample size on values of average kinetic energies H^{Dis} and $H^{\text{Dis}+R}$. As shown in Figure 1(b), different-sized concentric sphere samples are tested. The results indicate that with increase in sample size, $H^{\text{Dis}+R}$ does not converge but it continuously increases. It is obvious that as temperature measures, H^{Total} and $H^{\text{Dis+R}}$ violate *Condition 3*, because different reference frames lead to different H^{Total} and $H^{\text{Dis}+R}$. In contrast, average disturbance kinetic energy H^{Dis} seems a better choice to measure the temperature. However, H^{Dis} is only the average kinetic energy excluding the rigid motion. It might contain the mechanical vibration kinetic energy, and predict a wrong temperature.

3. WHY AND HOW TO FILTER OUT KINETIC ENERGY OF MECHANICAL VIBRATION IN TEMPERATURE COMPUTATION

In general situations, kinetic energy of a sample includes three parts: the rigid motion part, the mechanical vibration part, and the thermal motion part. It is easy to remove the rigid motion part from kinetic energy computation by choosing a comoving and corotating frame. However, it is not straightforward to decouple the mechanical vibration part and the thermal motion part.

We note the fact that when the sample becomes smaller, the fraction of the mechanical vibration part in the average disturbance kinetic energy H^{Dis} becomes lower until it can be ignored. Therefore, when H^{Dis} is used to measure the temperature, a smaller sample is preferred to filter out the contribution from mechanical vibration. On the other hand, if the temperature varies spatially in non-equilibrium systems, small samples should also be used to obtain the local temperature of a given point.

3.1. Size Dependence of the Average Disturbance Kinetic Energy of Small Samples

To demonstrate the sample-size dependence, we first discuss an extreme case, where the sample has only one atom in it. The velocity of this sample equals to the velocity of the atom, i.e., $\mathbf{v}_C = \mathbf{v}_i$. By removing the rigid motion, the average disturbance kinetic energy H^{Dis} becomes zero, while H^{Dis} is obviously non-zero for any larger samples.

More generally, we may also prove that the smaller sample corresponds to lower average disturbance kinetic energy. Assume there is a large sample with $2N$ atoms. We may use it to compute its average velocity $\bar{v}$, or divide this large sample into two small samples: Sample 1 with mass $M^{(1)}$ and Sample 2 with mass $M^{(2)}$, and compute the corresponding average velocities $\bar{v}^{(1)}$ and $\bar{v}^{(2)}$, respectively. The average disturbance kinetic energies in these two ways of computation are

$$
\begin{aligned}
H^{\text{Dis}}_{\text{large sample}} &= \frac{1}{2N}\sum_{i=1}^{2N}\frac{1}{2}m_i(v_i-\bar{v})^2 \\
&= \frac{1}{2N}\sum_{i=1}^{2N}\frac{1}{2}m_i\left(v_i-\frac{1}{M^{(1)}+M^{(2)}}\sum_{i=1}^{2N}m_iv_i\right)^2 \\
&= \frac{1}{2N}\sum_{i=1}^{2N}\frac{1}{2}m_iv_i^2-\frac{1}{2N(M^{(1)}+M^{(2)})}\frac{1}{2}\left(\sum_{i=1}^{2N}m_iv_i\right)^2
\end{aligned}
\tag{8}
$$

and

$$
\begin{aligned}
H^{\text{Dis}}_{\text{small sample}} &= \frac{H^{\text{Dis}}_{\text{sample1}}+H^{\text{Dis}}_{\text{sample2}}}{2} \\
&= \frac{1}{2}\left[\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_iv_i^2-\frac{1}{NM^{(1)}}\left(\sum_{i=1}^{N}\frac{1}{2}m_iv_i\right)^2\right] \\
&\quad+\frac{1}{2}\left[\frac{1}{N}\sum_{i=N+1}^{2N}\frac{1}{2}m_iv_i^2-\frac{1}{NM^{(2)}}\left(\sum_{i=N+1}^{2N}\frac{1}{2}m_iv_i\right)^2\right] \\
&= \frac{1}{2N}\sum_{i=1}^{2N}\frac{1}{2}m_iv_i^2-\frac{1}{2NM^{(1)}}\frac{1}{2}\left(\sum_{i=1}^{N}m_iv_i\right)^2 \\
&\quad-\frac{1}{2NM^{(2)}}\frac{1}{2}\left(\sum_{i=N+1}^{2N}m_iv_i\right)^2
\end{aligned}
\tag{9}
$$

The difference between Eqs. (8) and (9) is

$$
\begin{aligned}
H^{\text{Dis}}_{\text{smallsample}}-H^{\text{Dis}}_{\text{largesample}} &= -\frac{1}{2N}\frac{1}{2} \\
&\quad\times\frac{(P^{(1)}M^{(2)}-P^{(2)}M^{(1)})^2}{M^{(1)}M^{(2)}(M^{(1)}+M^{(2)})}\geq 0
\end{aligned}
\tag{10}
$$

where $P^{(1)}=\sum_{i=1}^{N}m_iv_i$ and $P^{(2)}=\sum_{i=N+1}^{2N}m_iv_i$ are momentums of Sample 1 and Sample 2, respectively. It should be pointed out that the above derivation also holds for other partitions with many smaller average volume elements. Equation (8) implies that the smaller local average volume has lower local disturbance kinetic energy, unless $P^{(1)}M^{(2)} - P^{(2)}M^{(1)} = 0$.

To further demonstrate the sample-size dependence, a system in simple equilibrium state without any rigid motion (Fig. 2(a)) is investigated. Figure 2(b) indicates that for the smaller sample, H^{Dis} is dependent on the sample size N_{sample}, i.e., the number of atoms in a sample. As we know, for this simple equilibrium case, the classical definition of temperature, $T = (2/3k_B)\langle H^{\text{Total}}\rangle$, is widely accepted (of course, this definition may fail for other complex situations, as discussed earlier). It is also found that although H^{Dis} for sufficiently large sample converges to H^{Total}, H^{Dis} of the smaller sample is significantly lower than H^{Total}. Therefore, directly using H^{Dis} leads to a lower temperature estimation and *Condition 4* is violated.

3.2. A Calibration Approach to Avoid Sample-Size Dependence in Local Temperature Computation for Dynamic Problems

We propose a calibration approach to compute temperature correctly in molecular dynamics simulations. The essential idea is based on the assumption that temperatures of two samples are the same if their sample size (N_{sample}) and average disturbance kinetic energy (H^{Dis}) are identical. Considering that a simple equilibrium system without rigid motion and mechanical vibration has a widely accepted temperature definition, it can be used as a thermometer or benchmark to calibrate temperature in non-equilibrium states.

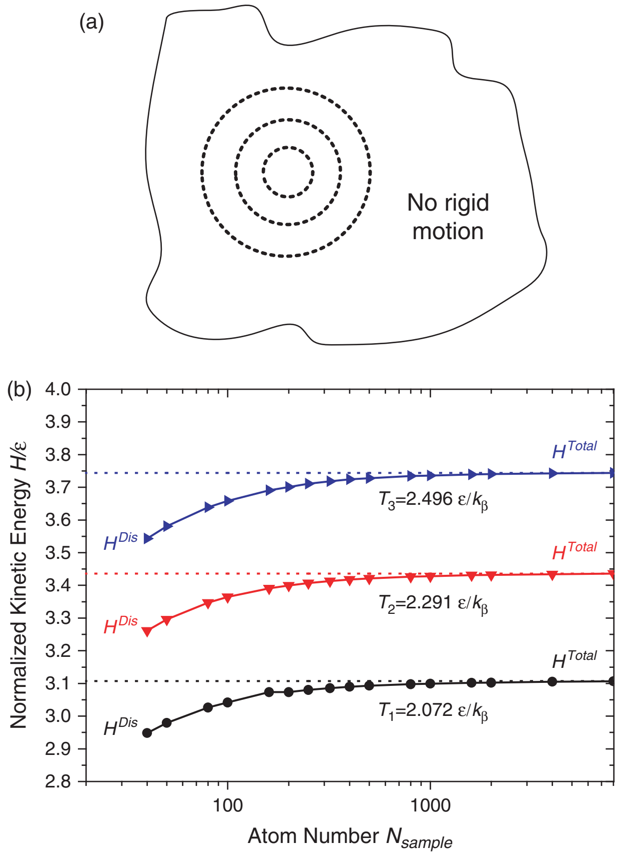

Fig. 2. (a) Schematic diagram of a system in simple equilibrium without rigid motion; (b) The average disturbance kinetic energy, H^{Dis}, as a function of sample size.

Figure 2(b) is a temperature contour map obtained from a system in equilibrium without rigid motion, and can serve as a calibration chart to predict the temperature for the non-equilibrium state. If average disturbance kinetic energy H^{Dis} (N_{sample}) and sample size N_{sample} are known, then the right temperature can be obtained by interpolation (Fig. 2(b)). With this calibration treatment, *Condition 4* is satisfied. Therefore, the definition of temperature based on the calibrated average disturbance kinetic energy has wide applicability, as the following dynamic example demonstrates.

3.3. A Dynamical Example Under Thermostat

We simulate the dynamic behavior of an atomic bar in isothermal environment (Fig. 3(a)) which includes 8000 atoms with a harmonic interatomic potential $(1/2)k(r_{ij} - b)^2$, where k is the harmonic force constant and b is the equilibrium bond length. The bar is initially under uniaxial static tension, and is in thermomechanical equilibrium at $T = 0.15\ kb^2/k_\beta$. The loading is then suddenly released, and the bar starts to vibrate, as shown in Figure 3(a). It is expected that this system will experience macroscopic quasi-harmonic vibration and related physical quantities will exhibit a regular periodic curve with respect to time, at least in the first several cycles.

Figures 3(b–d) show the kinetic energy of the whole system as a function of the normalized time, and four energy/temperature control modes with different number of samples are adopted to test the validity and convergence of various MD schemes. If this atomic bar is simulated as an isolated system in MD simulation, i.e., the total energy (including both kinetic and potential parts) is conserved, then the corresponding curve is really a regular periodic curve as denoted by the black solid line. According to our common sense, vibration behavior of the isolated system during the first several cycles is similar to that of the system under thermostat, which provides a reference in investigating various temperature controlled schemes.

Because there are mechanical vibration and thermal disturbance motion in this system, smaller samples are preferred to accurately obtain and control the temperature. On the other hand, too small a sample might lose its statistical feature. A good simulation should be independent of the arbitrary choice of researchers, such as the number of samples when evaluating and controlling temperature. The bar is then divided into different number of samples, such as 1, 5, 15, 40 and 80, to study the convergence. The Nose–Hoover temperature control method developed by Nose[16, 17]

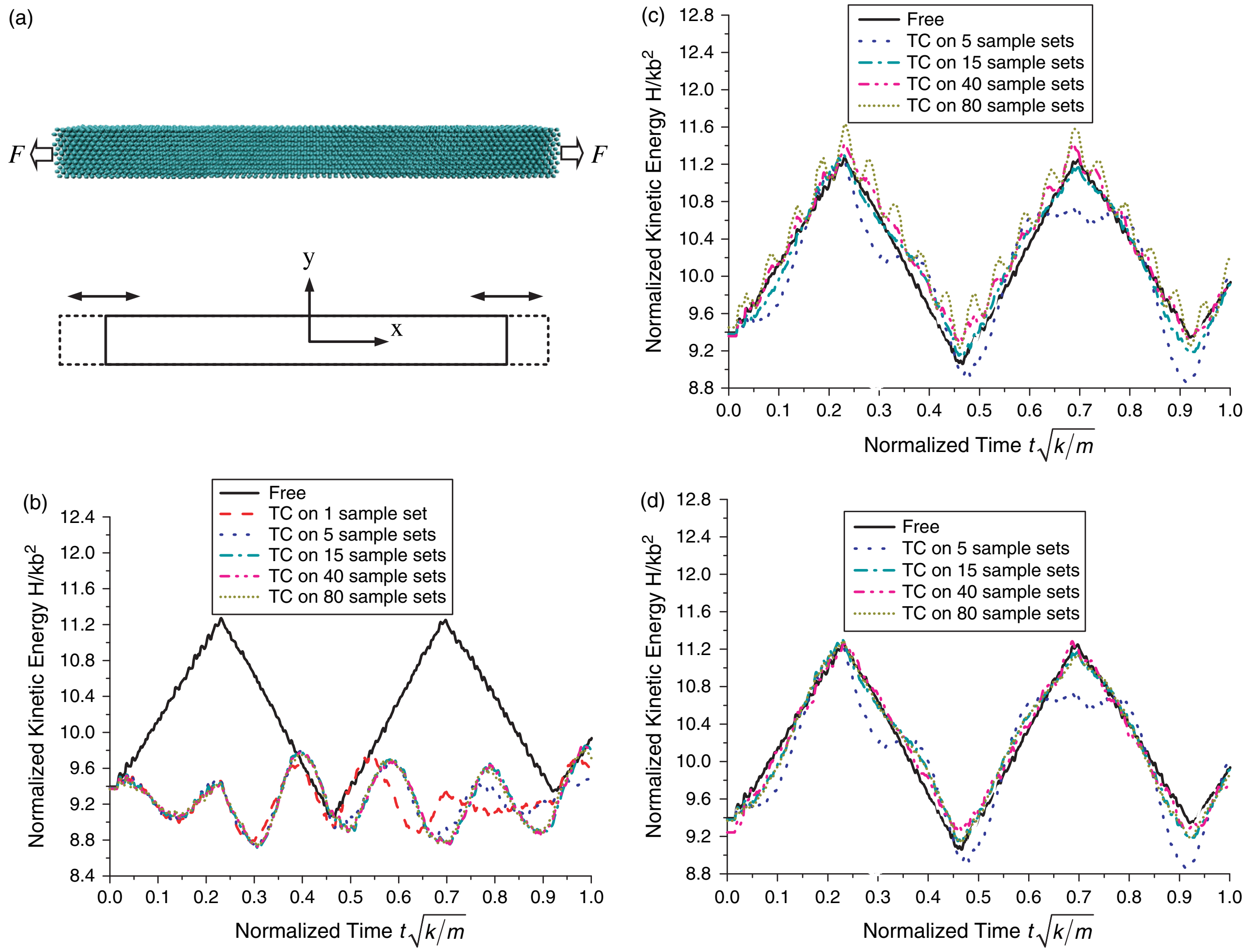

Fig. 3. (a) Schematic diagram of a vibrating atomic bar; The normalized kinetic energy of a bar versus the normalized time with different numbers of Nose–Hoover thermostat controlling (TC) samples based on average total kinetic energy (b), average disturbance kinetic energy (c) and the calibrated average disturbance kinetic energy (d).

and Hoover,[18, 19] is used to simulate an isothermal environment by adjusting the corresponding average kinetic energy in each sample. If the average total kinetic energy H^{Total} is adopted in the thermostat, as in many widely used MD softwares, curves for different numbers of samples shown in Figure 3(b) deviate significantly from the curve for the isolated system, which seems unreasonable. If we directly use the average disturbance kinetic H^{Dis} in temperature control, it can be observed from Figure 3(c) that the simulation is not converged with respect to the sample size. The corresponding curves exhibit many local zigzags and their amplitudes increase with reduction of sample size, which makes the curves different from the reference curve for isolated system. The reason is that directly using H^{Dis} always underestimates the local temperature and the thermostat tends to input the energy at intervals to keep the desired temperature. In contrast, if the calibrated average disturbance kinetic energy and small samples are adopted in the thermostat, as shown in Figure 3(d), MD simulations yield smooth regular periodic curves, which converge to the reference curve of isolated system. Therefore, our suggested calibration for the H^{Dis}-based definition of temperature is suitable for more complex situations in MD simulations.

4. CONCLUSIONS

To correctly obtain the local temperature in non-equilibrium systems, we propose a temperature definition based on the calibrated average kinetic energy of a sample. The validity of this and other kinetic-energy-based temperature definitions are discussed in this paper. The following related issues have been studied and clarified.

(1) The kinetic energy of a sample can first be divided into the rigid motion part and the disturbance part. However, it is not straightforward to further decouple the latter into mechanical vibration part and thermal motion part.

(2) The temperature should only be related to the kinetic energy of thermal motion; therefore, in a dynamic system, the smaller sample is preferred to filter out the contribution from mechanical vibration. However, it is proved and indicated by our simulation example that the average disturbance kinetic energy is sample-size dependent.

(3) This unwanted sample-size effect in temperature computation can be eliminated by calibrating with a corresponding simple equilibrium system, and using the assumption that temperatures of the two samples are the same if their sample size and average disturbance kinetic energy are identical. This approach has been validated in the dynamic example of this paper.

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