POSITIONAL AND ORIENTATIONAL CONFIGURATIONAL TEMPERATURES FROM COMPUTER SIMULATION

A. A. Chialvo[1,2], J.M. Simonson[1], P. G. Kusalik[5], and P. T. Cummings[2,3,4,6]
[1]Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6110
[2]Departments of Chemical Engineering, [3]Chemistry, and [4]Computer Science,
University of Tennessee, Knoxville, TN 37996-2200
[5]Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada
[6]Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181

Abstract

We define two configurational temperatures associated with the positional $\boldsymbol{r}^N$ and orientational ω^N portions of the configurational phase space of the molecules in a system according to Hirschfelder's hypervirial theorem, and implement their calculation by Monte Carlo and molecular dynamics simulations. We use a simple quadrupolar Lennard-Jones fluid at normal conditions and the TIP4P model at low temperature to illustrate the use of these quantities to test the correctness of Monte Carlo simulation protocols, and as a new tool in the study of the poorly understood behavior of supercooled water.

Keywords

Configurational temperatures, Monte Carlo simulation, Molecular dynamics.

Introduction

Constants of motion are suitable targets to check the validity and accuracy of the integration procedure in the simulation of dynamical systems. Unfortunately, while the conservation of these quantities is a necessary requirement, it is usually not a sufficient condition of correctness of the algorithm, as many practitioners have found out the hard way. For non-dynamical simulation approaches, such as Monte Carlo techniques, there is a need for additional checks of validity not only for the random translational (Butler et al., 1998), but also for orientational moves (Chialvo et al., 2000). A subtler situation rises when dealing with systems at very low temperature such as water at sub-ambient conditions, for which the configurational/orientational relaxation times are rather long. While the kinetic temperature (the measure of the time-average kinetic energy) might be at the set point, the corresponding average configurational (positional and orientational) temperature might not. Yet, there are other compelling reasons to be able to assess the temperature of a system by analyzing its average configuration. For instance, in the validation of microstructural information from x-ray, electron and neutron scattering spectra by means of reverse Monte Carlo techniques we require ways to diagnose the correctness of the procedure used in the processing and to test the internal consistency of the raw data (Tóth and Baranyai, 1999). Moreover, many researchers would like to be able to estimate the temperature of a system based on configurational information provided by those spectra (Heinze et al., 1997).

As a first step toward the achievement of those goals, in this paper we revisit an earlier theoretical development, the so-called *hypervirial theorem* developed by Hirschfelder (Hirschfelder, 1960), as a well-suited tool to make possible the molecular simulation route to *positional* and *orientational* configurational-temperatures. After

developing the corresponding algorithms, we analyze specific molecular dynamics and Monte Carlo illustrative simulation cases where the two configurational quantities can be used to check either the validity of the simulation methodology, the proper configurational equilibration of the system, and/or the correctness of the simulation codes.

Configurational Temperatures

Starting from the hypervirial expressions (Hirschfelder, 1960),

$$\left\langle (\nabla_r \phi)^2 \right\rangle = kT \left\langle \nabla_r^2 \phi \right\rangle \tag{1}$$

$$\left\langle (\nabla_\omega \phi)^2 \right\rangle = kT \left\langle \nabla_\omega^2 \phi \right\rangle \tag{2}$$

where $\phi(r,\omega)$ is the potential depending on distance (r) and orientation (ω), and $\nabla_\omega(...) \equiv \boldsymbol{l} \times \nabla_r(...)$ is the angular gradient operator, such that the torque τ becomes

$$\begin{aligned} \nabla_\omega \phi &\equiv \boldsymbol{l} \times \nabla_r \phi \\ &= -\tau \end{aligned} \tag{3}$$

In equation (3) the operator "$\times$" denotes the cross-product of two vectors, and $\boldsymbol{l} = l_x \hat{i} + l_y \hat{j} + l_z \hat{k}$ is the vector position of molecular sites with respect to the corresponding center of mass. Thus, the divergence of the torque becomes

$$\begin{aligned} \nabla_\omega \bullet \tau &= -\nabla_\omega \bullet \nabla_\omega \phi \\ &= -\nabla_\omega^2 \phi \end{aligned} \tag{4}$$

where the operator "$\bullet$" denotes a scalar product between two vector. Consequently, the configurational temperature associated with the orientational degrees of freedom (ω^N) reads,

$$\begin{aligned} kT &= \left\langle \tau^2 \right\rangle / \left\langle \nabla_\omega^2 \phi \right\rangle \\ &= -\left\langle \tau^2 \right\rangle / \left\langle \nabla_\omega \bullet \tau \right\rangle \\ &= -\left\langle \tau^2 \right\rangle / \left\langle (\boldsymbol{l} \times \nabla_r) \bullet (\boldsymbol{l} \times \nabla_r \phi) \right\rangle \end{aligned} \tag{5}$$

Note that the expression for the configurational temperature associated with the translational degrees of freedom ($\boldsymbol{r}^N$), Eqn. (1), is similar to that derived through rather different approaches by Rugh (Rugh, 1998, Butler et al., 1998), and Baranyai (Baranyai, 2000).

Simulation Results and Discussion

We have performed NVT-MC simulations of a simple quadrupolar Lennard-Jones fluid (Reed and Gubbins, 1991), and NVT-MD simulations of supercooled TIP4P water (Jorgensen, 1981). The detailed account of the methodology and findings of this ongoing investigation will be presented elsewhere (Chialvo et al., 2000).

For illustration purposes, we present in Figures 1-2 the comparison between the kinetic and the two configurational temperatures resulting from the NVT-MD simulation of supercooled and ambient water. This comparison highlights an interesting (and, so far not considered) simulation scenario, *i.e.*, one in which the average system configuration does not agree with the expected value from the kinetic temperature. In other words, even after several nanoseconds of simulation trajectory, the energy equipartition is not satisfied. Note that as the system (kinetic) temperature is increased, the two configurational temperatures approach the corresponding kinetic counterpart.

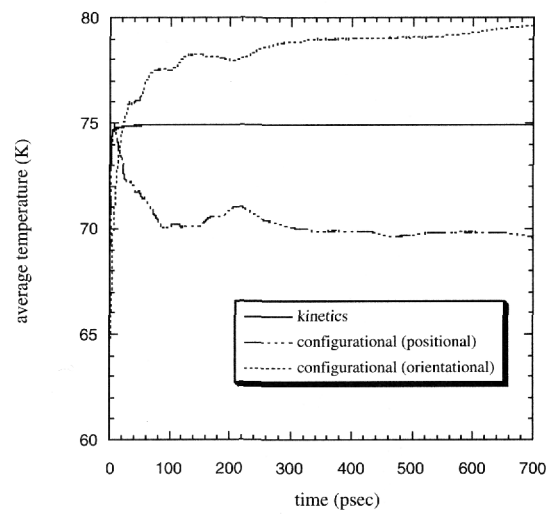

Figure 1. Configurational versus kinetic temperatures for supercooled TIP4P water at T=75K and ρ=1.0g/cc.

The TIP4P water sample at 75 K (Fig. 1) is in a highly metastable (glassy) state. Thermodynamic (energy) and kinetic (diffusion constant) data suggest that it is well below its glass transistion temperature, esitmated to be ~150 K. Structural analysis of the system reveals no indications of crystalline order.

Likewise, in Figure 3 we display the translational and orientational configurational temperatures from NVT-MC simulations of a quadrupolar Lennard-Jones fluid, and their response to an instantaneous change in the set-point simulation temperature. The corresponding responses for the pressure and configurational energies are given in Figure 4.

These pictures clearly indicate the difference between the structural relaxation associated with the translational and orientational degrees of freedom. While the translational configurational temperature adjusts almost instantaneously to the step function change, the

orientational counterpart exhibits a rather long asymptotic relaxation toward the set point temperature. This behavior, in turn, affects the corresponding responses of the pressure and configurational energy as shown in Figure 4. These illustrations suggest the need for further investigation in the behavior of the configurational temperatures and their role in the thermophysical behavior of fluids at low temperature and high density.

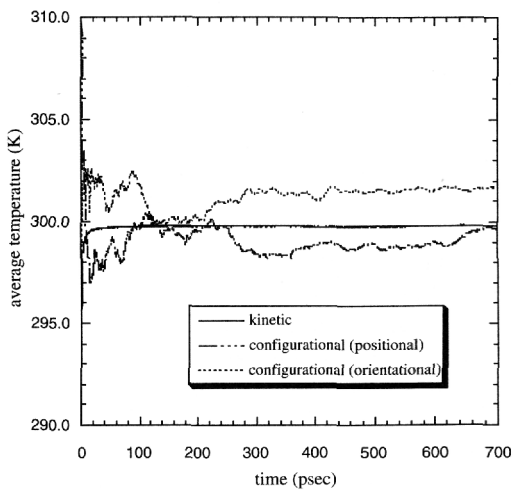

Figure 2. Configurational versus kinetic temperatures for ambient TIP4P water at T=300K and ρ=1.0g/cc.

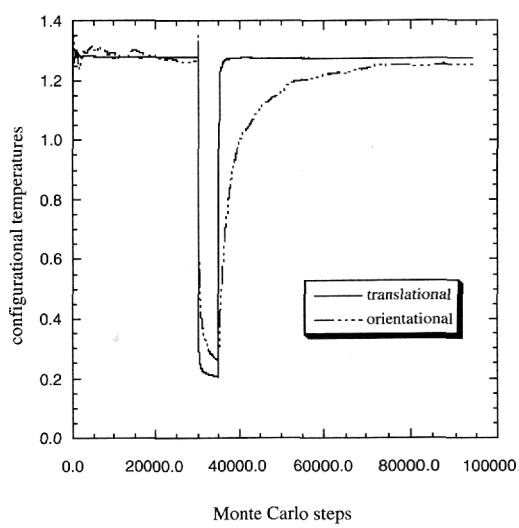

Figure 3. Response of the configurational temperatures (in units of ε / k) to a step function change (from 1.227 to 0.2 and back to 1.227) on the set point temperature for a Lennard-Jones quadrupolar fluid with Q=0.5 at T*=1.227 and ρ*=0.85.*

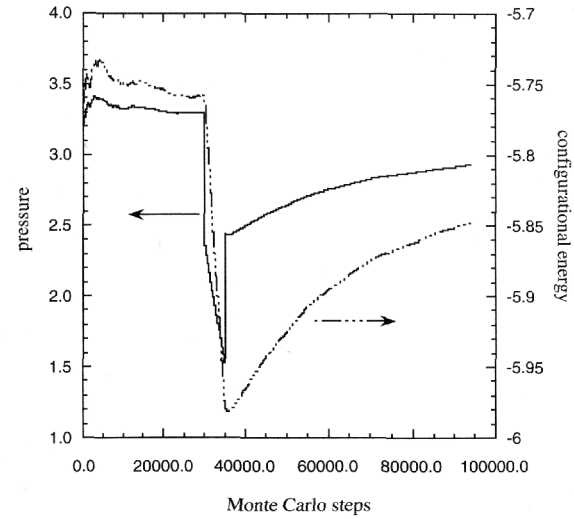

Figure 4. Response of the configurational energy and the pressure (in units of ε and σ) to a step function change (from 1.227 to 0.2 and back to 1.227) on the set point temperature for the same fluid as in Figure 3.

Acknowledgements

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