Int J Thermophys (2010) 31:766–773
DOI 10.1007/s10765-009-0698-8

Ergodic Convergence Times for Molecular Liquids

Raymond D. Mountain

Received: 12 May 2009 / Accepted: 30 December 2009 / Published online: 22 January 2010

Abstract A problem common to all molecular dynamics and Monte Carlo simulations used to estimate fluid properties is how to decide when adequate sampling of the phase space of the system has been realized. One procedure for addressing the sampling question is to construct the energy metric for the system. The energy metric provides an indication of when the time-averaged energies of the individual molecules converge to a common value (self-averaging). The time required for the value of the energy metric to decrease to 1 % of its initial value is a useful indication that adequate sampling has been realized. The energy metric based ergodic convergence times for the molecular liquids water, acetonitrile, methanol, and carbon dioxide plus mixtures of water and methanol and of water and acetonitrile are reported. The convergence time τ for water is about 100 ps at ambient conditions; for carbon dioxide it is about 300 ps while for methanol it is about 800 ps. The convergence times for water/acetonitrile mixtures are much longer due to the microheterogeneous structure of the mixtures. The ergodic convergence time is an increasing function of the mole fraction of methanol in the mixtures. The convergence times for water along the liquid side of the liquid–vapor coexistence curve are found to decrease strongly as the temperature increases.

Keywords Acetonitrile · Carbon dioxide · Energy metric · Liquid state · Methanol · Water

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R. D. Mountain (✉)
Chemical and Biochemical Reference Data Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8320, USA
e-mail: Raymond.mountain@nist.gov

1 Introduction

A concern with any molecular dynamics or Monte Carlo simulation of fluid thermal properties is the adequacy of the sampling performed to obtain estimates of the properties. This is independent of the adequacy of the model interactions used. For a system that is intended to be in thermal equilibrium, one usually invokes the quasi-ergodic hypothesis that time and phase space averages are equivalent [1]. This poses the concern in terms of how long should the simulation be run to obtain the approximate equivalence of time and ensemble averages. One way of estimating the necessary simulation time was developed to guide the simulation of strongly supercooled fluids. The method constructs the energy fluctuation metric, $M_{\mathrm{E}}(t)$ [2]. The long-time behavior of the energy fluctuation metric provides an estimate of when the individual molecules of the fluid have sampled most of the possible environments. The estimate is τ, the ergodic convergence time. For a fluid truly in thermal equilibrium, it should not be possible to find molecules with long-time average energies different from the average over all molecules of that type.

In this article, we obtain ergodic convergence times for water, methanol, aqueous mixtures of methanol, and for acetonitrile and aqueous mixtures of acetonitrile. The latter set will illustrate a limitation of the usefulness of the energy fluctuation metric.

The energy fluctuation metric is the variance of time-averaged individual particle energies relative to the overall average particle energy summed over all molecules in the fluid. Let $\varepsilon_j(t)$ be the time average energy of molecule j, then the energy fluctuation metric, $M_{\mathrm{E}}(t)$, is

$$M_{\mathrm{E}}(t) = 1/N \sum_{j=1}^{N} \left(\varepsilon_j(t) - \langle E \rangle\right)^2$$

where the sum is over all N molecules and $\langle E \rangle$ is the average energy per molecule at time t. This is a quantity that can be readily generated during a run. It is easy to show that the long-time dependence of the fluctuation metric goes as $1/t$ in the ensemble average sense. A useful conjecture is that the ergodic convergence time is estimated to be the time when the value of the fluctuation metric has decreased to 0.01 times the initial value, namely, $M_{\mathrm{E}}(\tau) = 0.01 M_{\mathrm{E}}(0)$. This will be referred to as the 0.01 criterion. As will be demonstrated below, an estimate of the ergodic convergence time can be obtained by extrapolating the linear portion of $M_{\mathrm{E}}(0)/M_{\mathrm{E}}(t)$ to longer times.

2 Simulation Details

The simulations of water, methanol, carbon dioxide, and the aqueous methanol mixtures are for systems of a total of 500 molecules, while the simulations involving acetonitrile are for systems of 730 molecules. The fluids are placed in a cubic simulation cell, and periodic boundary conditions are applied in all three spatial dimensions. The size of the simulation cell was adjusted so that the time-averaged value of the pressure was within a few MPa of 0.1 MPa. Water is modeled using the SPC/E potential [3], methanol is modeled using the potential of van Leeuwen and Smit [4], carbon dioxide is modeled using the potential of Potoff and Siepmann [5], and acetonitrile is modeled using the Edwards potential [6]. These models treat the molecules as rigid, three interaction site objects. The methyl groups in methanol and acetonitrile are represented as united atoms. The potential parameters and geometry of the objects are found in the cited articles. The interaction potentials have the Lennard–Jones plus Coulomb form. Each of the models provides reasonably good predictions for the liquid–vapor coexistence curves of the pure fluids. As is usually done, the unlike atom Lennard–Jones parameters are obtained using the Lorentz–Berthelot combining rules [7].

The equations of motion were integrated using the Velocity-Verlet algorithm, adapted to use quaternions to represent the orientational degrees of freedom of the molecules [8]. Separate Nose–Hoover thermostats were applied to the translational and orientational degrees of freedom to maintain the temperature of the system [9] so that sampling is from the NVT ensemble. The time step for the integration was 1 fs and the coupling time for the thermostats was set to 0.5 ps, as this was found to provide good temperature control. The long-range parts of the Lennard–Jones interactions were truncated at 1/2 the simulation cell edge, and the long-range part of the Coulomb interactions was obtained using the Ewald summation method with conducting boundary conditions [10]. The fluids were "equilibrated" before the production runs were made to determine the fluctuation metric. As each run provided a single trajectory, several sequential runs were made in some cases to obtain an estimate of the inherent uncertainties in the estimates of the ergodic convergence times.

The initial value of the fluctuation metric, $M_{\mathrm{E}}(0)$, was determined from the distribution of individual molecule energies, taken over the duration of the simulation, as this significantly reduced the uncertainty in the estimates of the ergodic convergence times. The distribution of individual particle energies is broad, and a single sample does not provide a reliable estimate of the width of the distribution. The accumulated value of the energy metric is determined at 1 ps intervals and written to a file for later processing, including determining $M_{\mathrm{E}}(0)$.

A possible measure of the adequacy of the 0.01 criterion for ergodic convergence is the convergence of time averages of specific properties to a stable, long-time average. Here, we use the cumulative time average value of the pressure, $p(t)$, and the cumulative time average standard deviation of the pressure, $\sigma_p(t)$, as a check on the convergence of the time and ensemble averages. This is done using 1 ps block averages of the pressure. For these liquids, 1 ps duration blocks are effectively statistically independent as determined by the time correlation function of the block averages relative to the long-time average value.

3 Results

In this section, we will present the results for the energy fluctuation metrics as the ratio $M_{\mathrm{E}}(0)/M_{\mathrm{E}}L(t)$ for single trajectories. For this reason, the curves are "noisy" and only approximately exhibit 1/*t* behavior for long times. The ergodic convergence time estimate is somewhat "rough" as a result. Two possible values are the time when the ratio reaches 100 and the time when a linear extrapolation of the short time part

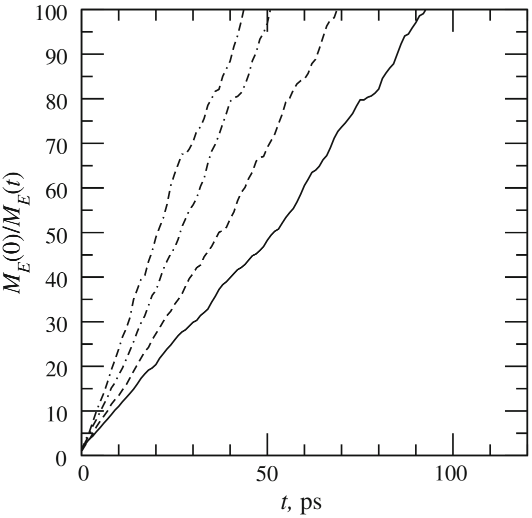


Fig. 1 Ratio of energy metric values is shown for liquid water at 293 K (*solid line*), 303 K (*dashed line*), 343 K (*dashed–dotted line*), and 393 K (*dashed–dashed–dotted line*)

of the curve reaches 100. These can differ by as much as 20 %. For some states, several trajectories have been run. These results, not shown here, also yield individual estimates that can vary by as much as 20 %. The conclusion is that any given estimate of the ergodic convergence time is inherently uncertain by up to 20 %. Since these estimates are intended to suggest how long a simulation should be, this is not a serious limitation. It is important to recognize that the ergodic convergence measure is not a substitute for careful analysis of simulation estimates for fluid properties to determine that the required accuracy is realized.

First, we examine the ergodic convergence times for water. Figure 1 exhibits the results for the energy fluctuation metric for four temperatures on the liquid side of the liquid–vapor coexistence line. The solid line is for 293 K, and the estimate for τ, based on a linear extrapolation from the short time part of the curve (0 to 40) ps is 105 ps. The dashed line is for 303 K with a τ of about 75 ps, the dashed–dotted line is for 343 K with a τ of about 55 ps, and the dashed–dashed–dotted line is for 393 K with a τ of about 42 ps. Although not shown here, similar results are obtained for states with increasing temperature at constant density. This indicates that temperature is the important quantity in determining the convergence time. Figure 2 exhibits the time-averaged pressure and standard deviation of the pressure as a function of the simulation time for 293 K. The pressure approaches the long-time average value in about 100 ps, indicating that for this system, the ergodic convergence time obtained using the “0.01 criterion” is appropriate for properties that are calculated directly. Pressure fluctuations, the square of the standard deviation $\sigma_p(t)$, will require longer simulations as the distribution of block average pressures takes longer than τ to be adequately sampled so that the variance of the block averages has converged. This also applies as well to the energy fluctuations and to the pressure–energy fluctuations.

Figure 3 compares the energy fluctuation metrics for water (solid line), CO_2 (dashed line), methanol (dashed–dotted line), and for acetonitrile (dashed–dashed–dotted line), all at 293 K for densities such that the calculated pressure is “close” to zero. The ergodic

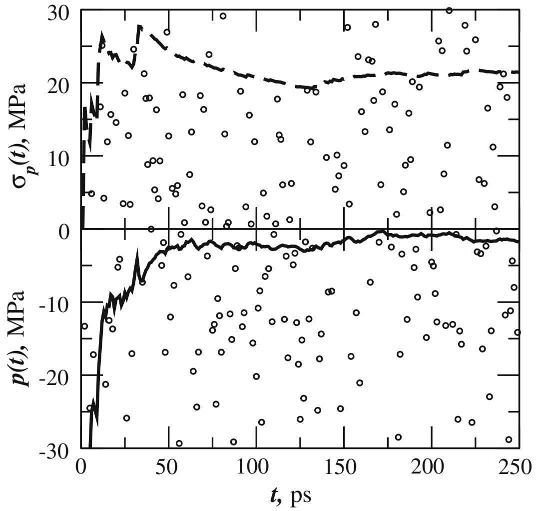


Fig. 2 Cumulative time average of the pressure, $p(t)$ (*solid line*), and the corresponding standard deviation, $\sigma_p(t)$ (*dashed line*), is shown as a function of the simulation time for water at 293 K. *Open circles* are the individual 1 ps duration block averages of the pressure

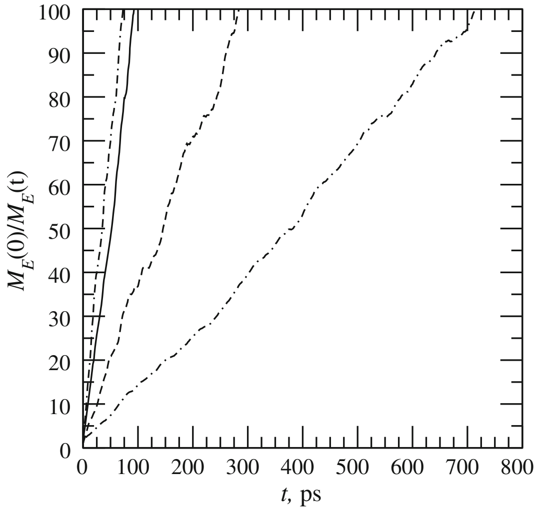


Fig. 3 Energy metric ratios are shown for water (*solid line*), CO_2 (*dashed line*), methanol (*dashed–dotted line*), and acetonitrile (*dashed–dashed–dotted line*), all at $T = 293$ K and densities so that the pressure is close to 0 MPa

convergence time for methanol is much larger than the times for the other liquids. The reasons for this are a subject for future study. A possible reason might be the presence of transient, chain-like configurations of hydrogen-bonded molecules as have been found in other alcohol liquids [12].

Next, we examine the results for mixtures of water and methanol. Figure 4 exhibits the results for systems with mole fraction water, X_W, equal to 0.8 (triangles), 0.6 (no symbol), and 0.4 (circles). The solid lines are the metric for the water molecules, and the dashed lines are the metric for the methanol molecules. The convergence times increase as the ratio of water to methanol decreases.

Finally, let us consider a situation where the energy metric is probably not a good indication of how long a simulation should be. Frenkel and Smit [11] point out that the time required for each molecule of an ice–water interfacial system to fully sample

Fig. 4 Energy metric ratios for water–methanol mixtures at 293 K as shown for three concentrations: $X_{\mathrm{W}} = 0.8$ (*triangles*), $X_{\mathrm{W}} = 0.6$ (*no symbol*), and $X_{\mathrm{W}} = 0.4$ (*circles*). The *solid lines* are the water metrics, and the *dashed lines* are the methanol metrics

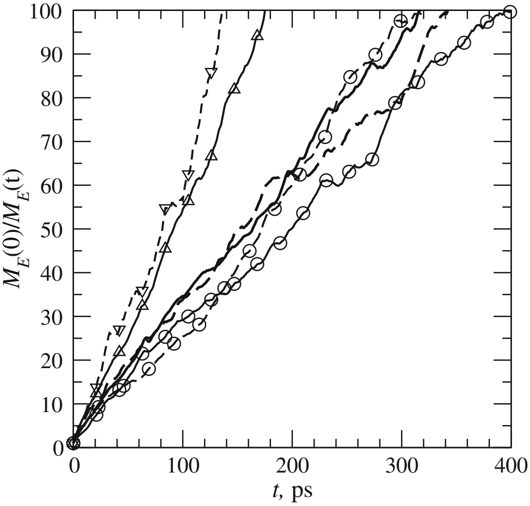
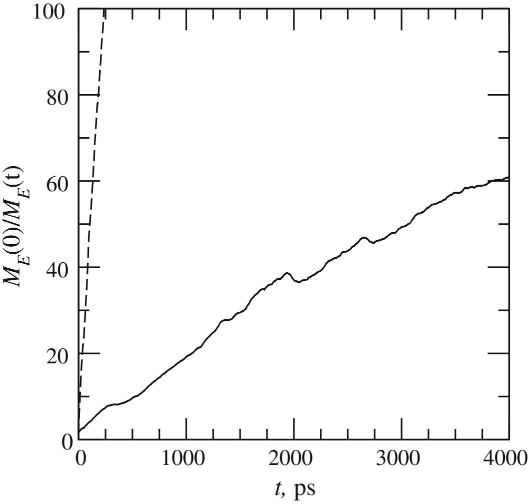


Fig. 5 Energy metric ratios for the water–acetonitrile mixture at 293 K with $X_{\mathrm{W}} = 0.167$ are shown for water (*solid line*) and acetonitrile (*dashed line*)



all environments would be much longer than any plausible equilibration time. The water–acetonitrile liquid mixture is another case where the local structure of the fluid makes the ergodic convergence time much longer than a useful "equilibration time." This is because the fluid is heterogeneous on the scale of several molecules with interpenetrating water-rich and acetonitrile-rich regions. Only on longer length scales is the liquid homogeneous [13].

Figure 5 exhibits the energy metric ratio for a water–acetonitrile mixture with X_{W} equal to 0.167. The solid line is the ratio for water molecules and suggests that the ergodic convergence time is on the order of 6 ns. The dashed line for the acetonitrile molecules puts the ergodic convergence time at about 250 ps. Figure 6 exhibits the

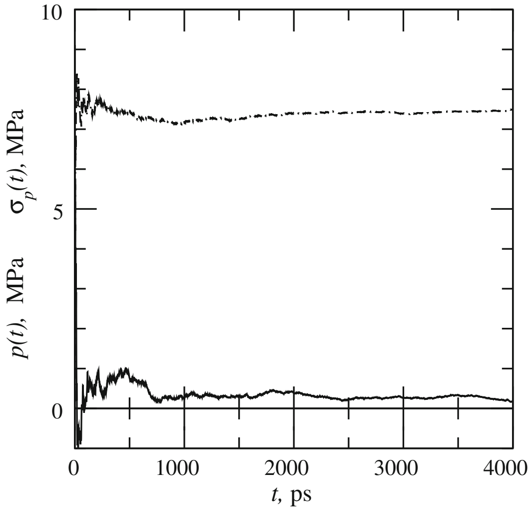


Fig. 6 Cumulative time averaged pressure, $p(t)$ (*solid line*) and the standard deviation for the pressure, $\sigma(t)$ (*dashed–dotted line*), are shown for the state used for Fig. 5. Averages are constructed using block averages for the pressure of 1 ps duration

time-averaged pressure and the standard deviation of the pressure for this system. From these plots, one would suggest that 1 ns is an adequate sampling time.

4 Discussion

The lesson from these studies is that the energy fluctuation metric is useful for estimating ergodic convergence times for systems that are homogeneous on the molecular scale. This predictive capability can be a useful feature when designing simulations that will require long running times. If there are small-scale structures present that constrain the overall motion of some of the molecules, such as a liquid–vapor interface [14], then some other criterion is needed to answer the question of how long is long enough.

The discussion has been in terms appropriate to a molecular dynamics simulation. It is also applicable to Monte Carlo simulations by replacing the progress variable time by the number of Monte Carlo cycles [15]. A common practice is to identify a cycle as a sequence of *N* proposed moves where *N* is the number of particles in the fluid.

References

1. D. Frenkel, B. Smit, *Understanding Molecular Simulation*, 2nd edn. (Academic Press, San Diego, 2002), pp. 15–17
2. D. Thirumalai, R.D. Mountain, Phys. Rev. A **42**, 4574 (1990)
3. H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, J. Phys. Chem. **91**, 6269 (1987)
4. M.E. van Leeuwen, B. Smit, J. Phys. Chem. **99**, 1831 (1999)
5. J.J. Potoff, J.I. Siepmann, AIChE J. **47**, 1676 (2001)
6. D.M.F. Edwards, P.A. Madden, I.R. McDonald, Mol. Phys. **51**, 1141 (1984)
7. J.P. Hansen, I.R. McDonald, *Theory of Simple Liquids*, 2nd edn. (Academic Press, San Diego, 1986), p. 179

8. N.S. Martys, R.D. Mountain, Phys. Rev. E **59**, 3733 (1999)
9. G.J. Martyna, M.L. Klein, M. Tuckerman, J. Chem. Phys. **97**, 2635 (1992)
10. M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1990), pp. 156–162
11. B. Chen, J.I. Siepmann, J. Phys. Chem. B **110**, 3555 (2006)
12. D. Frenkel, B. Smit, *Understanding Molecular Simulation*, 2nd edn. (Academic Press, San Diego, 2002), pp. 47–48
13. R.D. Mountain, J. Phys. Chem. A **103**, 10744 (1999)
14. R.D. Mountain, J. Phys. Chem. B **113**, 482 (2009)
15. R.D. Mountain, D. Thirumalai, Physica A **210**, 453 (1994)