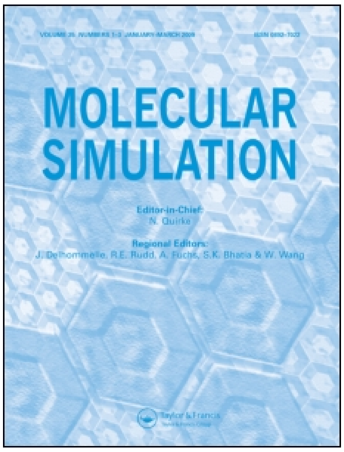

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CONFIGURATIONAL TEMPERATURE FOR BROWNIAN DYNAMICS

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Expressions for the configurational temperature are evaluated in Brownian dynamics simulations of a Lennard-Jones fluid and compared with the input temperature which is used to generate the random displacements. It is found that the two temperatures agree in the limit of large numbers of particles, and even for moderate system sizes the configurational temperature is a useful check on the correctness of the simulation algorithm. Investigation of the autocorrelation functions shows that for Lennard-Jones and power-law fluids, the correlation time of the configurational temperature is shorter than other typical thermodynamic quantities, and it generally increases with the range of the potential.

Keywords: Brownian dynamics; Configurational temperature; Statistical mechanics

INTRODUCTION

Expressions have recently been derived for the thermodynamic temperature of a system, using only configurational information [1-5] (the positions of the particles and the forces between them), and this has been called the configurational temperature. It has been shown that the configurational temperature is a useful tool for checking the correctness of Monte Carlo (MC) simulations [3], and it has also been tested in molecular dynamics (MD) simulations [5].

In this paper the configurational temperature is tested in Brownian dynamics (BD) simulations. BD is often implemented in a form in which

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only the positions and not the velocities of the particles are computed at each step [6]. This corresponds to a "high friction" limit in which the velocities are rapidly decaying, and the interest is in the long-time evolution of the system. The resulting algorithm is of the form [7]

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+\frac{1}{m\zeta}\mathbf{f}(t)\delta t+\delta\mathbf{r}^G$$

where $\mathbf{r}$ is the particle position, δt is the time step, $\mathbf{f}$ is the total *deterministic* force on the particle, m is the particle mass and ζ is the drag coefficient (the Einstein relation gives $m\zeta=k_BT/D$ where D is the diffusion constant of the particle). $\delta\mathbf{r}^G$ is the random force term, for which component δr^G_α is chosen independently from a Gaussian distribution with zero mean and variance $\langle(\delta r^G_\alpha)^2\rangle=2k_BT\delta t/(m\zeta)$. Thus the input temperature only enters explicitly through the variance of the random force term, and the equality of the input temperature to the resulting system temperature is really a test of the fluctuation dissipation theorem.

In this form of BD, as in MC, one cannot evaluate the usual kinetic temperature since velocities are not available, and so it might appear that there is no means of checking whether the simulated system indeed has a temperature which agrees with the input temperature. However the configurational temperature provides a route by which the temperature can be computed only from configurational information, and a comparison with the input temperature furnishes a check on the algorithmic correctness of the program.

In the context of MC simulations, it has also been observed that the configurational temperature responds rapidly to changes in the input temperature, even before thermodynamic equilibrium has been achieved [3]. Here BD is also used to examine the dynamics of the configurational temperature by studying the decay of various autocorrelation functions.

THEORY

Consider the microcanonical ensemble (NVE) with a given Hamiltonian. By evaluating the change in entropy associated with moving from a hypersurface with energy E to one with energy $E+\Delta E$, the temperature T can be obtained from the relation

$$\frac{1}{T}=\left.\frac{\partial S}{\partial E}\right|_V$$

Considering only the configurational part the result is [5]

$$\frac{1}{k_B T_{\mathrm{con}R}} = \left\langle \frac{-\sum_i \nabla_i \cdot \mathbf{F}_i}{\sum_i \mathbf{F}_i^2} - \frac{2\sum_{ij} \mathbf{F}_i \mathbf{F}_j : \nabla_i \mathbf{F}_j}{(\sum_i \mathbf{F}_i^2)^2} \right\rangle \tag{1}$$

where $\mathbf{F}_i$ is the total force acting on particle i and the angle brackets represent an ensemble average. If the particles interact *via* a pairwise additive pair potential u_{ij} between particles i and j, then

$$\mathbf{F}_i = -\sum_{j \neq i} \frac{\partial u_{ij}}{\partial \mathbf{r}_{ij}}$$

where $\mathbf{r}_{ij}$ is the vector from particle i to particle j. The notation $T_{\mathrm{con}R}$ is used for consistency with that of Ref. [5].

The proof has also been extended to the canonical ensemble, to systems with periodic boundary conditions and to the ensembles used in MD simulations [5]. A more general version of this result has also been proved [5], which shows that there are a class of phase functions whose ensemble averages yield the temperature. One such case is

$$\frac{1}{k_B T_{\mathrm{con}F}} = \frac{\langle -\sum_i \nabla_i \cdot \mathbf{F}_i \rangle}{\langle \sum_i \mathbf{F}_i^2 \rangle} \tag{2}$$

Temperature expressions related to Eq. (2) can easily be obtained which use only the forces on a single particle, or using only one Cartesian component of the forces. In general these behave in a similar fashion to Eq. (2), although the statistics are somewhat poorer, and so these will not be pursued further.

One additional temperature expression can be derived by observing that in Eq. (1) the second term is $O(1/N)$ for N particles, and so by neglecting this term one obtains

$$\frac{1}{k_B T_{\mathrm{con}1}} = \left\langle \frac{-\sum_i \nabla_i \cdot \mathbf{F}_i}{\sum_i \mathbf{F}_i^2} \right\rangle \tag{3}$$

Although these three expressions for the temperature (Eqs. (1) to (3)) agree in the thermodynamic limit (large N), it is not clear *a priori* how fast they converge or which is more practically useful in simulations. In this paper the focus will be on Eq. (2) and Eq. (3), since these are the simplest practical temperature expressions for use in simulations. In Ref. [5] it is found that the behaviour of $T_{\mathrm{con}R}$ is quite similar to that of $T_{\mathrm{con}F}$ in the cases examined.

Consider now a one component fluid of spherical particles with number density n and a pair potential given by $u(r)$, where r is the distance between particle centers. In the large N limit it is straightforward to derive from Eq. (2) the following expression for the temperature

$$\frac{1}{k_B T} = \frac{I_1}{I_2 + I_3} \tag{4}$$

where

$$I_1 = 4\pi n \int_0^{\infty} \nabla^2 u(r) g_2(r) r^2 dr \tag{5}$$

$$I_2 = 4\pi n \int_0^{\infty} \left(\frac{du}{dr}\right)^2 g_2(r) r^2 dr \tag{6}$$

$$I_3 = 8\pi^2 n^2 \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 \int_0^{\pi} d\theta \sin(\theta)\cos(\theta) g_3(r_1, r_2, \theta) \frac{du(r_1)}{dr_1}\frac{du(r_2)}{dr_2} \tag{7}$$

where g_2 is the pair correlation function, g_3 is the three particle correlation function and for three particles r_1 is the length of the vector from particle 3 to particle 1, r_2 is the length of the vector from particle 3 to particle 2, and θ is the angle between these two vectors. One might have thought that since the entropy depends on correlations of all orders so too might the temperature, but Eq. (4) shows that the temperature depends *only* on the two and three particle correlations. Equation (4) is also useful for computing corrections to the temperature expressions for long-range potentials. It is interesting to observe that $T > 0$ implies $I_1 > 0$. This last condition is clearly satisfied if $\nabla^2 u(r) > 0$ for all r, but it is less obvious if $\nabla^2 u(r)$ changes sign.

RESULTS

Figure 1 shows the ensemble averages from a Brownian dynamics simulation of the two configurational temperatures $T_{\mathrm{con}F}$ (from Eq. (2)) and $T_{\mathrm{con}1}$ (from Eq. (3)) as a function of N, the number of particles, for a three-dimensional fluid interacting through the Lennard–Jones potential

$$u_{ij} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

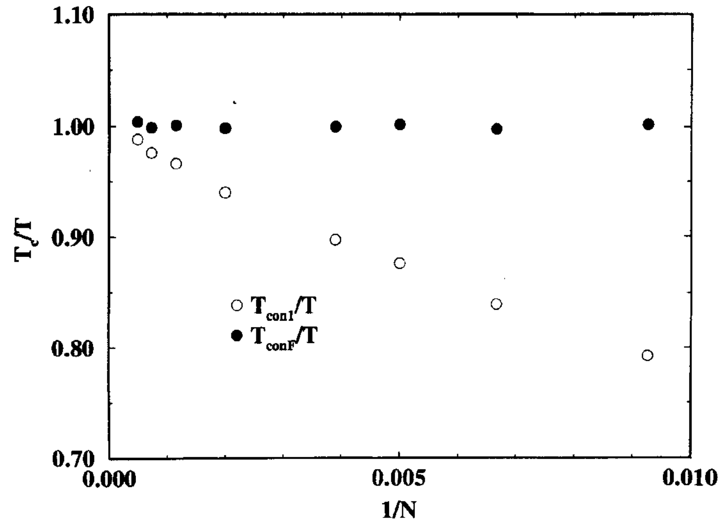

FIGURE 1 Configurational temperature as a function of system size for a 3D Lennard–Jones fluid at $\rho^* = 0.2$ and $T^* = 2.5$, computed from a Brownian Dynamics simulation. Open circles: configurational temperature $T_{\mathrm{con}1}$ computed from Eq. (3), Filled circles: configurational temperature $T_{\mathrm{con}F}$ computed from Eq. (2).

at the low density state point $\rho^* = 0.2$ and $T^* = 2.5$, where $\rho^* = N\sigma^3/V$ and $T^* = k_B T/\varepsilon$. The natural time-scale for the LJ fluid is $\sigma(m/\varepsilon)^{1/2}$ and the scale for the viscosity is $(m\varepsilon)^{1/2}/\sigma^2$ where m is the particle mass. The fluid viscosity was $\eta^* = 200$ for which the high friction limit is valid. A cutoff of 4σ was used for the Lennard–Jones potentials, and the time step was chosen such that the particles moved less than 0.01σ in a single step. The length of the runs was chosen so that the errors at each value of N were less than 1% or about the size of the symbols in Figure 1. At this state point $T_{\mathrm{con}F}$ is within error equal to the input temperature over the range of N shown, whereas $T_{\mathrm{con}1}$ shows an obvious $1/N$ convergence to the thermodynamic limit. This is probably related to the fact that at low densities there are much greater fluctuations in the denominator of Eq. (3) for small values of N and this has a consequent effect on $T_{\mathrm{con}1}$, whereas when the denominator is averaged first before taking the ratio, as for $T_{\mathrm{con}F}$, the effect of these fluctuations is reduced. Qualitatively similar results have been obtained testing the configurational temperature in MC simulations of a 2D Lennard–Jones fluid [3] and MD simulations of a WCA fluid [5]. Tests on inverse power law fluids at the same density indicate that the differences between $T_{\mathrm{con}1}$ and the input temperature are relatively smaller if the potential has longer range, although the behavior of $T_{\mathrm{con}F}$ is still superior. Thus at low densities the temperature expression in Eq. (3) is often less suitable as an algorithmic check, due to the dependence on system size, and instead the expression in Eq. (2) is to be preferred since it gives values of the configurational temperature which are close to the input temperature even for small system sizes.

The agreement of the ensemble average of the configurational temperature with the input temperature is a useful check on the correctness of the Brownian dynamics algorithm. However the equilibrium averages must of course be independent of the dynamics, and the same answers could be obtained from canonical MC simulations on the same system. The configurational temperature T_{con1} can be evaluated at each step of the simulation, and so it is interesting to investigate the fluctuations of this quantity. In particular the normalized autocorrelation function $C_{TT}(\delta 1/T_c(t), \delta 1/T_c(0))$ indicates how fast fluctuations in $1/T_{\mathrm{con1}}$ decay. In the high friction limit of BD, the short-time dynamics are not very realistic, so the interest is more from a simulation perspective regarding the equilibration and relaxation of the configurational temperature. Figure 2 shows the logarithm of the normalized autocorrelation functions for various quantities for a 3D Lennard–Jones fluid with $N = 500$ at the $\rho^* = 0.85$ $T^* = 2.5$ state point and with $\eta^* = 200$. These were collected on a run of 1×10^6

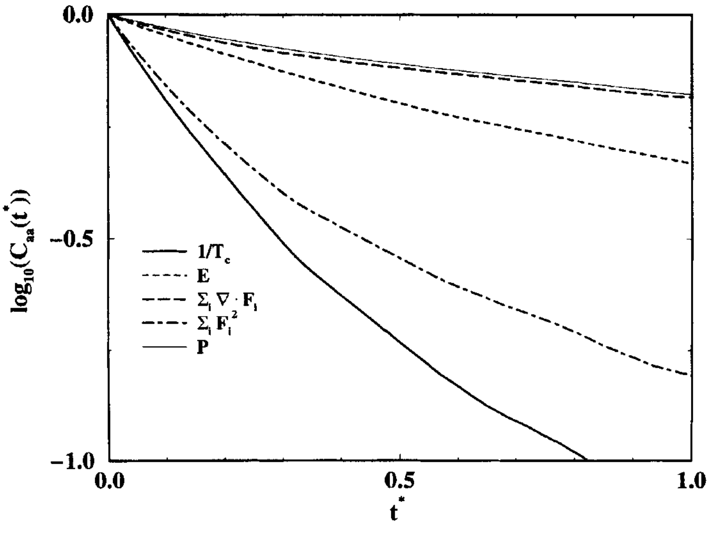

FIGURE 2 Logarithm of the normalized autocorrelation functions for a BD simulation of a 3D Lennard–Jones fluid with 500 particles at $\rho^* = 0.85$, $T^* = 2.5$ and $\eta^* = 200$. Thick solid line: $1/T_{\mathrm{con1}}$. Dotted line: internal energy E. Dashed line: $(1/N)\Sigma_i \nabla \cdot \mathbf{F}_i$ (numerator of expression for $1/T_{\mathrm{con1}}$). Dot-dash: $(1/N)\Sigma_i \mathbf{F}_i^2$ (denominator of expression for $1/T_{\mathrm{con1}}$). Thin solid line: configuration part of the pressure P.

time steps. It is evident that the fluctuations in $1/T_{\text{con}1}$ decay much faster than the fluctuations in either the internal energy E or the configurational part of the pressure P. This agrees with the observation that the configurational temperature responds very rapidly to temperature quenches, and that it can be equal to the input temperature even while the system is not at thermodynamic equilibrium [3].

The normalized autocorrelation functions for the fluctuations in the numerator and denominator of the temperature expression (see Fig. 2) have larger correlation times than their ratio, and so it is clear that the short correlation time of $T_{\text{con}1}$ must be due to the cross-correlation between the numerator and denominator. In Ref. [3] it was suggested that the phase functions which depend on the highest derivatives of the potential relax fastest to their equilibrium values, but in the current system this does not hold, since the fluctuations in the $\sum_i \nabla \cdot \mathbf{F}_i$ term decay much more slowly than those in $1/T_{\text{con}1}$ or $\sum_i \mathbf{F}_i^2$. The same qualitative behavior of the correlation times was also observed in simulations of 3D inverse power-law fluids, and so appears not to be specific just to the 3D Lennard–Jones fluid.

Comparing potentials of different ranges, one might expect that the configurational temperature would relax more slowly for potentials of longer range. In Figure 3, the normalized autocorrelation functions for $1/T_{\text{con}1}$ are given for the 3D Lennard–Jones fluids and inverse power law potentials of the form

$$u_{ij} = \varepsilon\left(\frac{\sigma}{r_{ij}}\right)^p$$

for $p = 4, 6, 12$, and with $N = 500$. The Lennard–Jones state point is $\rho^* = 0.85$ and $T^* = 2.5$, while the inverse power law fluids have $k_BT/\varepsilon = 0.625$ and $N\sigma^3/V = 0.85$ in order to give a comparable state point, and the time and viscosity scales must be similarly adjusted. The cutoff is chosen at 6.786σ, equal to half the box length, to minimize problems arising from truncation of the inverse power-law potentials. In the figure the autocorrelation functions are all plotted on the same time scale (t^* in Lennard–Jones units) in order to be properly comparable. It is clear that amongst the inverse power law fluids, the configurational temperature relaxes more quickly as the potential becomes of shorter range. This is because the configurational temperature will be dominated by force contributions from nearby pairs of particles, and so less time will be required for a disturbance to propagate over this distance. The relaxation

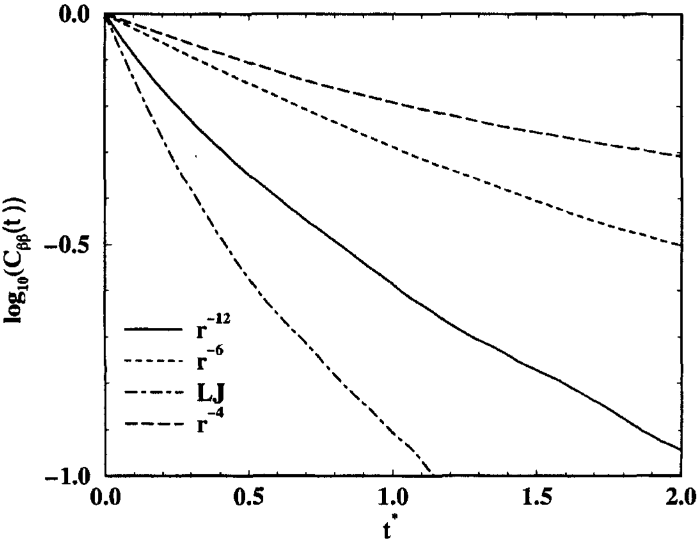

FIGURE 3 Logarithm of the normalized autocorrelation function of $1/T_{\text{con}1}$ for a BD simulation with 500 particles and for different potentials. The inverse power law fluids are at the state point $k_BT/\varepsilon = 0.625$ and $\rho^* = 0.2$, while the LJ fluid is at $T^* = 2.5$ and $\rho^* = 0.2$. The horizontal scale is in LJ units. Solid line: r^{-12} potential. Dotted line: r^{-6} potential. Dot-dash: LJ potential. Dashed line: r^{-4} potential.

time in the LJ fluid is even shorter than for the r^{-12} potential, which suggests some cancellation of the effects on the relaxation time due to the attractive and repulsive parts of the LJ potential.

CONCLUSION

It is possible to express the thermodynamic temperature of a system in terms of configurational information only (*i.e.*, positions of particles and the forces between them), and the expressions derived depend upon both two and three particle correlations in the system. This configurational temperature is a useful algorithmic check in Brownian Dynamics simulations, as in Monte Carlo simulations, since it enables one to check that the thermodynamic temperature of the system matches the input temperature. The temperature expression given in Eq. (2), and referred to as $T_{\text{con}F}$, is found to be most useful in practice, since its dependence on system size in weak even for small systems. The relaxation time of the configurational temperature is short in comparison to other thermodynamic quantities, which means that it cannot be used as a test for achieving an equilibrium state, while on comparing various inverse power law fluids, it is found that the relaxation time increases with the range of the potential.

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