Replica-Exchange Monte Carlo Method for Ar Fluid

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Lennard-Jones fluid systems such as Ar fluid have a huge number of states of energy local minima. Hence, a simulation by conventional algorithms based on the NVT canonical ensemble tends to get trapped in these local-minimum states. *Generalized-ensemble algorithms* alleviate this difficulty by performing a random walk in energy space. Multicanonical algorithm [1] and simulated tempering [2] are two of the most well-known such methods. However, in these methods we have to make iterations of preliminary runs in order to determine the (non-Boltzmann) weight factors. This process can be tedius and time-consuming. The *Replica-Exchange method*[3)-7)] (the method is also referred to as *replica Monte Carlo method*,[4)] *multiple Markov chain method*,[6)] and *parallel tempering*[7)]), is a new promising algorithm in which the above complicated procedure of weight determination is not necessary. We have applied the *Replica-Exchange Monte Carlo method, REMC*, to an Ar fluid system. We show that the new algorithm is indeed very effective and that accurate low-temperature canonical distributions can be obtained much more efficiently than conventional methods.

The generalized ensemble for replica-exchange method consists of M *non-interacting* replicas of the original system in the canonical ensemble at M different temperatures T_m $(m = 1, \cdots, M)$. Because the replicas are non-interacting, the weight factor for the state X in this generalized ensemble is given by the product of Boltzmann factors for each replica (or at each temperature). We now consider exchanging a pair of replica i and replica j which are at temperatures T_m $(= 1/k_B\beta_m)$ and T_n $(= 1/k_B\beta_n)$, respectively. In order for this exchange process to converge towards an equilibrium distribution, it is sufficient to impose the detailed balance condition on the transition probability $w(X \to X')$:

$$W_{REMC}(X)\ w(X \to X') = W_{REMC}(X')\ w(X' \to X)\ . \tag{1}$$

The transition probability, $w(X \to X')$ which satisfies the detailed balance condition is then given by:[3)-8)]

$$w(X \to X') \equiv w\left(x_m^{[i]}\ \middle|\ x_n^{[j]}\right) = \begin{cases} 1\ , & \text{for } \Delta \le 0\ , \\ \exp(-\Delta)\ , & \text{for } \Delta > 0\ , \end{cases} \tag{2}$$

where

$$\Delta \equiv (\beta_n - \beta_m)\left(U\left(q^{[i]}\right) - U\left(q^{[j]}\right)\right)\ , \tag{3}$$

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and $U(q^{[i]})$ and $U(q^{[j]})$ are the potential energies of replicas i and j, respectively. The effectiveness of the method was tested with Ar fluid. We remark that the exchanged quantity does not have to be temperature as long as it is in one-to-one correspondence with the replica (for instance, we can simulate the same system of M replicas with M different volumes). This is why we prefer the name replica-exchange method [3] to parallel tempering [7] (likewise, we prefer the term replica-exchange method to multiple Markov chain method, [6] because molecular dynamics algorithm is also possible [8]).

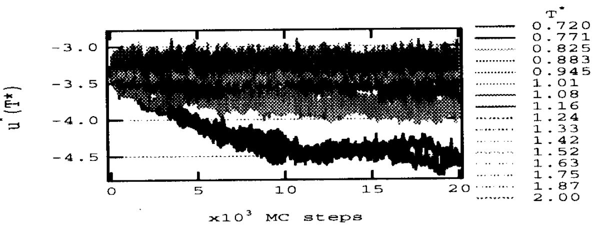

Fig. 1. Energy of *REMC* method.

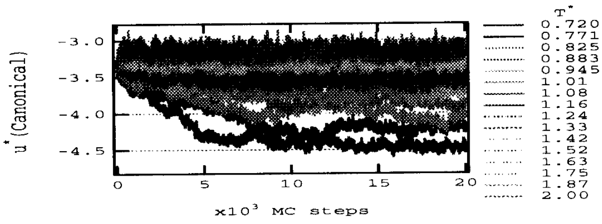

Fig. 2. Energy of canonical MC.

We now present the results of our simulations based on the *REMC* algorithm and conventional canonical MC algorithm. We used the sixteen temperatures between $T_H^* = 2.0$ and $T_L^* = 0.72$. Each replica consists of $n^* = 0.5, N = 256$, Ar fluid. All the simulations were started from random configurations. Compared with conventional method, *REMC* method seems to achieve fast thermalization (compare Fig. 1 with Fig. 2) and explores energy-surface without getting trapped in states of energy local minima at low temperature (see Fig. 3).

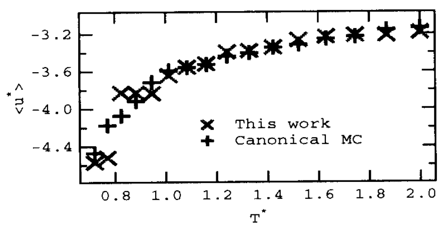

Fig. 3. Average energy as a function of temperature.

The *Replica-Exchange* method is indeed very effective and that accurate low-temperature canonical distributions can be obtained much more efficiently than conventional methods.

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