PHYSICAL REVIEW E VOLUME 59, NUMBER 3 MARCH 1999

Method for enhanced sampling in the simulations of dynamical systems

Igor M. Svishchev
Department of Chemistry, Trent University, Peterborough, Ontario, Canada K9J 7B8

Peter G. Kusalik
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

(Received 1 September 1998)

An algorithm for enhanced configurational sampling in molecular dynamics simulations based on stochastic scaling of the intermolecular potential is described. It is implemented in simulations of homogeneous nucleation of a supercooled molecular liquid, carbon dioxide, resulting in significant savings of computer time. This method preserves a canonical form for the potential energy distribution and does not alter average dynamical properties for equilibrium systems. [S1063-651X(99)06603-9]

PACS number(s): 02.70.−c, 61.20.Ja, 64.70.Dv, 61.66.−f

Configurational sampling of ‘‘difficult’’ regions of the phase space (those that are important yet rarely sampled through thermal fluctuations) is a major challenge in computer simulations of systems whose potential energy surfaces (PES's) exhibit a complex landscape. Typical examples include macromolecules, metastable liquids, spin glasses, polymorphic solids, etc. Simulated annealing is perhaps the most straightforward approach that can be used to probe their PES's [1]. In recent years a variety of refined techniques, such as umbrella sampling, multicanonical sampling, genetic algorithms, force- (antiforce-) biased methods, etc., has been implemented for their study, both in Monte Carlo (MC) and molecular dynamics (MD) simulations [2–13]. These advanced simulation techniques help enhance (accelerate) the configurational search through a coarse graining of the phase space, generally by lowering (or even eliminating) the potential barriers between local minima on the PES's. Incorporation of quantum degrees of freedom (‘‘diffuse’’ particles) into the system's classical Hamiltonian has been shown to achieve similar effects (improved sampling) in computer simulations of Lennard-Jones systems and proteins [14,15].

This Brief Report describes a simple and practical method with which to perform an enhanced configurational sampling in molecular dynamics simulations. The homogeneous crystallization of a molecular liquid, carbon dioxide (CO_2), will be the focus of this study, our main goal being to achieve a faster crystallization of a supercooled CO_2. Although simulations of the crystallization of simple monoatomic liquids can be performed almost routinely, the crystallization of molecular liquids still poses principal difficulties, similar to those encountered in studying protein folding—a large number of translational and rotational degrees of freedom which tend to relax into metastable ‘‘traps’’ of the PES's. Metastable disordered (‘‘glassy’’) states which emerge upon a reduction of temperature usually prevent the nucleation of a regular molecular crystal on the time scale of a typical simulation. A molecular system in which the spontaneous nucleation can be detected upon simple quenching is carbon dioxide; yet, as we have previously shown, the observed nucleation times range from hundreds of picoseconds to several nanoseconds [16].

We have achieved a faster crystallization of a supercooled molecular liquid by inducing small stochastic perturbations to the intermolecular potential as the system moves along its phase space trajectory (simulation details for CO_2 can be found in Ref. [16]). In this method, the intermolecular potential for the system, $u(r)$, is scaled at each MD time step by a random number α,

$$u_n(r)^* = \alpha_n u(r), \tag{1}$$

so that

$$\langle u_n(r)^* \rangle = \langle \alpha_n \rangle u(r) = u(r), \tag{2}$$

where $u_n(r)^*$ and α_n are, respectively, the scaled intermolecular potential and its scaling multiplier at the time step n, $\langle \cdots \rangle$ denotes the usual ensemble average, and the first equality in Eq. (2) follows from the requirement that $\langle \alpha_n \rangle = 1$. The numerical value for α is determined through a recurrent random walk procedure around unity where each step of the random walker is performed at each new MD step. Essentially, this approach combines a stochastic sampling in the parameter space for the interaction potential with the regular MD procedure (see Ref. [16]). It should be noted that this potential scaling procedure is equivalent to applying a small stochastic force to each particle *parallel* (or antiparallel) to the force resulting directly from the unperturbed interaction potential.

Formally, our restricted random walker α, or the potential multiplier, can be defined as

$$\alpha_{n+1} = \alpha_n + \Delta\alpha_{n+1} \tag{3}$$

and

$$\Delta\alpha_{n+1} = \sigma(2R - \alpha_n), \tag{4}$$

where α_{n+1} is the potential multiplier at the next $(n+1)$ time step, $\Delta\alpha_{n+1}$ is the size of the step of the random walker, R is the random number generated in the interval [0,1], and σ is the numerical constant determining the width of the distribution sampled by α. We have shown numerically that the probability distribution for α has a normal (Gaussian) form with a mean and dispersion of 1 and 3.04σ,

1063-651X/99/59(3)/3753(3)/$15.00

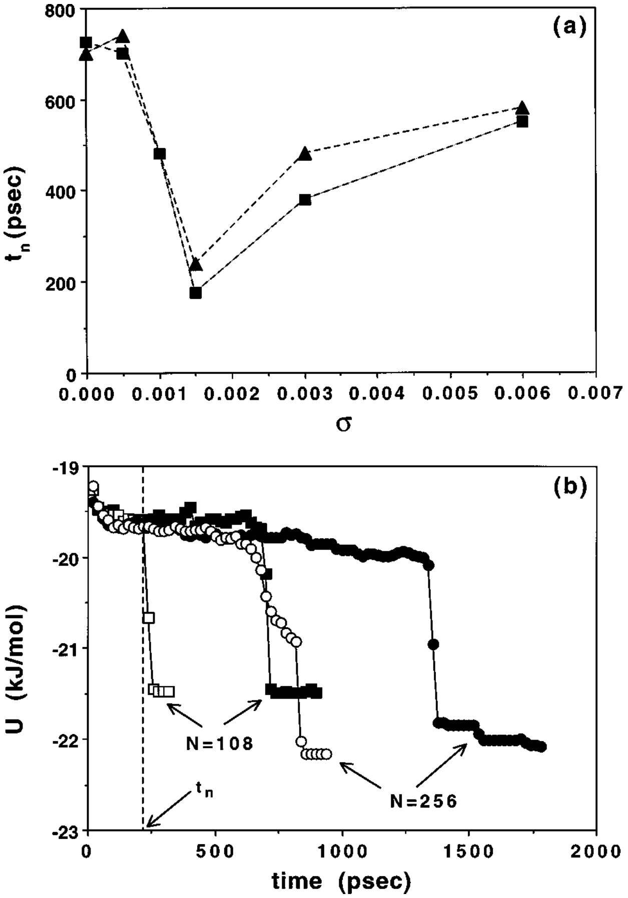

FIG. 1. Effect of the potential perturbations on the nucleation times t_n of supercooled liquid carbon dioxide at a fixed quench temperature of 75 K. (a) Nucleation times for 108-particle samples of carbon dioxide obtained with different values of the normalization constant σ. In this plot the triangles and squares are results obtained in two independent series of simulations. (b) Time dependences of the total configurational energy for 108 and 256 carbon dioxide samples (the squares and circles, respectively). Each point represents a block average taken over 19.0 ps. The solid symbols represent a standard MD simulation ($\sigma=0$), while the open symbols are results obtained with $\sigma=0.0015$. As an illustration, the nucleation time is specified for one of the simulation runs.

respectively. In each of our simulation runs, the initial value for α was set to 1. We remark that thermostatted equations of motion, as used in this study, can accommodate these small stochastic perturbations to the regular intermolecular forces since at each time step the random force experiences only a small change in magnitude. Different values for the constant σ, which determines the range of magnitudes of these perturbations, were tested. Our stochastic forces were typically less than 1% of those resulting from the intermolecular interactions (i.e., α fell within the range 0.99–1.01).

The main results of these MD runs are shown in Figs. 1 and 2. Two 108-particle samples of liquid CO_2 were prepared at 180 K and served as *independent* starting configurations. These two samples could then be rapidly quenched (at a rate of 30 K/ps) to their final temperatures and monitored for the onset of crystallization. Several different trajectories were thus generated using different values for σ, ranging from 0 to 0.006. Figure 1 illustrates the effect of the potential perturbations on the nucleation times of supercooled liquid carbon dioxide at a fixed quench temperature of 75 K. The nucleation times observed appear to depend significantly on σ, as shown in Fig. 1(a). In particular, using $\sigma=0.0015$ (to determine the width of the sampling distribution for α) results in approximately a threefold reduction in the crystallization time, as compared with the standard ($\sigma=0$, $\alpha\equiv1.0$) simulation at 75 K. Similar results have been obtained for 256-particle samples. Typical time dependences for the configurational energy at 75 K for $N=108$ and 256 are shown in Fig. 1(b).

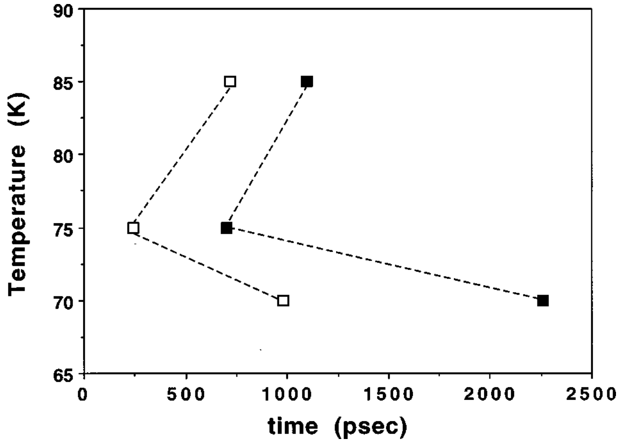

FIG. 2. Nucleation times for 108-particle samples of carbon dioxide obtained at different quench temperatures. In this time-temperature-transformation plot the solid symbols are results of a standard MD simulation, while the open symbols are results obtained with $\sigma=0.0015$.

Further 108-particle simulations have been carried out, now at different quench temperatures 70 and 85 K, using our optimum value for σ (i.e., $\sigma=0.0015$). The nucleation times are plotted versus final temperature in Fig. 2 (time-temperature-transformation plot). A significant speedup in the crystallization dynamics has been accomplished at all temperatures studied.

An important test of our simulation technique was carried out with a "vitrified" sample of carbon dioxide. This sample was produced by *slow* cooling (within 1 ns) a liquid configuration from 180 to 85 K. In the absence of perturbations, it did not exhibit the spontaneous crystallization over the next 4 ns. (Contrary to our initial expectations, gradual cooling appears to inhibit the nucleation events in a dynamical simulation; virtually all our CO_2 configurations did not tend to crystallize after slow annealing at temperatures at which they would normally undergo the crystallization after a rapid quench.) In the test simulation the same starting CO_2 configuration and cooling procedure were used. We engaged our stochastic perturbations (with $\sigma=0.0015$) only after reaching the final temperature of 85 K. The crystallization now followed at approximately 0.82 ns.

A notable feature of our simulation method is that it preserves the canonical (Gaussian) form for the potential energy distribution $P(U)$. Figure 3 displays the potential energy distributions for liquid CO_2 at 180 K accumulated in a standard MD simulation and in a simulation with $\sigma=0.0015$; at this temperature, the system is far from phase instabilities [16]. Also shown in Fig. 3 are the results obtained at 75 K for supercooled liquid prior to the nucleation event and for

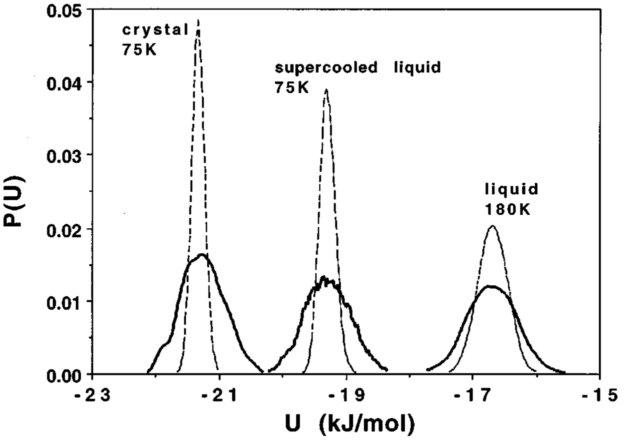

FIG. 3. Potential energy distributions for carbon dioxide system accumulated in a standard MD simulation (dashed lines) and in a simulation with $\sigma = 0.0015$ (solid lines). Liquid carbon dioxide at 180 K, supercooled liquid at 75 K prior to the nucleation event, and the crystal that emerges from this liquid after the nucleation are represented.

crystal that emerges from this liquid after the nucleation. This figure illustrates that the energy distribution for a perturbed system is broader, but it has the same mean value. The incorporation of a random energy scaling, or a perturbing random force [as defined by Eqs. (1)–(4)], into the constant-temperature equations of motion effectively increases the energy fluctuations experienced by the system, yet without changing average properties such as the energy or pressure. The resulting potential energy distribution for an equilibrium system, $P(\alpha U)$, broadened by a restricted random walk in α, can be deconvoluted back to the original distribution $P(U)$, since

$$P(\alpha U) = \int_{-\infty}^{\infty} P(U) P(\alpha) d\alpha. \tag{5}$$

This broader energy distribution must span more configurational states of the system. Upon quenching, the liquid state trajectory encounters a ‘‘maze’’ of metastable glassy ‘‘traps’’ which encompass a global minimum domain (the crystalline state) [17]. Random, yet small, distortions (perturbations) of the PES’s enable the trajectory to escape metastable ‘‘traps’’ by making accessible those high (and hence low) energy configurations that would not be normally sampled through the inherent thermal fluctuations, eventually leading to a faster nucleation. Hence the system can be viewed as if it were effectively at a higher configurational temperature, while its kinetic temperature is unchanged.

We have also computed the average self-diffusion coefficients for liquid CO_2 at 180 K both in the absence and presence of stochastic perturbations. We have found their values to be equal within statistical uncertainties. This fact implies that the local translational dynamics of molecules subject to small random perturbations (with $\sigma < 0.006$) is similar to that in the original canonical ensemble.

From a mechanistic viewpoint, this work illustrates an important effect of random perturbations of the PES’s on the phase instabilities of dynamical systems [18]. This effect has been exploited in simulations of the liquid-to-solid transformation. In principle, our simulation method has a wider applicability, not being restricted to a particular system or process. Work is underway to study ice nucleation and growth.

We are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada.

---

[1] S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science **220**, 671 (1983).
[2] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
[3] D. E. Goldberg, *Genetic Algorithms in Search, Optimization and Machine Learning* (Addison-Wesley, Reading, MA, 1989).
[4] P. G. Wolynes, J. N. Omuchic, and D. Thirumalai, Science **267**, 1619 (1995).
[5] C. Bartels and M. Karplus, J. Phys. Chem. **102**, 865 (1998).
[6] E. Leontidis and U. W. Suter, Mol. Phys. **83**, 489 (1994).
[7] J. P. K. Doye and D. J. Wales, Phys. Rev. Lett. **80**, 1357 (1998).
[8] B. A. Berg and T. N. Neuhaus, Phys. Rev. Lett. **68**, 9 (1992).
[9] U. H. E. Hansmann, Y. Okamoto, and F. Eisenmenger, Chem. Phys. Lett. **259**, 321 (1996).
[10] D. Borgis and A. Staib, J. Chem. Phys. **104**, 4776 (1996).
[11] T. P. Straatsma and J. A. McCammon, J. Chem. Phys. **101**, 5032 (1994).
[12] E. M. Boczko and C. L. Brooks III, Science **269**, 393 (1995).
[13] J. Lee, Phys. Rev. Lett. **71**, 211 (1993).
[14] R. L. Somorjai, J. Phys. Chem. **95**, 4141 (1991).
[15] J. Ma, D. Hsu and J. E. Straub, J. Chem. Phys. **99**, 4024 (1993).
[16] I. M. Svishchev and P. G. Kusalik, Phys. Rev. Lett. **75**, 3289 (1995).
[17] F. H. Stillinger, Phys. Rev. B **41**, 2409 (1990).
[18] M. I. Freidlin and A. D. Wentzell, *Random Perturbations of Dynamical Systems* (Springer-Verlag, New York, 1984).