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RESEARCH ARTICLE

On computational efficiency of the hybrid Monte Carlo method applied to the multicanonical ensemble

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In the present paper, computational efficiency of the hybrid Monte Carlo (HMC) method applied to the multicanonical ensemble is studied; the HMC is an equation of motion guided Monte Carlo method. As in the standard HMC for the canonical ensemble, the multicanonical HMC calculations with high acceptance ratio show better efficiency; about 60 % acceptance yields the best performance for the system examined.

Keywords: multicanonical ensemble; hybrid Monte Carlo; Lennard-Jones liquids; statistical inefficiency

1. Introduction

Molecular processes surmounting high potential energy barriers are widely known to be hard to sufficiently sample configurations using the standard molecular simulation techniques. Phase transitions and chemical reactions fall into this type of category. Extended ensemble methods have been developed to overcome this type of sampling problems by introducing artificial statistical ensembles [1]; a multicanonical method is a promising extended ensemble method, which realizes the random walk in the potential energy space. The multicanonical Monte Carlo (MC) method has originally been developed by Berg and Neuhaus [2, 3]; then, the molecular dynamics (MD) [4, 5] and hybrid Monte Carlo (HMC) [4] algorithms to generate the multicanonical ensemble have been proposed. Compared to conventional MD and MC methods, the multicanonical MC and MD can sample a broader range of potential energy landscape without having the system trapped in local minima; even global minimum energy structures could be visited in a single calculation without examining various structures as the initial input. Okumura and Okamoto have extended the multicanonical method to efficiently sample the volume space as well as the potential energy space, which is referred to be the multibaric-multithermal ensemble [6]. Then, Mitsutake and Okamoto have generalized the formulation for multidimensional multicanonical ensembles [7], which enables us to perform a wider-range sampling in parameter spaces besides the potential energy and the volume. The multicanonical method and its generalization have been applied to basic Lennard-Jones systems: solid–liquid phase transition by the multicanonical method [8] and by the multibaric-multithermal method [9], and gas–liquid interfacial tension [10]. Then, the extended ensemble methods have been applied to address various challenging problems including protein folding [11], residual entropy of ice [12], liquid–solid phase transition of water in finite system [13–15], aggregation of polymers [16], hydration free energy change [17], and phase diagram of a fluid in porous materials [18].

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In the present study, computational efficiency of the HMC method applied to the multicanonical ensemble is examined. The HMC method is an equation of motion guided Monte Carlo method [19]. The equation of motion is used to generate trial configurations; the proposed trial configuration is accepted according to a generalized Metropolis criterion. The hybrid Monte Carlo method has been developed to solve sampling problems related with a non-ergodicity found in numerical simulations of quantum field theory [20]. Then, the method has been extended to treat condensed matters such as liquids [21] including quantum many-body systems [22–28]. In the present study, dense rare gas fluid such as fluid argon is chosen to be a model system to examine the computational efficiency of the multicanonical HMC method.

2. Method

In this section, we briefly review the multicanonical ensemble method. We consider the system consisting of N particles whose coordinates and momenta are represented by $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and $\{\mathbf{p}_1, \dots, \mathbf{p}_N\}$, respectively; the potential energy of the system is denoted to be E . In the canonical ensemble for systems at a temperature T , the distribution function $P_c(E, T)$ is written by

$$P_c(E, T) \propto n(E)e^{-E/k_B T} \quad (1)$$

where k_B is the Boltzmann constant and $n(E)$ is the density of potential energy state. The distribution function has a bell-type shape whose peak is located at the ensemble average $\langle E \rangle$. The standard Monte Carlo and molecular dynamics methods primarily sample configurations around the peak. Low energy configurations apart from the peak, for example, are hardly visited by the standard methods. To overcome this type of sampling problems, the multicanonical method has been developed. The distribution function of the multicanonical ensemble $P_{\text{mc}}(E)$ is given by

$$P_{\text{mc}}(E) \propto n(E)e^{-W(E)} = \text{constant} \quad (2)$$

where $W(E)$ is a weight function to realize the constant distribution regarding the potential energy. The following function clearly generates the constant distribution:

$$W(E) = \ln n(E). \quad (3)$$

Since the function $n(E)$ is not known *a priori*, we must first numerically evaluate the weight function $W(E)$; the method will be described in the Results section.

The normalization constant of the distribution function $P_{\text{mc}}(E)$ is given using Eq. (2),

$$\begin{aligned} Z_{\text{mc}} &= \int dE n(E) e^{-W(E)} \\ &= \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-W(E(\{\mathbf{r}_i\}))} \end{aligned} \quad (4)$$

where $n(E) = \int d\mathbf{r}_1 \dots d\mathbf{r}_N \delta(E - E(\{\mathbf{r}_i\}))$. As is evident from the above expression, the multicanonical density in the configuration space is given by $e^{-W(E(\{\mathbf{r}_i\}))}$. The Metropolis Monte Carlo method can be applied to the multicanonical ensemble; the Metropolis criterion is given by $\min(1, e^{-\Delta W})$ where ΔW is the change in the function W after the trial move.

To devise the molecular dynamics and hybrid Monte Carlo methods, we regard the multicanonical distribution to be an artificial canonical distribution at a temperature T_0 using the following

effective potential $E_{\text{mc}}(E)$:

$$E_{\text{mc}}(E(\{\mathbf{r}_i\})) = k_B T_0 W(E(\{\mathbf{r}_i\})). \quad (5)$$

Then, the multicanonical density can be written by $e^{-E_{\text{mc}}/k_B T_0}$. We can use the canonical molecular dynamics and hybrid Monte Carlo methods [19] to generate the artificial canonical distribution. To this end, we define the following Hamiltonian H_{mc} :

$$H_{\text{mc}} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + E_{\text{mc}} \quad (6)$$

where m_i is the mass of an i -th particle. Then, we obtain the following equations of motion:

$$\begin{aligned} \frac{d\mathbf{r}_i}{dt} &= \frac{\partial H_{\text{mc}}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \\ \frac{d\mathbf{p}_i}{dt} &= -\frac{\partial H_{\text{mc}}}{\partial \mathbf{r}_i} = -\frac{\partial E_{\text{mc}}}{\partial E} \frac{\partial E}{\partial \mathbf{r}_i}. \end{aligned} \quad (7)$$

To introduce the multicanonical molecular dynamics method, we attach the thermostat to the physical system as in the canonical molecular dynamics. The hybrid Monte Carlo is another method to generate the canonical distribution. The hybrid Monte Carlo (HMC) [20–22] is a method that combines molecular dynamics (MD) and Monte Carlo (MC) techniques. Unlike the standard MC, whole system coordinates are simultaneously updated by equations of motion. The trial configuration is then accepted or rejected by an appropriate Metropolis criterion as in MC. The HMC algorithm has been proved to yield the canonical distribution as long as a time-reversible and volume-preserving numerical integration algorithm is employed to solve the equations of motion; this condition is needed to guarantee the microscopic detailed balance [21]. To construct the HMC method for the multicanonical ensemble, the above Hamiltonian H_{mc} is used to introduce the equations of motion. The hybrid Monte Carlo method is outlined as follows. We start with an initial state of the system $(\{\mathbf{r}_i\}, \{\mathbf{p}_i\})$ and re-sample momenta $\{\mathbf{p}_i\}$ from Maxwell distribution at the temperature T_0 . Molecular dynamics based on Eq. (7) is then used to move the whole system for time increment of $n_{\text{MD}} \times \Delta t$, where Δt is the time increment of the MD calculation and n_{MD} is the number of MD steps in one HMC cycle. The trial configuration is then accepted by the probability P_A ,

$$P_A = \min\{1, e^{-\Delta H_{\text{mc}}/k_B T_0}\} \quad (8)$$

where ΔH_{mc} is the change in the total Hamiltonian H_{mc} after the move of n_{MD} steps.

Here, we comment on advantages of HMC over MD. It is possible to get better computational efficiency than MD using suitably chosen HMC parameters n_{MD} and Δt . Usually, larger Δt than that of MD can be used in HMC calculations, biases introduced by the resulting Hamiltonian error are removed by the Metropolis criterion Eq. (8). Optimized HMC parameters and comparison on the computational efficiency can be found, for example, for standard Lennard-Jones fluids [21] and quantum many-body systems described by the path integral method [23, 28].

3. Computational details

In the present study, fluid argon is chosen to be a model system. The system is composed of $N = 108$ particles interacting with the Lennard-Jones potential. The following potential parameters

are adopted: $\sigma = 3.41 \text{ \AA}$ and $\epsilon/k_B = 120 \text{ K}$. Density of the system is set to be $\rho = 0.02237 \text{ \AA}^{-3}$, corresponding to high density states near the triple point and the temperature $T_0 = 180 \text{ K}$ for the artificial canonical ensemble with the multicanonical effective potential E_{mc} Eq. (5). To calculate the force appeared in Eq. (7), the coefficient $\partial E_{mc}/\partial E$ is numerically evaluated using Lagrangian cubic interpolation technique. For each multicanonical HMC run, 1.0×10^6 molecular dynamics steps are carried out.

4. Results

We first show the multicanonical distribution function. The multicanonical weight function $W(E)$ can be evaluated using the canonical distribution at a temperature T_0 :

$$W(E) = \ln n(E) = \frac{E}{k_B T_0} + \ln P_c(E, T_0) \quad (9)$$

where energy independent terms are omitted. Since usually the numerical canonical simulation for the temperature T_0 does not cover a sufficiently large E range, we must refine the function $W(E)$ iteratively using the following relation:

$$W^{(n+1)}(E) = W^{(n)}(E) + \ln P_{mc}^{(n)}(E) \quad (10)$$

where the n -th multicanonical distribution $P_{mc}^{(n)}(E)$ is obtained by the weight function $W^{(n)}(E)$. Detailed description on the method of the refinement can be found in Ref. [29]. The distribution by the refined $W(E)$ is presented in Fig. 1. In the energy range $[-648\epsilon, -540\epsilon]$, a flat distribution is found to be obtained. Outside the range, the system is designed to obey the canonical distribution. This weight function $W(E)$ is used to perform HMC calculations for examining the computational efficiency.

We next discuss the computational efficiency of the multicanonical HMC method. We examine the sampling efficiency of the multicanonical HMC method by a quantity called a statistical inefficiency [30, 31]. This quantity expresses the number of correlated steps needed to obtain independent sampling for a physical quantity. We calculate the statistical inefficiency in units of the number of molecular dynamics steps, which means the number of the correlated HMC steps multiplied by n_{MD} . The parameter n_{MD} is first fixed to be 10. In Fig. 2, we show the time step Δt dependence of the statistical inefficiency for the potential energy together with the associated acceptance ratio; the acceptance ratio is found to decrease with increasing Δt , because large Δt causes the large Hamiltonian error when integrating the equations of motion. If the equations of motion are accurately integrated, corresponding to the high acceptance ratio, the movement in the phase space is small; this results in the long correlation. On the other hand, if we adopt large Δt corresponding to low acceptance ratio, the system moves widely in phase space; however, many of the trial configurations are rejected due to the large Hamiltonian error, resulting in the long correlation again. Thus, the statistical inefficiency has a minimum value between high and low acceptance ratio. For the present system, minimum correlation is found to be given by $\Delta t = 30 \text{ fs}$. Corresponding acceptance ratio is 64 %. In Fig. 3, the statistical inefficiency and the associated acceptance ratio is presented for various n_{MD} with $\Delta t = 30 \text{ fs}$. We find the case of $n_{MD} = 10$ yields minimum number of correlated steps. The trend is similar with that found for dense LJ fluids under the canonical ensemble [21]; slightly smaller acceptance ratio gives better efficiency for the multicanonical ensemble. This is partly due to the fact that Δt giving the good efficiency depends on the energy range. Indeed, the canonical HMC calculation for the system at 180 K is found to show best efficiency for $\Delta t = 25 \sim 30 \text{ fs}$, while the system at 100 K for $\Delta t = 40 \text{ fs}$.

After multicanonical HMC calculations have been performed, we can estimate the canonical

average for any temperature. The canonical distribution is represented by the multicanonical distribution:

$$P_c(E, T) \propto P_{\text{mc}}(E)e^{W(E)-E/k_B T}. \quad (11)$$

Then, the canonical average of a physical quantity $A(E)$ is estimated by

$$\langle A(E) \rangle = \frac{\int dE A(E) P_{\text{mc}}(E) e^{W(E)-E/k_B T}}{\int dE P_{\text{mc}}(E) e^{W(E)-E/k_B T}}. \quad (12)$$

In Fig. 4, the average potential energy as a function of temperature is presented for thermodynamic states covering from near the triple point to the supercritical condition. The averaged potential energy evaluated by the above reweighting technique is found to be in very good agreement with the canonical HMC results.

5. Concluding remarks

In the present paper, the computational efficiency of the hybrid Monte Carlo method is examined to generate the multicanonical ensemble. Dense Lennard-Jones fluid is chosen to be a model system. As in the standard HMC method for the canonical distribution, higher acceptance ratio around 60 % is found to be computationally efficient. In a HMC step, several molecular dynamics steps are needed to achieve efficient sampling; for the system examined, 10 molecular dynamics steps are found to yield best efficiency.

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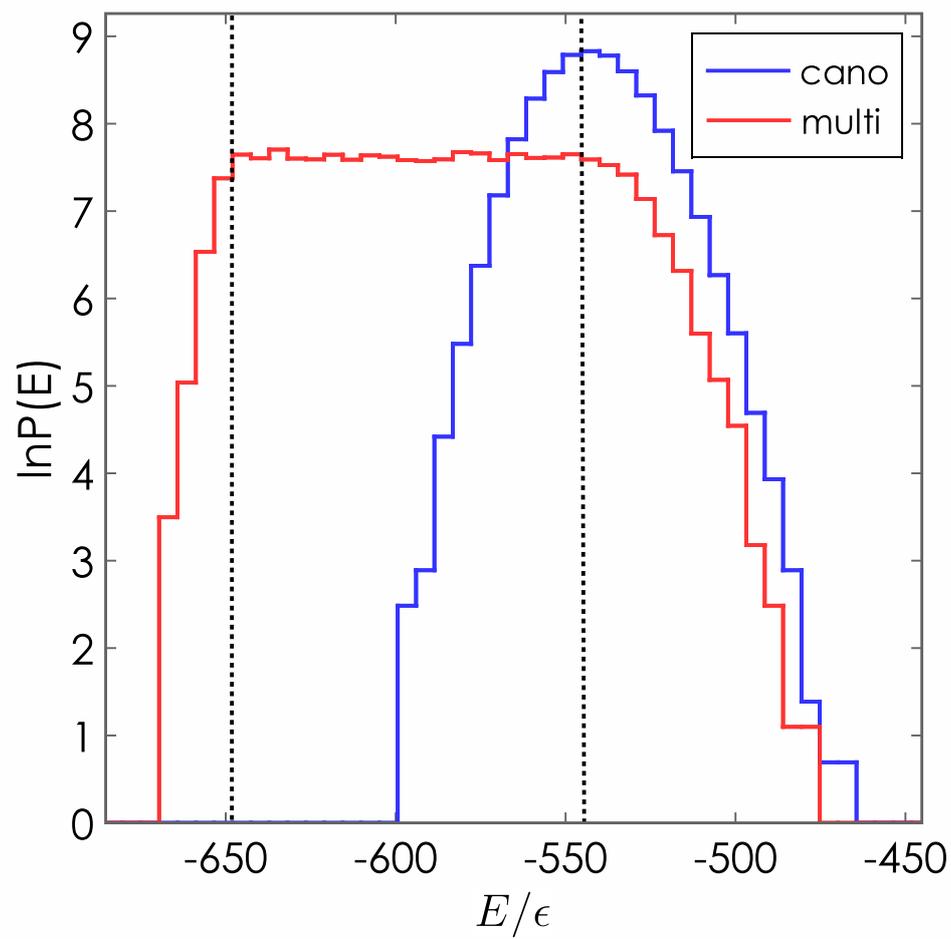


Figure 1. Unnormalized distribution function for the multicanonical ensemble is plotted, together with the canonical result at $T = 180$ K for comparison. While inside dotted vertical lines the distribution is tuned to be flat, outside the range the distribution is designed to obey the canonical distribution.

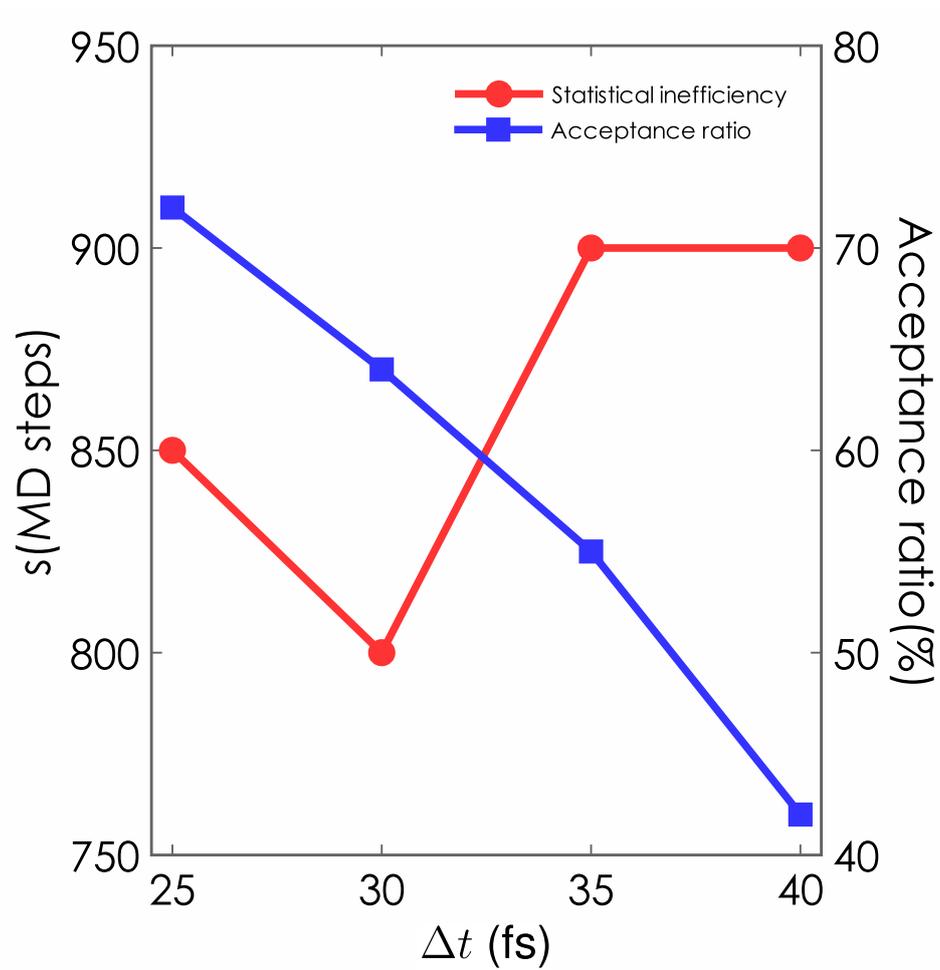


Figure 2. The statistical inefficiency s for the potential energy is presented as a function of Δt ; n_{MD} is fixed to be 10. The statistical inefficiency is calculated in units of molecular dynamics step. The acceptance ratio is also presented as a function of Δt .

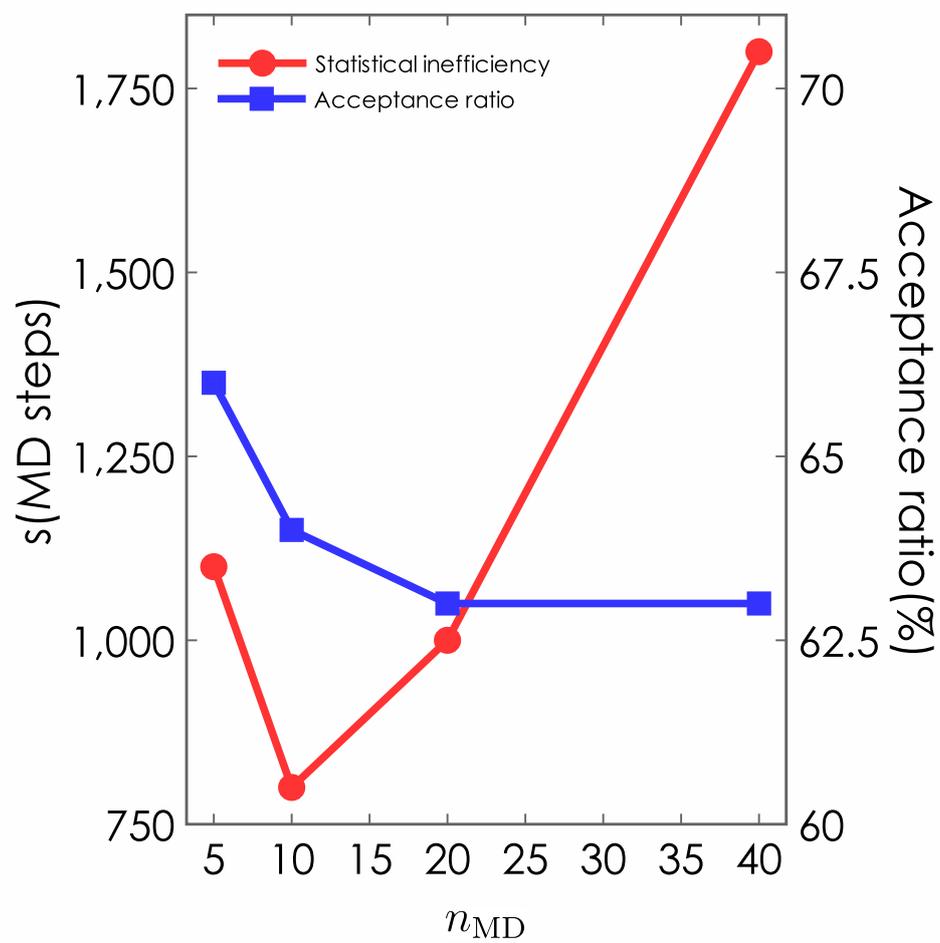


Figure 3. The statistical inefficiency s for the potential energy is presented as a function of n_{MD} ; Δt is fixed to be 30 fs. The statistical inefficiency is calculated in units of molecular dynamics step. The acceptance ratio is also presented as a function of n_{MD} .

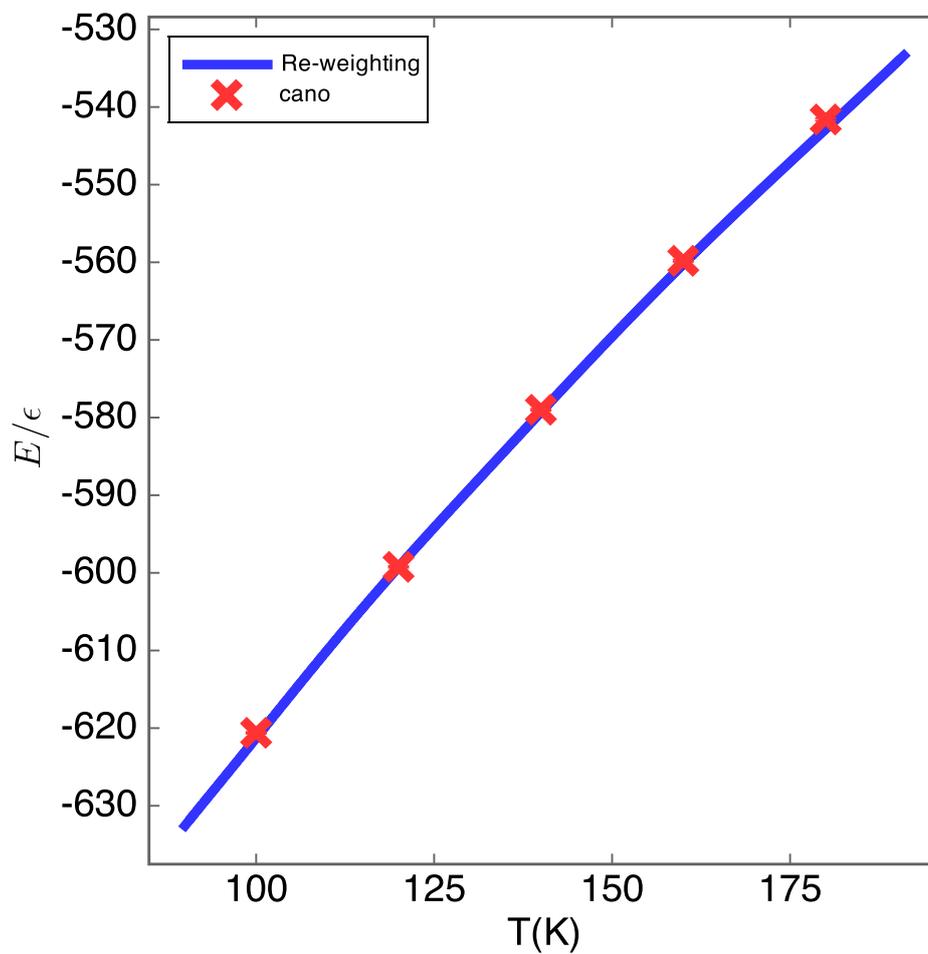


Figure 4. The average potential energy as a function of the temperature is presented. Blue curve is obtained by the multi-canonical HMC calculation with the reweighting technique. Red crosses are the results of separately performed canonical HMC calculations. Error bars for the canonical HMC results are smaller than the size of the cross symbols.