

RESEARCH ARTICLE

Density of States Estimation for Soft Core System

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The density of states (DOSs) for the soft core system is calculated by the multicanonical molecular dynamics simulation. We found the DOS of this system has a concavity. Owing to this concavity, the probability distribution has double peaks near the temperature where the system undergoes the solid–fluid phase transition.

Keywords: density of states, phase transition, soft core system, multicanonical molecular dynamics

1 Introduction

According to thermodynamics, phase transition is characterised by some anomaly (discontinuity or divergence) of the derivative of the free energy. Experimentally, the liquid–gas transition and solid–liquid transitions are categorized with the first-order phase transition, which has a discontinuity of entropy and volume. The transition between the ferromagnetic phase and paramagnetic phase is categorized with the second-order phase transition, in which the heat capacity or magnetic susceptibility diverges at the transition. The entropy and the volume are the first derivative of the free energy and the magnetic susceptibility is the second derivative of the free energy. Therefore, the existence of the phase transition is known by obtaining the free energy of the system. Statistical mechanics tells us that the free energy is obtained by the partition function, $Z(T, V)$. Let H be the Hamiltonian of the system with N classical identical particles, the dynamical state of the system is specified by the $3N$ coordinates $\mathbf{r}^N \equiv \mathbf{r}_1, \dots, \mathbf{r}_N$ and $3N$ momenta $\mathbf{p}^N \equiv \mathbf{p}_1, \dots, \mathbf{p}_N$. $Z(T, V)$ is obtained by carrying out the integration over the entire phase space, Ω , as follows:

$$Z(T, V) = \int g(E, V) \exp\left(-\frac{E}{k_B T}\right) dE, \quad (1)$$

$$g(E, V) = \frac{1}{N! h^{3N}} \iint_{\Omega} \delta(H(\mathbf{r}^N, \mathbf{p}^N) - E) d\mathbf{r}^N d\mathbf{p}^N, \quad (2)$$

where $g(E, V)$ is the density of states (DOSs) and V is volume of the system. Equation (1) indicates $Z(T, V)$ is merely the Laplace transformation of $g(E, V)$. Thus, the thermodynamic property of the system is intrinsically included in $g(E, V)$. From the formulae of Helmholtz free energy, $F(T, V)$, and Gibbs free energy, $G(T, p)$,

$$F(T, V) = -k_B T \ln \int g(E, V) \exp\left(-\frac{E}{k_B T}\right) dE, \quad (3)$$

$$G(T, p) = -k_B T \ln \iint g(E, V) \exp\left(-\frac{E + pV}{k_B T}\right) dE dV, \quad (4)$$

the anomaly of $F(T, V)$ and $G(T, p)$ must be caused by a certain property of $g(E, V)$. In this study, we obtain $g(E, V)$ by performing the multicanonical molecular dynamics (MMD) simulations[1] to the soft core system to clarify the relation between the property of $g(E, V)$ and

phase transitions.

2 Model and Methods

The Hamiltonian of this study is the soft core system with the softness parameter $n = 12$.

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^N \sum_{j>i}^N \varepsilon \left(\frac{\sigma}{r_{ij}} \right)^n. \quad (5)$$

This system is known to show a first-order phase transition between a fcc-solid phase and a fluid phase at which the scaled density $\rho^\dagger \equiv (N\sigma^3/V)(\varepsilon/k_B T)^{3/n} = 1.15 - 1.19$. [2, 3] Hereafter, length, temperature and energy are scaled by σ , ε/k_B and ε , respectively. The Helmholtz free energy of this system are expressed as follows:

$$\frac{F(T, V)}{NT} = -\frac{3}{2} \ln(2\pi m \varepsilon T) - \frac{1}{N} \ln \int \tilde{g}(\Phi, V) \exp\left(-\frac{\sigma^n \Phi}{T}\right) d\Phi, \quad (6)$$

$$\tilde{g}(\Phi, V) = \frac{\sigma^{3N}}{N! h^{3N}} \int_V \delta\left(\sum_{i=1}^N \sum_{j>i}^N r_{ij}^{-n} - \Phi\right) d\mathbf{r}^N, \quad (7)$$

where $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$, Φ is the scaled potential energy and the integrand of Equation (7) is Dirac's δ function. The MMD simulation enables us to evaluate the partial DOS of potential energy, $\tilde{g}(\Phi, V)$, which can never be obtained by the conventional molecular dynamics simulations. Once $\tilde{g}(\Phi, V)$ is obtained, Helmholtz free energy, the internal energy and the specific heat of the system is calculated. Although, $\tilde{g}(\Phi, V)$ is different from $g(E, V)$ of Equation (2), $g(E, V)$ is also calculated from $\tilde{g}(\Phi, V)$. [1] The detailed procedure of MMD simulations is described in Ref. [1]. In this study, all particles are arranged in a cubic box to which periodic boundary conditions are applied as usual. Temperature \mathcal{T} is controlled by Gaussian thermostat. [4] The simulations are performed with $N = 108$, $\rho \equiv N/V = 0.8$ and $\mathcal{T} = 0.10, 0.24, 0.60$ and 0.80 . As $\phi \equiv \Phi/N$, the flatness of probability distribution, $\mathcal{P}_{\mathcal{T}}(\phi)$ is estimated by

$$\Delta = \int_{\phi_{\min}}^{\phi_{\max}} \left| \mathcal{P}_{\mathcal{T}}(\phi) - \frac{1}{\phi_{\max} - \phi_{\min}} \right| d\phi, \quad (8)$$

where the potential energy is changed within the range ϕ_{\max} and ϕ_{\min} during the MMD simulation. The MMD simulations are executed after a conventional canonical MD simulation with the MD step $N_t = 10^7$ for all \mathcal{T} . The total number of MMD iterations (N_{MMD}) and the MD steps (N_t) for each iteration are described in the following section.

3 Results

Figure 1 shows the time evolution of potential energy and its probability distribution for $\mathcal{T} = 0.10$. It can be seen that the random walk is realized within the range $0.7 \leq \phi \leq 1.1$. The MMD iterations are executed $N_{\text{MMD}} = 44$ times in total for $\mathcal{T} = 0.10$. Initially, the MMD iterations are executed 38 times with $N_t = 10^7$. Next, the MMD iterations are executed five times, $N_{\text{MMD}} = 39 - 43$, with $N_t = 5 \times 10^7$. The final MMD iteration is executed with $N_t = 2 \times 10^8$. Δ decreases by repeating the MMD iterations and finally converges to $\Delta \sim 3.0 \times 10^{-3}$. N_{MMD} , N_t , Δ and the potential energy range for other \mathcal{T} s are tabulated in Table 1. According to Equations (2) and (7), The DOS is intrinsically independent of \mathcal{T} . The choice of \mathcal{T} affects on the energy range,

ϕ_{\max} and ϕ_{\min} , which the system accesses during the simulation time. Figure 2 shows that DOSs obtained by different \mathcal{T} agree well with each other, except for the difference of energy range. It is found that the shape of DOS is concave at $\phi \sim 1$. The simulation results are omitted, however, the same property is found in the DOS for the soft core system with $N = 32$ and $N = 256$. Helmholtz free energy and the internal energy are evaluated as a function of temperature, T , as shown in Figure 3. The internal energy significantly changes around $T \sim 0.23$ while Helmholtz free energy has no peculiar property. In order to investigate the reason of this anomalous property of the internal energy at $T \sim 0.23$, the (unnormalized) probability distribution of ϕ , which is the integrand of the second term of Equation (6), is shown in Figure 4. The probability distribution of ϕ , $P_T(\phi)$, has a single peak at $\phi \sim 0.92$ when $T = 0.22$ and $P_T(\phi)$ has a single peak at $\phi \sim 1.08$ when $T = 0.24$. On the other hand, $P_T(\phi)$ has two peaks at $\phi \sim 0.93$ and $\phi \sim 1.07$ when $T = 0.23$. This double peak comes out from the concavity of DOS at $\phi \sim 1.0$. When the temperature passes through $T \sim 0.23$, the peak position of $P_T(\phi)$ changes suddenly. This sudden change of $P_T(\phi)$ induces the sudden change of internal energy. The MMD simulation results when $\mathcal{T} = 0.60$ and $\mathcal{T} = 0.80$ cover the energy range $\phi \geq 1.20$. Thus, these simulation results can be used to investigate the thermodynamical properties of this system at higher temperature.

4 Conclusion

In this study, we have obtained the DOS for the soft core system with $N = 108$ and have found out that the DOS has a concavity at $\phi \sim 1.0$. That concavity produces a double peak in the probability distribution when the temperature is $T \sim 0.23$. The scaled density estimated by assuming $T = 0.23$ is $\rho^\dagger \sim 1.155$, which is quite similar to the value obtained by Hoover et al.[2, 3] Therefore, the origin of solid–fluid first-order phase transition of this system must be ascribed to the concavity of the DOS. The system size, $N = 108$, is smaller than that commonly used in the conventional molecular dynamics simulation. In order for the system to access a wide area of the phase space, the MMD simulation requires not only a much longer simulation time, N_t , than the conventional MD, but also a large number of iterations, N_{MMD} . In addition, the system needs a long simulation time to escape from the local minimum of the potential energy surface when the temperature, \mathcal{T} , is low. This is the reason that N_{MMD} and N_t for $\mathcal{T} = 0.10$ and 0.24 become larger than those for $\mathcal{T} = 0.60$ and 0.80 . (Table 1) But the simulation with larger N systems is required to ensure the existence of concavity of DOS and the relation between the concavity of DOS and the first-order phase transition. Furthermore, this study is only for the soft core system with the softness parameter $n = 12$. In order to clarify the relation between the DOS and the phase transition, it is also necessary to investigate the other system which shows a phase transition.

References

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Table 1. MMD iteration number (N_{MMD}), MD step (N_{t}), the minimum potential energy (ϕ_{min}) and the maximum potential energy (ϕ_{max}), and the measure of flatness (Δ) for each temperature \mathcal{T} .

\mathcal{T}	N_{MMD}	N_{t}	ϕ_{min}	ϕ_{max}	Δ
0.10	44	*	0.70	1.10	3.0×10^{-3}
0.24	9	2×10^9	0.80	1.33	2.4×10^{-2}
0.60	11	1×10^8	1.20	2.20	6.0×10^{-4}
0.80	9	1×10^8	1.30	3.40	7.0×10^{-4}

* N_{t} for $\mathcal{T} = 0.10$ is described in the text.

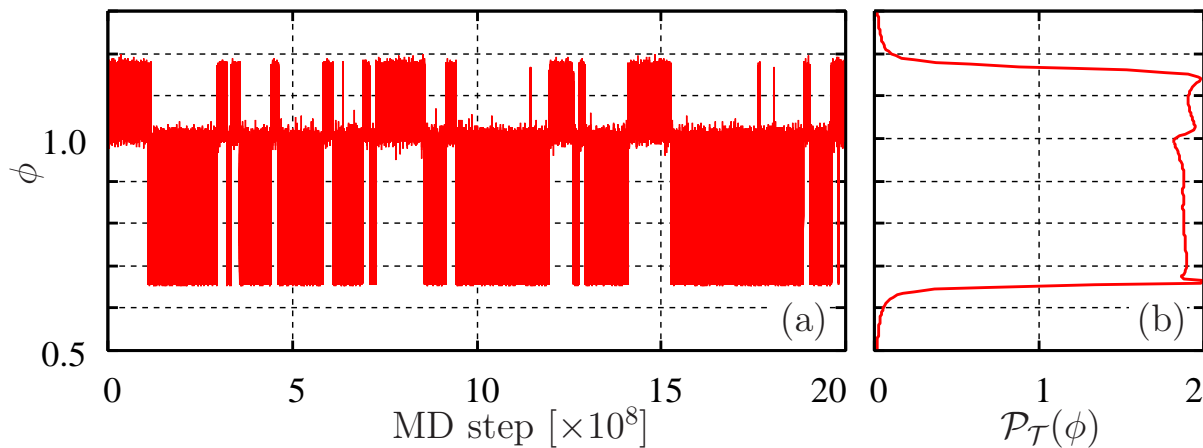


Figure 1. The time evolution of the potential energy (a) and the probability distribution (b) which is obtained by the last iteration of MMD simulation when $\mathcal{T} = 0.10$.

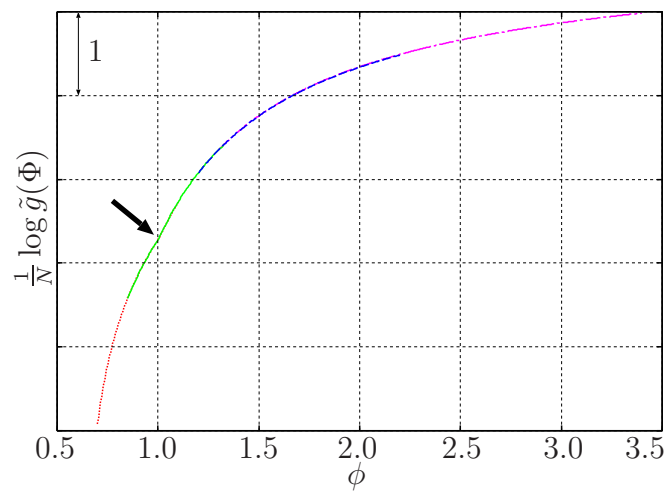


Figure 2. DOS as a function of ϕ . The dotted red line, the solid green line, the dashed blue line and the magenta dashed-dotted line correspond to the MMD simulation results when $\mathcal{T} = 0.10, 0.24, 0.60$ and 0.80 , respectively. The arrow indicates the concavity of DOS.

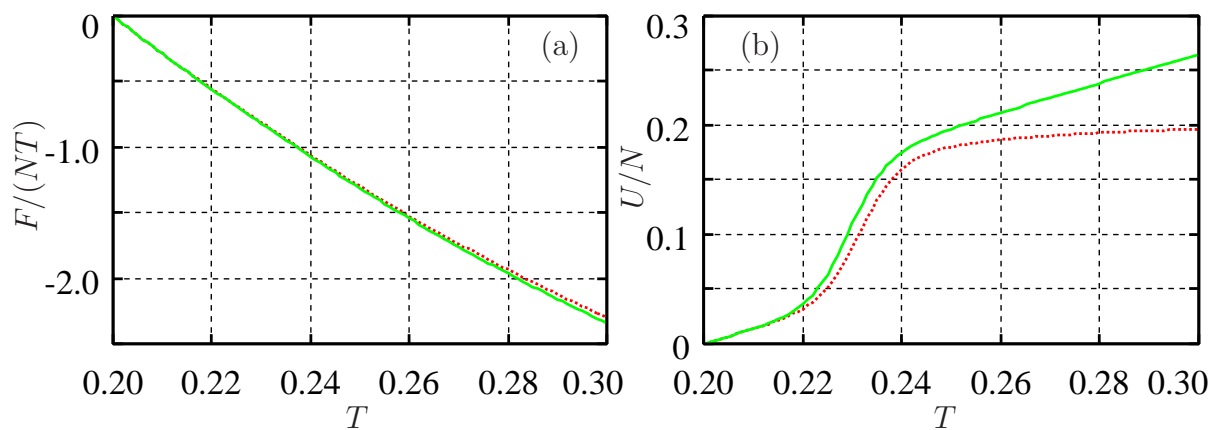


Figure 3. Helmholtz free energy (a) and the internal energy (b) as a function of temperature. The dotted red line is calculated by the MMD simulation result when $T = 0.10$ and the solid green line is calculated by the MMD simulation result when $T = 0.24$.

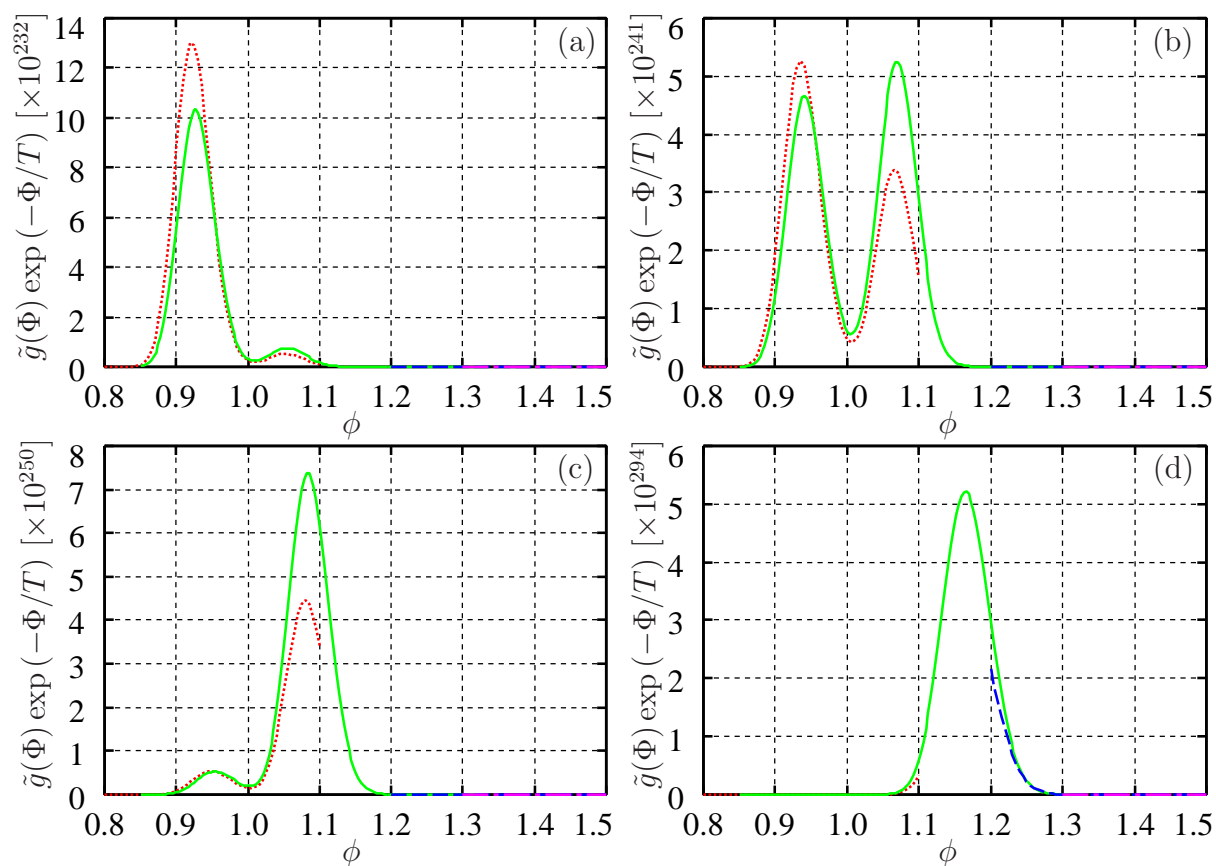


Figure 4. The unnormalized probability distribution of ϕ at four different temperatures. (a) $T = 0.22$, (b) $T = 0.23$, (c) $T = 0.24$ and (d) $T = 0.30$, respectively. The meaning of each line is the same as Figure 2.