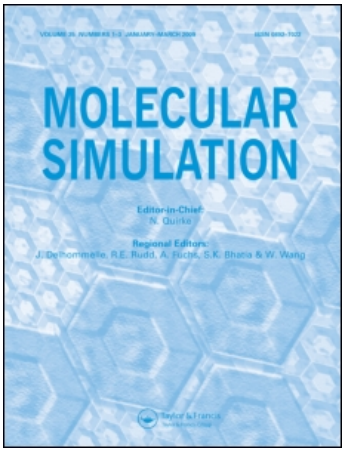

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Use of Control Quantities in Computer Simulation Experiments: Application to the Exp-6 Potential Fluid

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To cite this Article Nezbeda, Ivo and Kolafa, Jiř(1995) 'The Use of Control Quantities in Computer Simulation Experiments: Application to the Exp-6 Potential Fluid', Molecular Simulation, 14: 3, 153 — 163
To link to this Article: DOI: 10.1080/08927029508022013
URL: http://dx.doi.org/10.1080/08927029508022013

Molecular Simulation, 1995, Vol. 14, pp. 153–163
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THE USE OF CONTROL QUANTITIES IN COMPUTER SIMULATION EXPERIMENTS: APPLICATION TO THE EXP-6 POTENTIAL FLUID

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(Received May 1994, accepted July 1994)

Important quantities, which should be computed in the course of computer experiments in order to maintain the control over the development of the studied system, are summarized and their properties are discussed. The usefulness of these quantities is demonstrated by reference to published data for the exp-6 potential model. The ease with which it is possible to confuse solid and liquid states is illustrated.

KEY WORDS: Control quantities, convergence profile, structure factor, autodiffusion, orientational-order parameter, exp-6 fluid.

1 INTRODUCTION

It has long been an unwritten requirement for experimentalists to describe in detail in their papers the experimental equipment, the experimental method employed, and to present their results with estimates of errors. Furthermore, before embarking on new experiments, they performed several tests to reproduce known bench-mark data to ensure that their equipment and methods performed as required.

Computer experiments may be viewed as a modern-day counterpart of laboratory experiments [1] and similar rules should thus also apply to them. In papers from the pioneering era of computer simulations, when only a handful of enthusiasts was experimenting with this new technique and improving the methods, we always find every detail of their simulations so that anyone may be able to reproduce the published results. Unfortunately, this is no longer true. Computer simulations have become, to a certain extent, a routine 'experimental' method to produce results for a variety of purposes. With both commercial and public-domain software available, as well as with an access to fast computers, anyone can 'study' nowadays a system of his own interest by means of computers, even without proper understanding of the underlying methods.

The results of computer simulations are physical quantities, which may also typically be calculated theoretically and/or are available from real experiments. However, in addition to collecting numbers which ultimately produce these quantities, it is also necessary to monitor, in the course of the simulation, certain auxiliary quantities, which provide indispensable information on the development of the system. Surprisingly, little attention, if any at all, is paid to these in the published literature; we shall refer to them as control quantities.

The first purpose of this communication is to demonstrate that simulations carried out routinely with disrespect for the basic rules of experimental methodology may lead to erroneous results which, however, need not be immediately evident and, consequently, may mislead theorists and other users of such data. To accomplish this goal, we summarize definitions and properties of the control quantities which, we think, should always be computed in computer simulation pseudoexperiments. The second purpose is to demonstrate the use of some of these quantities, in showing that some of the recently published extensive data (altogether 504 state points) on the exp-6 potential fluid [2, 3] at very high pressures and high temperatures are not fluid but rather solid states.

II FLUID, GLASS, OR A SOLID?

A principal concern in computer simulations on fluid is to guarantee that the simulated system is in a single thermodynamically equilibrated fluid phase. This becomes especially very important when we perform the simulation at conditions near phase boundaries. Secondly (which seems so obvious that it should not be even mentioned), we must be sure that the configuration space is sampled properly.

There are several, more or less standard, tools available which detect different phases, states far from equilibrium, improper sampling, etc.; some of them are briefly mentioned in [4], others may be found scattered in original papers. To be specific, we will exemplify the use of these general tools for the exp-6 fluid, which is defined by the potential

$$u(r) = \varepsilon \left\{ \frac{6}{\alpha - 6} \exp\left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \frac{\alpha}{\alpha - 6} \left(\frac{r_m}{r} \right)^6 \right\} \tag{1}$$

where r_m and ε determine the position of the potential minimum and its depth, respectively; throughout the paper we shall use units such that $\varepsilon/k_B = r_m = 1$ where k_B is the Boltzmann constant. The dimensionless parameter α measures the repulsive stiffness and varies, for real fluids, between 11 and 15 [2, 3, 5, 6].

The exponential term is a more realistic characterization of interatomic repulsive forces at very high pressures [5] than *e.g.* the inverse twelfth power (Lennard-Jones) potential, leading to the use of the exp-6 potential in geochemical (rock inclusions) and military (detonations) applications. From the point of purposes of this paper, the exp-6 potential is more suitable than the usually used 12-6 Lennard-Jones potential, since it makes certain features less distinctive and thus requires more careful procedures.

A Convergence profile

The convergence profile shows the time development of quantities of interest. Typical quantities to monitor are different parts of the energy (configurational, intra- and intermolecular, kinetic in molecular dynamics) or virial pressure (or the contact value

of the pair correlation function in the case of a fluid of hard bodies). When the simulation is started from an initial configuration (*e.g.* a crystal, a random configuration, a configuration equilibrated at other temperature or density), gradual changes of these quantities from their initial values to their equilibrium values are observed. After reaching equilibrium, the measured quantities then begin to fluctuate around the equilibrium values.

The typical time in molecular dynamics (MD), or number of steps in Monte Carlo (MC), simulations within which the quantities fluctuate is important for estimating the errors of the measured quantities, and in turn for determining the necessary minimum length of the entire pseudo-experiment. It is further recommended that one carefully analyze the resulting time series and calculate, for instance, the time correlation functions and the correlation time (integral of the time autocorrelation function) [7].

A "cumulative convergence profile" or "running average" showing averaged values from the start of the simulation run is some times used instead of a "running" profile. The recorded quantities converge to their expectation mean values (they must converge by definition), but information on the actual time development is hidden. In our opinion, this type of convergence profile is more misleading than useful and cannot be recommended.

The usefulness of monitoring the convergence profile is demonstrated by Figure 1. The recorded quantity is the kinetic temperature T_{kin} (the kinetic energy divided by half the number of degrees of freedom) obtained by running a microcanonical MD simulation on 800 exp-6 atoms (with $\alpha = 13.9$ and at high number-density $\rho = 2.6881$, which is a state point corresponding to CO_2 [3]) at the total energy per particle $E_{tot} = 40$. The illustrated convergence profile starts from a state that seems to be well equilibrated, since the kinetic temperature fluctuates around a constant value. Then, a sharp change occurs, and the kinetic temperature begins to fluctuate around a new value; henceforth no further trends are observed. The interpretation of this observation is that in the first part of the simulation a metastable state was simulated. Consequently, if we stop the simulation run *before* the jump occurs (too short run), the results are questionable. If we do not monitor the convergence profile (*i.e.* are not aware of the transition which takes place) and evaluate the average from the entire run, the results will be incorrect.

B Autodiffusion

The autodiffusion describes the mobility of molecules and can thus detect different thermodynamic states. We define the autodiffusion of molecule i by

$$D_i = \lim_{t \to \infty} \frac{\delta_i(t)}{6t} \tag{2}$$

where the mean square displacement δ is given by

$$\delta_i(t) = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle^{1/2} \tag{3}$$

and $\mathbf{r}_i$ is vector of position of particle i. In MC or MD experiments, in addition to the ensemble average $\langle . \rangle$, averaging over all molecules (possibly weighted if a mixture is

simulated) is performed. It is also worth noting that with the periodic boundary conditions the molecule may travel over several periodic images and thus the path of the molecule should be followed in order to obtain the correct 3D autodiffusion.

If the limit (2) converges rapidly to a nonzero value, the system contains a fluid phase. The mobility of molecules in glassy or solid states is much lower and in such cases (2) converges slowly or not at all, while (3) fluctuates around a constant value describing a molecule vibrating in a cage.

Table 1 shows the autodiffusion and the mean square displacement as a function of time interval for both parts of the simulation of Figure 1. It is seen that the autodiffusion in the first part of the simulation (A) converges slowly to a value around 0.009. Slow convergence can be explained by long relaxation times in the sample; in fact, the autodiffusion cannot be measured more accurately because metastable fluid undergoes a spontaneous phase transition. The autodiffusion in the relaxed state (B) is lower, but neither the autodiffusion nor the mean square displacement seem to converge clearly to a constant value. This 'mixed behaviour' can be explained by the presence of a two-phase region or a solid state with a lot of perturbations.

C *Structure factor*

The structure factor detects regular lattice ordering in the system (or in a part of it). For a system of N identical particles described by vectors $\mathbf{r}_i$, $i \in \{1, \ldots, N\}$, the structure factor, as a function of a reciprocal space vector $\mathbf{k}$, is defined by [8]

$$S(\mathbf{k}) = \left\langle \frac{1}{N} |Q(\mathbf{k})|^2 \right\rangle \tag{4}$$

where

$$Q(\mathbf{k}) = \sum_{j=1}^{N} \exp(i\mathbf{k}\cdot\mathbf{r}_j) \tag{5}$$

It can also be expressed as the Fourier transform of the radial distribution function $g(\mathbf{r})$:

$$S(\mathbf{k}) = 1 + \rho \int \exp(i\mathbf{k}\cdot\mathbf{r}) g(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{6}$$

where ρ denotes the number density. From the computational point of view it is worth mentioning that the algorithm to calculate $\mathbf{Q}(\mathbf{k})$ is the same as for the k-space part of Ewald sums [9].

Table 1 The mean square displacement δ and the autodiffusion D as a function of time interval t. Exponents A and B refer, respectively, to the first and second parts of the simulation of Figure 1.

t	δ_t^A	D_t^A	δ_t^B	D_t^B
0.25	30.6	0.0255	25.7	0.0214
0.50	40.0	0.0167	29.9	0.0124
0.75	49.3	0.0137	31.9	0.0089
1.50	69.0	0.0096	42.6	0.0059
2.25	99.8	0.0092	53.3	0.0049

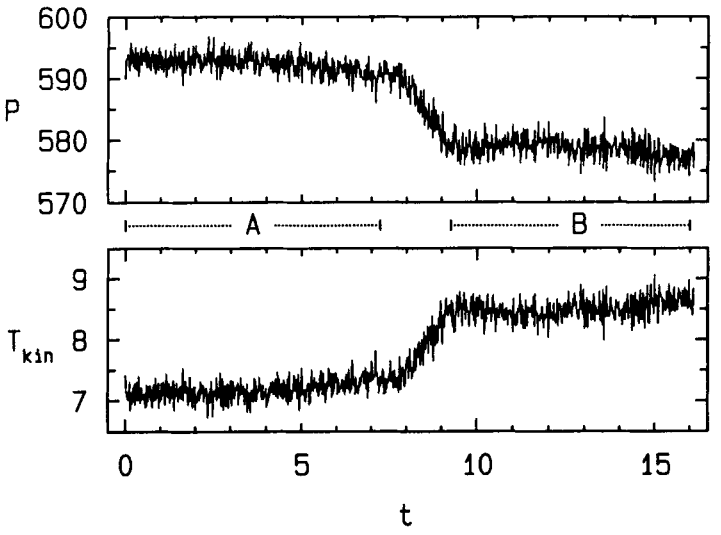

Figure 1 Example of the convergence profile for the microcanonical MD simulation on the exp-6 potential system with $\alpha = 13.9$ at $\rho = 2.6881$ and $E_{tot} = 40$. A first-order phase transition from a metastable fluid phase to a solid is observed.

If the structure factor is calculated from a sample contained in a periodic box of edge L, the k-vectors can be only discrete multiples of integer vectors $\mathbf{n}$:

$$k = 2\pi\mathbf{n}/L \tag{7}$$

For the fully homogeneous fluid phase the structure factor is a smooth (with respect to grid) function of the k-vectors. The presence of an ordered phase in the sample is reflected by sharp peaks in the directions of the respective k-vectors. As it is difficult to observe a 3D function (and also to reduce the amount of data) we define the structure factor as a function of scalar $k = |\mathbf{k}|$ by

$$S(k) = \sum_{k=|\mathbf{k}|} S(\mathbf{k}) \Big/ \sum_{k=|\mathbf{k}|} 1 \tag{8}$$

Though the 3D information is lost, the fluid-lattice difference is still discernible from this angle-averaged function.

Figure 2 shows a typical fluid-phase structure factor for the same α and density of Figure 1, $N = 250$ and temperature $T = 19.83 \pm 0.01$. The departure from smoothness is due to several factors: (1) statistical errors, (2) grid errors, and (3) influence of periodic boundary conditions on the liquid structure (which is, for as low number of particles as 250, quite high). The first two factors are evident and the last statement is easily deduced from the radial distribution function: its value for distances close to half the box size differs significantly from unity. On the other hand, the influence of the boundary conditions on the pressure, correctly predicted by the HNC theory [10], is negligible (less than 0.05% for $N \in \langle 250, \infty)$ and $T = 12$) because the dominant contribution at high pressures comes from atoms close to contact.

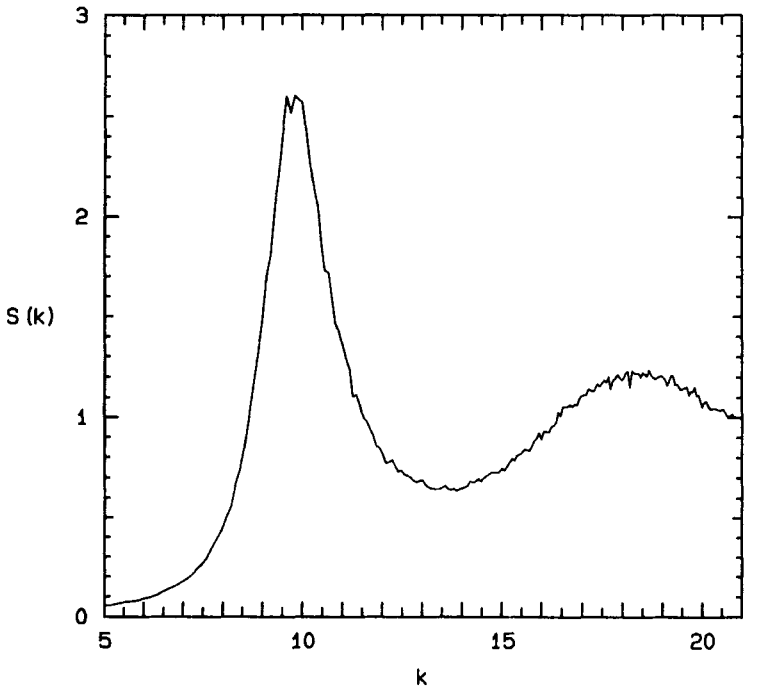

Figure 2 Typical fluid structure factor obtained from a high-temperature configuration of 250 exp-6 atoms in the periodic boundary conditions.

Figure 3 shows the structure factors for both parts of the simulation run of Figure 1. The structure factor A is, within the grid and statistical errors, a fairly smooth function of the reciprocal space vector, suggesting thus that the system is in a disordered phase; its first maximum is, however, rather high suggesting that the system is likely in a glassy state. Small peaks over the smooth function are probably caused by the onset of crystallization; in fact, the examination of the 3D configurations at the end of interval A shows islands of an ordered phase. The second structure factor contains sharp peaks, which provides clear evidence that the system contains a large crystal. Further analysis reveals a body centered cubic crystal squeezed by the periodic boundary conditions (which causes splits of the peaks).

We have mentioned that the structure factor is the Fourier transform of the radial distribution function. The distribution itself provides also useful insight into the structure: For instance, a crystal at sufficiently low temperatures should exhibit sharp peaks in this function. This, however, need not be the case for soft repulsive potentials. The exp-6 potential is so soft that it may be difficult (if not impossible) to distinguish fluid and crystalline phases by examining $g(r)$ only. With increasing temperature the peaks become wider and gradually merge; for the studied density at temperatures around 10, only a split of the second maximum on the radial distribution function is seen. At even higher temperatures the radial distribution function is quite fluid-like even if the sample is still a (possibly superheated) crystal.

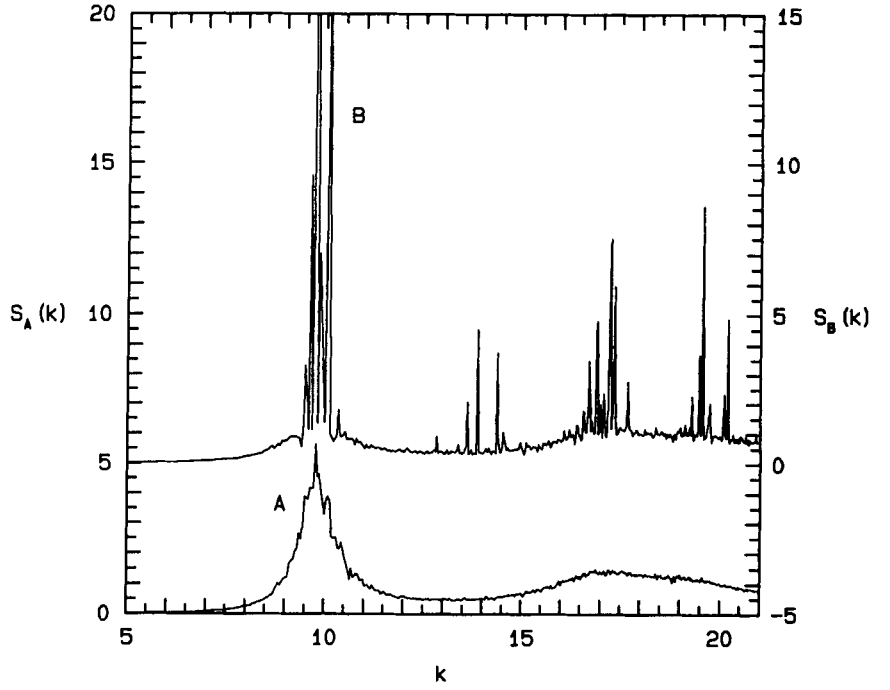

Figure 3 The structure factors corresponding to both parts of the simulation shown in Figure 1.

In the present study we did not know in advance the translation vectors of the lattice resulting from spontaneous freezing. If the pseudoexperiment is started from an ordered lattice (which was the case of [2, 3]), it is enough to monitor $S(\mathbf{k})$ for one chosen translation vector of the initial lattice; $S(\mathbf{k})$ is then also called the translation order parameter [4].

D Orientational-order parameter

Although this parameter is associated only with systems made up of linear molecules, we will give here, for completeness, its definition and basic properties.

The orientation-order parameter M is defined by

$$M = \frac{3}{2}\langle \mathrm{Tr} O^2 \rangle \tag{9}$$

where O stands for the traceless orientation tensor [11], the components of which are

$$O^{\alpha\beta} = \frac{1}{N}\sum_{i=1}^{N} v_i^{\alpha} v_i^{\beta} = \frac{1}{3}\delta^{\alpha\beta} \tag{10}$$

with v_i^{α} being the components of the unit vector of the axis of the linear molecule.

This parameter measures the alignment of the molecular axes and varies between zero and unity: for a completely oriented phase it equals unity, and is of the order of $1/N$

in the completely isotropic phase. It is a natural extension of the structure factor to orientational degrees of freedom, and is similarly useful. For instance, although the generation of rotational moves in MC simulations provides no fundamental problems, it is not without pitfalls (for a discussion of erroneous algorithms used in early simulations on linear molecule fluids see, for example, [2] and M can then detect a possible defect in the MC code.

III ANALYSIS OF THE SIMULATION DATA

Recently we published a paper [13] on a simple volume-explicit equation of state (EOS) applicable to compressed supercritical fluids and applied it successfully to real experimental data. We also attempted to make use of the extensive tables of new simulation data on the exp-6 potential supercritical *fluids* published by Belonoshko and Saxena [2, 3] but soon encountered difficulties. Although the data for a given density seemed to fall on a smooth curve (within the published error bars), some discrepancies between the data and our EOS, as well as observed trends, were somewhat incomprehensible. These findings prompted us, in addition to questioning first the EOS, to also check the simulation data itself and to make a deeper analysis of the published data by carrying out our own simulations. Special attention was paid to the aforementioned control quantities in order to closely follow the development of the studied system with the goal of detecting potential structural changes. In this paper we use some of our new data for an analysis of the properties of the exp-6 potential fluid; the complete set of these data will be published elsewhere [14].

In Figure 4 we compare typical results of Belonoshko and Saxena (BS) with our simulations along a selected isochore. The figure shows the pressure of the exp-6 system with $\alpha = 13.9$ along the isochore $\rho = 2.6881$ which is a state point for CO_2 at $V = 16\,\mathrm{cm}^3/\mathrm{mol}$ [3]. We see that there are two disconnected branches belonging to (either stable or metastable) crystal and liquid phases, respectively. Though the BS data (filled circles) lie, within their large error bars, on a smooth curve, they are far removed from our data (open circles) corresponding to the fluid phase, which were obtained under very similar conditions (250 exp-6 atoms in periodic boundary conditions); it is seen that data are in much better agreement with our data for the solid phase. In the figure we distinguish crystals obtained by spontaneous freezing of metastable liquid (diamonds) where the crystal may contain dislocations and may be distorted, and data obtained by starting from an ideal bcc lattice filling regularly the space (squares). The arrows in Figure 4 show cases when a spontaneous transition from a metastable state to a stable one occurred; an increase in temperature and decrease in pressure indicates freezing (latent heat is released) and *vice versa*. It should be noted that the periodic boundary conditions for $N = 250$ atoms stabilize artificially the lattice structure and thus give a biased estimate of the melting point. Neither 250 nor 800 atoms are sufficient to observe a stable two-phase region; nevertheless, our own simulations with 800-atom configurations containing a piece of crystal in the fluid phase suggest that the melting point, for the considered density, is located, roughly, at $T \approx 11$.

To understand the discrepancies between the two sets of data it is sufficient to follow Belonoshko and Saxena's description of their simulations and to recall Figures 1 and 4.

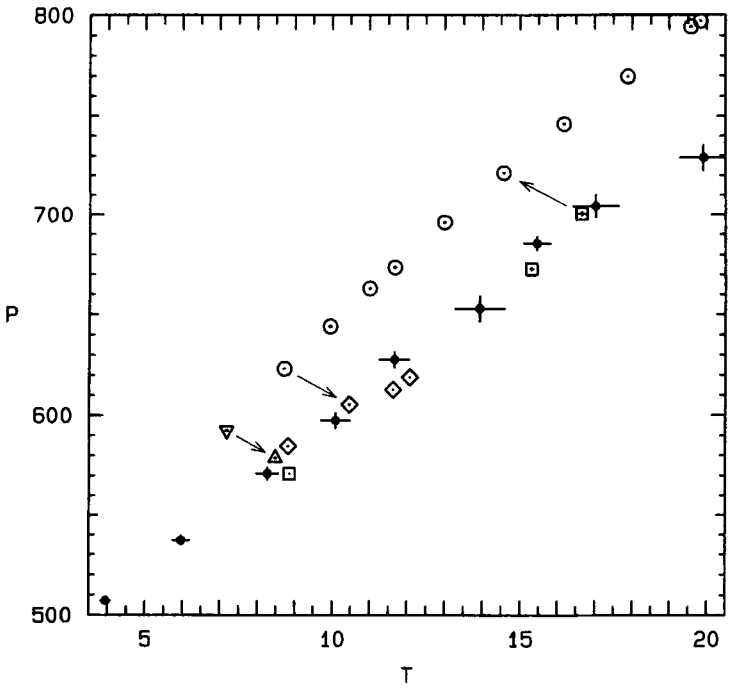

Figure 4 Simulation results for the exp-6 potential system at density $\rho = 2.6881$ and with $\alpha = 13.9$. Filled symbols denote the data from ref. [3], and open symbols denote the data obtained in this paper. ○: fluid phase of 250 particles; ◇: solid phase, obtained by freezing a supercooled fluid of 250 particles; □: solid phase started from a bcc lattice of 250 particles; △: fluid phase (part A of Figure 1) of 800 particles; ▽: solid phase (part B of Figure 1) of 800 particles. The arrows denote freezing of a supercooled liquid or melting of an overheated bcc crystal.

They started from a regular bcc lattice arrangement and first attempted to melt it. They did not use any microscopic (control) property to check whether the system did in fact reach the stable fluid phase, and after a predetermined fixed time (when it seemed that the fluctuations in pressure had stabilized) they began to collect the required histograms. The final configuration they used then as the initial configuration for the next run at a higher temperature, and so on. From our own simulations and from examining the control quantities (in this case basically the structure factor) it is easy to find the explanation of the discrepancies between our data and theirs. The simulation runs they used were too short to reach the stable fluid phase and their results thus correspond to a solid glassy phase, as confirmed by our simulations (*cf.* Figure 4).

The result of the analysis of the BS data, carried out as described above for one selected isochore, applies to other isochores as well. We thus conclude that the published simulation data do not describe the properties of the exp-6 potential fluid phase. (We recall that BS do not explicitly claim that *all* the data in their tables are for the homogeneous fluid phase although the titles of their papers may imply it).

IV CONCLUSIONS

In this paper, dealing with technical aspects of computer simulations, we have focussed on frequently overlooked aspects of the simulation procedure. Control quantities, which do not necessarily produce data corresponding to physical (measurable) quantities but which provide indispensable information on the development of the studied system, have been summarized and discussed in detail. The usefulness of these control quantities has been demonstrated by their application to the exp-6 potential fluid and solid.

With a generally observable trend in the current literature to devote less and less space to the technical details of simulations, there exists a potential danger that these technical aspects of simulations may also be ignored in the simulations themselves. This may lead to inaccurate (at best) or even erroneous results, of which the simulator, and more importantly the unwary user of such data, may be unaware. The findings discussed in this paper concerning the exp-6 potential system should be a sufficient warning.

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APPENDIX: SIMULATION DETAILS

We used the standard microcanonical ensemble with the periodic boundary conditions. The potential cutoff was one half of the box size, 2.266, for $N = 250$ and 2.81 for

$N = 800$; the potential was smoothed close to the cutoff. The Newton equations of motion were integrated by the four value Gear predictor-corrector method; since this method is not time reversible, the energy exhibits a tiny systematic drift which was corrected by velocity rescaling. The time step was 0.001–0.00125 of reduced time units (a reduced time unit is 1.91 ps for CO_2). The equilibration was monitored using the convergence profile and typically required a few time units. The productive run was at least 10 time units long; only if a phase transition occurred, the averages had to be calculated separately from shorter portions of the run. One MD step for $N = 250$ required 0.8–0.9s of CPU time on a 486/33MHz PC. The measured data were statistically analyzed by a combined method using averaging in blocks of increasing lengths and calculation of the correlation time [7, 15].