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Can the Pruned-Enriched Method be Used for the Simulation of Fluids?

Jianguo Jiang · Yineng Huang · Jichun Wu

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Abstract The flat histogram version of pruned and enriched Rosenbluth method (FLATPERM) is an effective Monte Carlo method for calculating densities of states of polymers on a lattice. In this paper we generalize this method to calculate the densities of states of off-lattice systems. To demonstrate the feasibility of the approach, we perform sample calculations for the Lennard-Jones fluids. The densities of states of Lennard-Jones fluids simulated by Pruned-enriched method, i.e., the generalization of FLATPERM, agree with the densities simulated by Wang-Landau method in the range of high potential energy. However the direct extension of FLATPERM fails at low energy and a useful extension still needs to be found.

Keywords Density of states · Monte Carlo simulations

1 Introduction

The density of states is very important in statistical physics. Some Monte Carlo algorithms such as multi-canonical sampling and Wang-Landau method have been proposed to calculate densities of classical states [1–9]. Many important thermodynamic quantities, e.g., mean energy, free energy, entropy and specific heat, can be directly calculated if densities of states are known. At a critical temperature some thermodynamic quantities vary violently. In conventional Metropolis method many temperature points near the critical point should be selected, which is rather inefficient. Therefore algorithms for simulations of densities of states are particularly useful to study phase transitions.

P. Grassberger et al. proposed the pruned and enriched Rosenbluth method (PERM) to simulate end-to-end distance and partition function of polymers on a lattice [10–12], which

J. Jiang (✉) · J. Wu
Department of Hydrosciences, Nanjing University, Nanjing, 210093, China
e-mail: jianguo.jiang@gmail.com

Y. Huang
Department of Physics and National Lab of Solid State Microstructures, Nanjing University, Nanjing, 210093, China

could adjust weight factors of configurations by pruning and enrichment procedures. Based on PERM, the flat histogram version of PERM (FLATPERM) and the multi-canonical chain growth method were developed to calculate the densities of states of polymers on a lattice [13, 14], which relate densities of states with weight factors. The principle of FLATPERM is that the densities of states are proportional to the weighted average times of visiting them in random simulations. The weight of each configuration is adjusted to the estimated value of the density of corresponding states by pruning and enrichment procedures. In this paper we generalized FLATPERM to off-lattice systems and tested its feasibility in comparison with Wang-landau method. For simplicity, the generalization of FLATPERM is called as Pruned-enriched method.

2 Method

The density of states with N particles, energy E and volume V in phase space is represented by $\Omega(N, V, E)$, which may be written as the product of ideal gas and configurational components, i.e.,

$$\begin{aligned}\Omega(N, V, E) &= \frac{\epsilon}{h^{3N} N!} \int \delta(E - K(p^{3N}) - U(q^{3N})) dp^{3N} dq^{3N} \\ &= \frac{q_0^{3N} N!}{\epsilon V^N} \int \Omega_{ig}(N, V, E - t) \Omega_{config}(N, V, t) dt, \end{aligned} \tag{1}$$

where Ω_{ig} is the ideal-gas density of states, Ω_{config} is configurational density of states (t is potential energy), ϵ is a constant with units of energy and q_0 is a constant with units of length [4]. Ω_{ig} and Ω_{config} are defined as

$$\Omega_{config}(N, V, E) = \frac{\epsilon}{q_0^{3N} N!} \int \delta(E - U(q^{3N})) dq^{3N} \tag{2}$$

and

$$\Omega_{ig}(N, V, E) = \frac{\epsilon V^N}{h^{3N} N!} \int \delta(E - K(p^{3N})) dp^{3N} = \left[\left(\frac{4\pi m E}{3h^2} \right)^{3/2} \frac{V e^{5/2}}{N^{5/2}} \right]^N, \tag{3}$$

respectively, where m is the mass of particles and e is the base of the natural logarithm [4, 15, 16]. Once Ω_{config} is known, $\Omega(N, V, E)$ may be calculated by (1) and partition function for any temperature T can be obtained by $Z(T) = \sum \Omega(N, V, E) e^{-\beta E}$.

One idea for calculating configurational densities is that configurational densities are proportional to the visited times of corresponding states if configurations are generated randomly. In this paper configurations are generated by the procedure that particles are placed randomly in a box with fixed volume one after another. Hence the simulations only include insertion of particles. The configurational densities of a fluid can be written as

$$\Omega_{config}(N, V, E) = \frac{1}{K} \sum_{i=1}^{K} W^i(N, V, E), \tag{4}$$

where K is the number of tours of insertions from the first particle to the last particle. $W^i(N, V, E)$ is the weight factor of corresponding configuration, which is given by

$$\begin{cases} W^i(N, V, E) = W^i(N - 1, V, E') \times \frac{V}{N}, & N \geq 2, \\ W^i(N, V, E) = V, & N = 1. \end{cases} \tag{5}$$

Here $E = \sum_{j=1}^{N-1} U(r_{Nj}) + E'$ and $U(r_{Nj})$ is the potential energy between the Nth particle and the jth particle. V appearing in $W^i(N, V, E)$ is from the fact that the allowable sites for a new particle is proportional to the box volume V. N in the denominator of above formula results from that these particles are identical. For a given configuration of N particles, it can be generated from N configurations of $N-1$ particles. When there is only one particle in the box, the potential energy of the system is equal to 0 and the possible position for the particle is proportional to V. Neglecting a constant, We define $W^i(1, V, E) = V$.

In (5) $W^i(N, V, E)$ of each configuration of N particles has the same value of $V^N/N!$. However, in practice configurational densities vary widely in magnitude with potential energy E [1–3, 5–7]. T. Prellerg et al. developed the FLATPERM method to overcome this difficulties [13]. In the original FLATPERM method $W^i(N) \equiv \prod_{n=1}^{N} m_n$, where m_n is the number of allowable sites for the nth step in a self-avoiding walk on a lattice [12, 13]. For a fluid of identical particles, $W^i(N, V, E)$ is calculated by (5). The idea of FLATPERM is that every configuration is accompanied with a weight factor and these weight factors are adjusted according to estimated densities. Suppose a new particle is inserted into a configuration with $N-1$ particles and potential energy E', the weight factor of the new configuration is obtained from (5). Then $\Omega_{config}(N, V, E)$ is updated by (4). The weight factor for next step is adjusted as follows. We define

$$r \equiv \frac{W^i(N, V, E)}{\Omega_{config}(N, V, E)}. \tag{6}$$

If $r > 1$, we make this configuration r copies and each copy with a new weight $W^i(N, V, E)/r$ will continue grow. If $r \leq 1$, the configuration with a new weight $W^i(N, V, E)/r$ will continue grow with probability r [13]. The change of weight is compensated by the continuing growth times. So this method is called Pruned-enriched method. A tour of simulations will be finished after all enriched branches end. Then next tour will begin.

Before simulations we should determine the potential energy range of the system. For a Lennard-Jones fluid, the potential energy range has no upper bound. The lower the temperature is, the lower the range of energy contributing to the partition function is. For a given temperature range, the potential energy range can be obtained by the method proposed by Qiliang Yan et al. [5]. During simulations trial configurations may be beyond the energy range. In this case configurations outside the energy range continue growing without being pruned or enriched. However, if the energy of a configuration is far above the energy range, say 50% of the energy window for each N, the configuration has a very small probability to grow within the energy range again and can be neglected for efficiency.

3 Simulations and Results

A truncated-and-shifted Lennard-Jones fluid is used to test this method. This model can exhibit main features of realistic fluids. The potential energy function between a pair of particles is written as

$$U(r) = \begin{cases} 4\epsilon[((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6) - ((\frac{\sigma}{r_c})^{12} - (\frac{\sigma}{r_c})^6)], & r < r_c, \\ 0, & r \geq r_c. \end{cases} \tag{7}$$

The length of the cubic box is set to $L = 5\sigma$ and the truncated length $r_c = 2.5\sigma$.

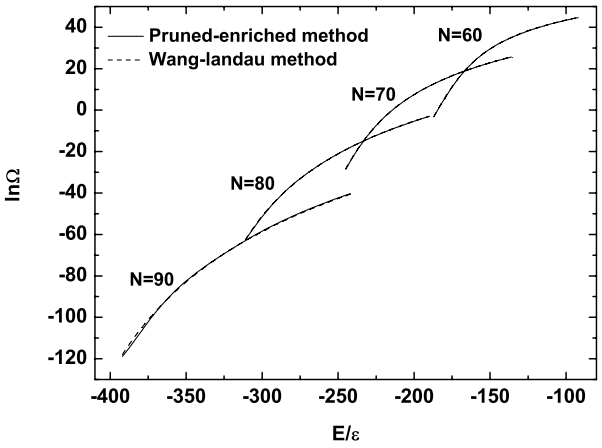

Fig. 1 The densities of states of truncated Lennard-Jones fluids simulated by Pruned-enriched method and Wang-Landau method. The corresponding range of temperature is $1.5 \sim 2.5$

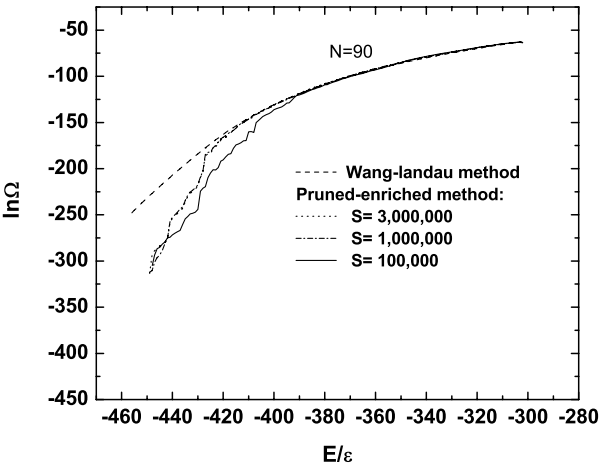

Fig. 2 The density of states of truncated Lennard-Jones fluid as calculated by Wang-Landau method and pruned-enriched method. The number of particles is 90 and s is the times of tours in simulations. The corresponding range of temperature is $0.5 \sim 1.5$

In Fig. 1 the range of T is taken as $1.5 \sim 2.5$ and the range of potential energy is high. The results simulated by Wang-landau method and Pruned-enriched method are shown in Fig. 1. In Pruned-enriched method we simulated 10^5 tours and in Wang-landau method the final modification factor is $e^{10^{-6}}$. In Fig. 1 the results given by Pruned-enriched method and Wang-Landau method agree well. This illustrates that Pruned-enriched method is applicable to off-lattice system. When modification factor of Wang-landau method decreases, the calculations per iteration become increasingly long. Contrary to Wang-landau method, all stages of the simulation of Pruned-enriched method contribute equally to the construction of the density of states. This is one merit of Pruned-enriched method. Another merit of Pruned-enriched method is that it does not need flatness criterion. If some states with small densities are not visited during simulations, densities of other states can still be given.

However, if the range of T is low, corresponding potential energy range will be low and Pruned-enriched method can not work well. This can be seen from Fig. 2 that the densities of low energy states of 90 particles obtained from Pruned-enriched method are systematically lower than that from Wang-landau method. Even though we do 3×10^6 tours of simulations, the discrepancy between them decreases little. But the time spent is

longer than that of Wang-landau method. Therefore Pruned-enriched method is rather inefficient as the energy of states is low. This inefficiency maybe result from the selection of weight. To search a configuration of $N+1$ particles, the minimal weight is approximately equal to $\Omega^{min}_{config}(N,V,E)\times V/N$, where $\Omega^{min}_{config}(N,V,E)$ is the smallest density of the energy window of N particles. If the energy E' of a state $(N+1,V,E')$ is very low and $\Omega_{config}(N+1,V,E')$ is much less than the minimal weight, then the state $(N+1,V,E')$ will be seldom visited. Therefore Pruned-enriched will give a systematically smaller result if $\Omega^{min}_{config}(N,V,E)$ decreases quickly as N increases. This will happen in the lower part of energy windows when N is large or the temperature range is low.

In its original version FLATPERM is used to calculate densities of states of polymers on lattices. The allowable sites for a new polymer monomer are finite. However, the allowable sites for particles are infinite in an off-lattice system. The simulation of fluids shows that FLATPERM can partly solve the problems with infinite sites. In this paper the growth process is that particles are randomly inserted into a box one after another, which is adverse for the generation of states with low densities. Maybe a new growth process is needed to conquer the difficulties of states with low energy.

In summary we have generalized the FLATPERM method from systems on a lattice to off-lattice systems. The Pruned-enriched method, i.e., the generalization of the FLATPERM, provides us a new tool to estimate the densities of states of off-lattice systems. We have applied it to Lennard-Jones fluids and obtained the densities of states. Compared with Wang-Landau method, the Pruned-enriched method has two merits. One is that all stages of the simulation do equal contributions to densities of states. The other merit is that programs can run well even if some states can not be visited. However, the Pruned-enriched method is rather inefficient for low energy levels, which are responsible for the phase transitions at low temperatures. Therefore this method needs to be improved in future research.

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