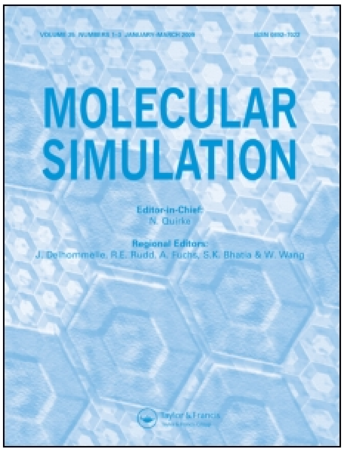
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

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

The Glass Transition in a Simple Model Glass: Numerical Simulations

P. Jund[a]; D. Caprion[a]; R. Jullien[a]
[a] Laboratoire des Verres, Université Montpellier, Montpellier, France

To cite this Article Jund, P. , Caprion, D. and Jullien, R.(1997) 'The Glass Transition in a Simple Model Glass: Numerical Simulations', Molecular Simulation, 20: 1, 3 — 15

To link to this Article: DOI: 10.1080/08927029708024164

URL: http://dx.doi.org/10.1080/08927029708024164

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1997, Vol. 20, pp. 3-15
Reprints available directly from the publisher
Photocopying permitted by license only

THE GLASS TRANSITION IN A SIMPLE MODEL GLASS: NUMERICAL SIMULATIONS

P. JUND, D. CAPRION and R. JULLIEN

Laboratoire des Verres - Université Montpellier 2, Place
E. Bataillon, Case 069, 34095 Montpellier, France

(Received October1996; Accepted November 1996)

In order to improve our understanding of the glass transition we performed constant-energy molecular dynamics simulations on a soft-sphere system quenched from the liquid state to zero temperature. The temperature dependence of static (radial pair distribution function) and dynamic quantities (self-diffusion constant) has been investigated together with the temperature evolution of relevant structural properties deduced from the Delaunay-Voronoi tessellation of these samples. This study permits to shed new light on the structural freezing below the glass transition temperature and the evolution of the local structure through the transition.

Keywords: Glass transition; soft-spheres; Delaunay-Voronoi tessellation

I. INTRODUCTION

Even though the glass transition is well defined and represents "a general phenomenon observed when a liquid is cooled beyond it's freezing temperature and does not crystallize" [1] its understanding still represents a scientific challenge. Together with experimental studies emphasis has been put on the theoretical study of this transition with basically two ways of tackling the problem: on the one hand the use of realistic interatomic potentials to reproduce the experimental results as closely as possible [2], on the other hand the use of simplified interactions to extract the general behavior of a system when it undergoes the glass transition [3]. Our work finds its place in the second approach since we use an inverse sixth power potential defined by Laird and Schober [4] to reproduce a model glass. We have chosen this potential rather than the commonly used Lennard-Jones interaction to avoid the crystallization effects which have been reported in earlier studies [5]. This choice can be discussed because of the purely repulsive character of this potential but it has been proven to be well suited to describe the vibrational spectrum of glasses at low temperatures [6]. The scope of this review is to present both standard results (obtained previously with the same potential) as well as original findings to give a comprehensive picture of part of our theoretical work on the glass transition.

All the results will be presented for an assembly of 1000 soft-spheres since no noticeable size effects have been detected. One of the major differences with previous work done with this potential is the way we prepared our glass samples which will be the topic of the following section together with computational details. Results regarding the pair distribution function and the self-diffusion constant will be given in Section III. We discuss the structural characteristics of the glass samples in Section IV. In Section V, we present our conclusions.

II. METHOD

We performed molecular dynamics simulations for systems of soft spheres interacting via the inverse sixth power potential defined by Laird and Schober [4]:

$$U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^6 + Ar^4 + B \tag{1}$$

To simplify the simulations the potential was cut off at $r/\sigma = 3.0$ and A and B were chosen so that the potential and the force are zero at the cut off. Our simulations used $N = 1000$ atoms in a rigid cubic box of edge length L, with periodic boundary conditions (PBC) at a density such that $(N/L^3)\sigma^3 = 1$. In order to give some physical meaning to the simulations and to be able to give the temperatures in Kelvin we have chosen $\sigma = 3.405$ Å and $\varepsilon = 0.0103$ eV, which are the Lennard-Jones values of Argon [7] (of course we do not pretend to simulate *real* Argon!). Similarly we took the atomic mass of Argon ($m = 40$ amu) and consequently we used a time step $\Delta t = 0.004\tau = 10^{-2}$ ps to integrate the equations of motion using the fourth order Runge-Kutta algorithm ($\tau = (m\sigma^2/\varepsilon)^{1/2}$ is the standard Lennard-Jones unit of time).

The glass configurations were obtained by quenching a well equilibrated initial liquid sample obtained by melting a simple cubic crystal at a temperature of about 50 K, well above the melting temperature which is about

23 K at this density [8]. After full equilibration of the liquid the system was cooled down to zero temperature at a quench rate of 10^{12} K/s which was obtained by removing $\Delta E = 8.6\ 10^{-7}$eV from the total energy of the system at each iteration.

At several temperatures during the quenching process the configurations (positions and velocities) were saved. Each configuration was used to start a constant-energy molecular dynamics calculation during which the temperature was recorded as a function of time. In all cases, we have observed a relaxation process typical of such a system [9] during which a slight increase of the temperature was observed before a saturation regime was taking place. As shown in Figure 1, we found that typically 10000 iterations (i.e. 100 ps) were enough to insure a well defined constant temperature for each sample. After these 10000 relaxation steps we have started to calculate all the physical quantities reported below which have been monitored during 20000 additional steps. It is worth mentioning that during the total run time of 30000 steps (= 300 ps) we have never observed, in all our 1000-particles samples, any anomalous increase of the temperature associated

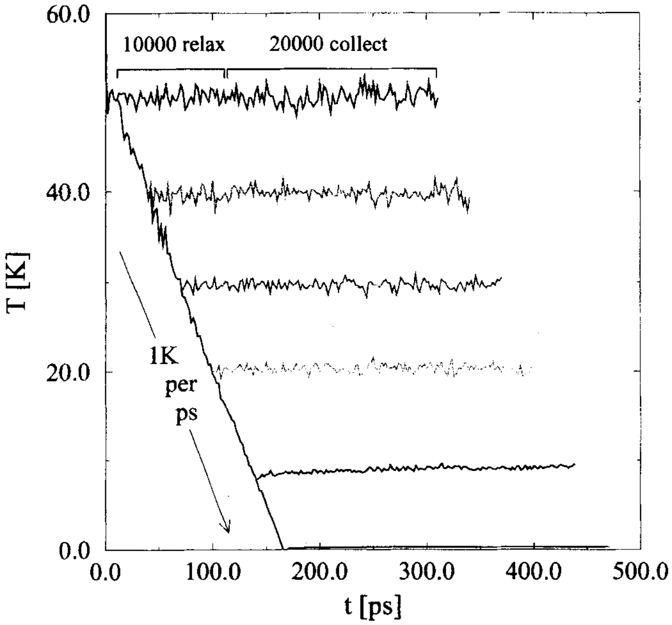


FIGURE 1 Time evaluatio fo the temperature during the quenchign process at 50 K (red), 40 K (orango), 30 K (green), 20 K (light blue, 10 K (purple) and 0 K (deep blue) (See Color Plate).

with crystal nucleation [5]. This quenching technique and the fact that configurations were saved all along enable us to study the characteristics of our system as a function of temperature contrarily to what has been done before. This study of relevant physical quantities versus the temperature will be presented in the following sections.

III. STANDARD RESULTS

The aim of our study is to detect the glass transition in a model system through the change of behavior of well chosen physical quantities. Therefore we studied both the static and the dynamic properties of the system defined earlier.

A. Static Properties

Since an important amount of structural information is contained in the Pair Distribution Function (PDF) $g(r)$ (obtained experimentally from radiation diffraction techniques [10]) we calculated the average $g(r)$ as a function of temperature (it should be noted that this quantity is very accurately determined, the error being less than 0.5%). As an example the PDFs as a function of system temperature are represented in Figure 2a as well as their Fourier transforms corresponding to the structure factor $S(q)$ in Figure 2b. As expected at low temperature ($T < 5$ K) the second peak splits, indicating an amorphous atomic packing [11]. Nevertheless $S(q)$ presents a sharp maximum at $q_m\sigma \approx 7.5$. The apparent and unphysical shrinking of the nearest neighbor distances with increasing temperature is simply an artifact due to the purely repulsive character of our potential. Following the earlier work of Wendt *et al.* [12] we reproduce in Figure 2c the ratio $R = g_{\min}/g_{\max}$, where $g_{\max}$ and $g_{\min}$ are the magnitudes of the first maximum and first minimum of the PDF, as a function of temperature. These authors argued that two linear branches corresponding to the liquid and amorphous states are present in the function $R = f(T)$, their intersection defining the glass transition temperature T_g. As shown in Figure 2c this clear distinction between the liquid and glassy states is not visible in our simulations. Moreover we found no size effect in the determination of R indicating that this quantity is probably not a good and reliable criterion to define the glass transition temperature. Nevertheless a small bump is visible in the curve $R = f(T)$ around T_g ($T_g \approx 10.3$ K for our system [13] but it is worth mentioning that this bump exists only if one lets

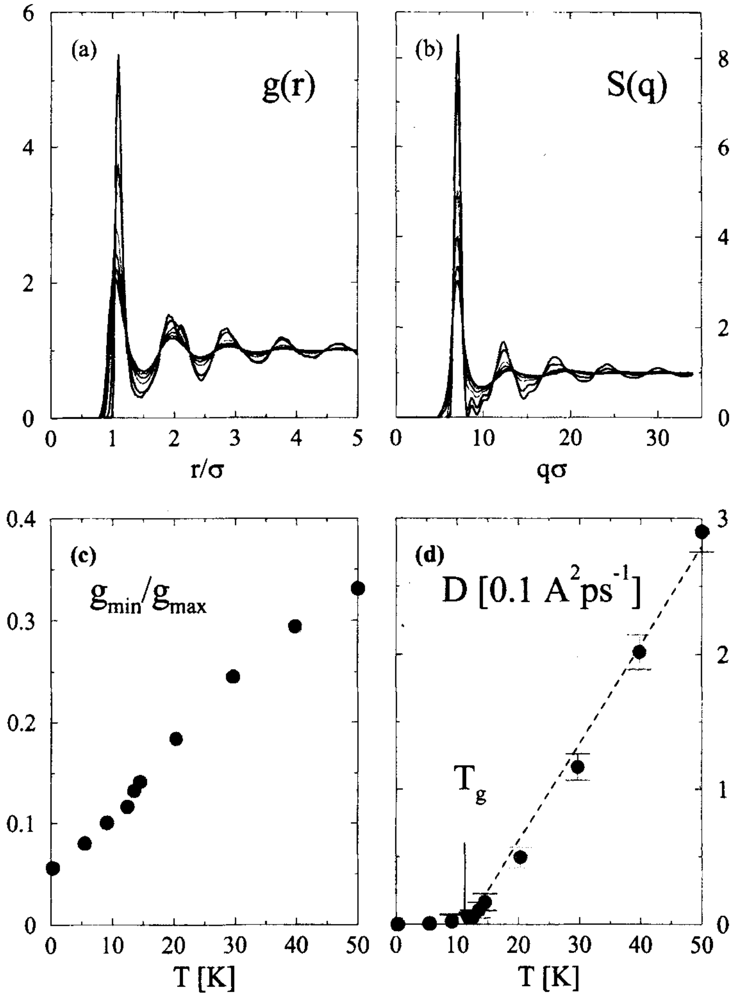


FIGURE 2 Standard quantities: (same color code as in Fig. 1
a) Pair distribution function
b) Structure factor
c) Empirical criterion $R = g_{\min}/g_{\max}$ versus temperature
d) Self diffusion constant D as a function of temperature (See Color Plate).

the system relax long enough (more than 5000 time steps). To get a better estimate of T_g we calculated the self diffusion constant which is supposed to be a good indicator of the glass transition.

B. Dynamic Properties

An estimate of the glass transition temperature was obtained by calculating the diffusion constant D as a function of temperature using the relation

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle | \vec{r}(0) - \vec{r}(t) |^2 \rangle \tag{2}$$

where $\vec{r}(t)$ is the time dependent position vector of a particle and $\langle \cdots \rangle$ denotes a configurational average.

As shown in Figure 2d, D follows the relation $D = C(T - T_g)$ for $T \geqslant 12$ K and tends to zero for $T < 10$ K (even when taking into account the relative error shown in the figure). The extrapolated value of T_g (≈ 10.5 K) can be taken as a lower limit for the glass transition temperature, since below T_g diffusive motion tends to be frozen out. This value of T_g is consistent with previous results and permits us to be confident in the generation of our glass samples which will be used in more original studies.

IV. STRUCTURAL PROPERTIES OF GLASSES

This section is dedicated to the results obtained in recent work which has been undertaken to tackle the difficult problem of the structure evolution through the glass transition [14]. To study this transition at a local level we combined the molecular dynamics scheme described in Section I and the so-called "Voronoi-Delaunay tessellation" which has been originally introduced to analyze random close packings of spheres [15–17]. The Voronoi cell is the extension of the Wigner-Seitz cell for a disordered structure: it is defined as the ensemble of points closer to a given atom than to any other and it is characteristic of the local environment around this atom. The first step in the tessellation process is to determine the Delaunay tetrahedral simplicial cells for a given configuration. These cells are among all the tetrahedra formed with four atomic centers the ones such that no other atomic center lies inside their circumscribed spheres. This part is the most computer time demanding but our algorithm which takes care of the PBC is efficient enough to be included inside the molecular dynamics code. As an input one has to provide a cut-off distance which is supposed to be larger than the longest edge of all the simplicial tetrahedra. If this is not the case, the basic requirement, namely that the sum of the volumes of all the simplicial tetrahedra is equal to the volume of the simulation box, is not fulfilled and the algorithm has to be ran again with a new and larger cut-off. Once the simplicial tetrahedra are obtained, the Voronoi cell of a given atom is determined knowing that its vertices are the centers of the circumspherical spheres of all the simplicial tetrahedra sharing this atom. We have checked that the cell vertices have always three edges in common, as expected in random structures. This leads to relations between the total number of edges E, the total number of vertices V and the total number of faces F which have all been verified by our numerical results. For example $2E=3V$ or with the help of the Euler formula ($V-E+F=2$ [18, 19]), $F=2+V/2=2+E/3$. Another formula, $\langle F\rangle=12/(6-\langle e\rangle)$, has been verified. It relates the mean number of faces $\langle F\rangle$, also called coordination number z, to the mean number of edges per face $\langle e\rangle$ [19]. Not only V, E and F and their mean over the N atoms have been calculated but also, the volume v of each cell, its total area s, as well as their statistical distributions over the N atoms. Since all the Voronoi cell statistics were found to be time independent after the relaxation period of 10000 time steps, the mean quantities were also averaged over different time intervals.

In Figure 3 we show the temperature variation of the coordination number $z=\langle F\rangle$ calculated on the *instantaneous* positions, which can be

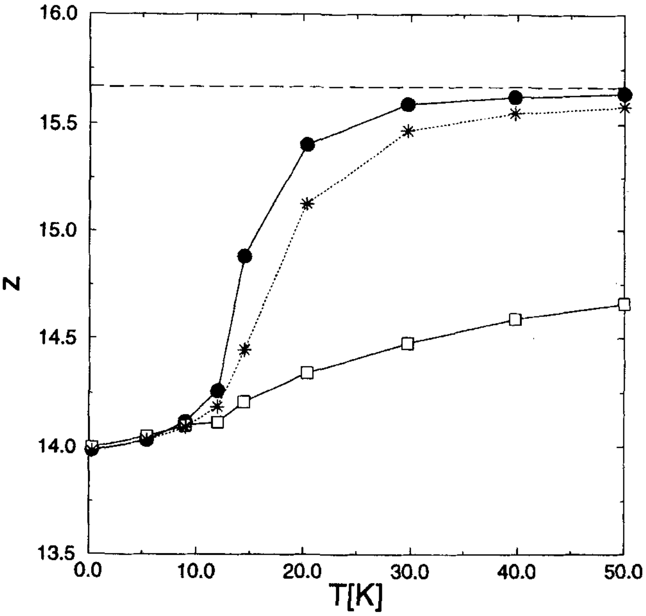


FIGURE 3 Coordination number $z=\langle F\rangle$ as a function of temperature □: instantaneour position; ★: mean position after 10000 iterations: ★: mean positions after 20000 iterations (the dashed line indicates z for a random packing).

identified as a measure of the intensity of disorder [18, 19]. For an ideal icosahedral structure with dodecahedral Voronoi cells, one should find the minimum value $z = 12$, but it is known that such a value cannot be realized in our standard three-dimensional space, due to the geometrical frustration of the five fold symmetry [18, 19]. Therefore here we find a value close to 14 at zero temperature, typical of quite a large disorder. The coordination number is increasing with temperature, as a consequence of thermally induced disorder and only a change of slope is observed when crossing T_g. To characterize better the glass transition we have also performed the Voronoi tessellation on the *averaged* positions of the atoms obtained after either 10000 or 20000 iterations after the initial relaxation period. For $T < T_g$ these $z(T)$ curves are nicely almost superimposed with the preceding ones, because the atoms are all vibrating around their fixed mean positions. On the contrary, for $T > T_g$, the curves corresponding to the averaged positions are strongly different from the ones corresponding to the instantaneous positions. This is a manifestation of the absence of long range correlations in the liquid phase due to atomic diffusion. As a comparison, we have depicted by the dashed horizontal line what would be the value of the coordination number for a perfect disorder, i.e. for the same number of points randomly packed inside the simulation box. These results indicate that for an infinite amount of simulation time the curve $z(T)$ corresponding to the averaged positions would be a perfect step function located at T_g.

In Figures 4 and 5, we report on the cell-volume and cell-surface distribution functions (in reduced units $\sigma = 1$) h_v and h_s, respectively, defined such that $h_v(v)dv$ is the fraction of cells having a volume lying between v and $v + dv$ and similarly for $h_s(s)$. With decreasing temperature, the distribution h_v becomes more and more peaked around the mean atomic volume, which is here precisely equal to 1, due to our particular choice of the density. A quantity of physical interest (shown in the inset of Fig. 4) is the standard deviation σ_v of this distribution since it measures the amplitude of the local density fluctuations. While σ_v is varying like $\sqrt{T}$ in the liquid phase, as is expected for classical thermally activated density fluctuations, this variation is slower in the glass phase, and, as T vanishes, σ_v tends to a non-zero value, characteristic of spatial disorder. Such a low temperature saturation of the density fluctuations is a signature of the glass transition [10, 20]. The same qualitative behavior is found for h_s, except that, now the mean surface $\langle s \rangle$ (close to the location of the maximum) is slowly varying with temperature. This variation is shown in the inset of Figure 5. For comparison, the surface s_d of the regular dodecahedron of volume 1 is indicated by the full square. The data can be interpreted as if, when decreasing the temperature from the

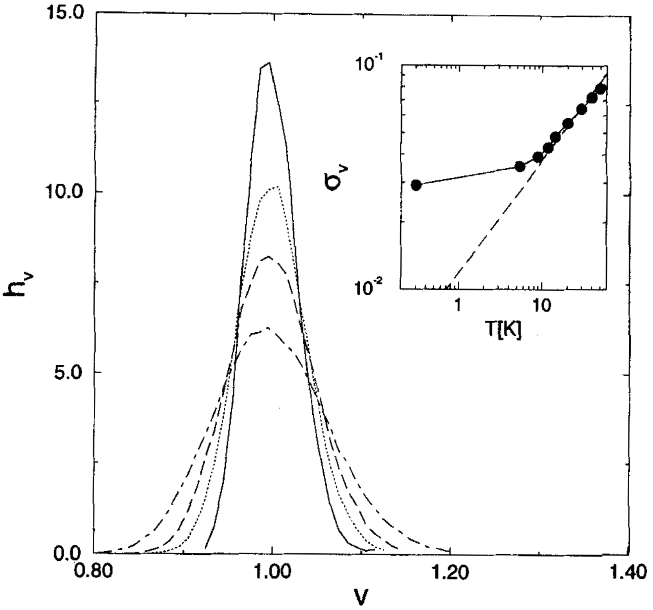


FIGURE 4 Cell volume distribution function:
Solid line 0.3 K; dotted line 9 K; dashed line: 14.5 K; dot-dashed line: 29.7 K.
Inset: Standard deviation σ_v as a function of temperature (the dashed line indicates a $T^{1/2}$ behaviour).

liquid phase, the mean surface would try to reach the one of the dodecahedron, but, since it is impossible to fill the space with dodecahedra only, a glass transition takes place and below T_g the mean surface saturates towards a value higher than s_d as T goes to zero.

We decided to analyze more precisely the deviations of the shell shapes from a regular dodechahedron. Therefore we calculated the fractions f_e's of cell faces having a given number e of edges ($e \geqslant 3$). Only the quantities f_4, f_5 and f_6 have been reported as a function of temperature in Figure 6, the other contributions being very small. In the geometrical approach [18, 19], a non-pentagonal face corresponds to a "defect" (compared to perfect icosahedral order) and the corresponding face encircles a segment of "disclination line". Consequently it is interesting to note that the proportion of pentagons is larger than the one ($\simeq 41.4\%$ [21]) of the most compact random packing of hard spheres (Bernal's packing [15]) as if the presence of a soft potential favors five fold order. On the other hand the large number of negative ($e > 5$) disclination lines is due to the lack of curvature of the regular three dimensional space (one needs a little *more* than five regular tetrahedra to fill the space around a common edge).

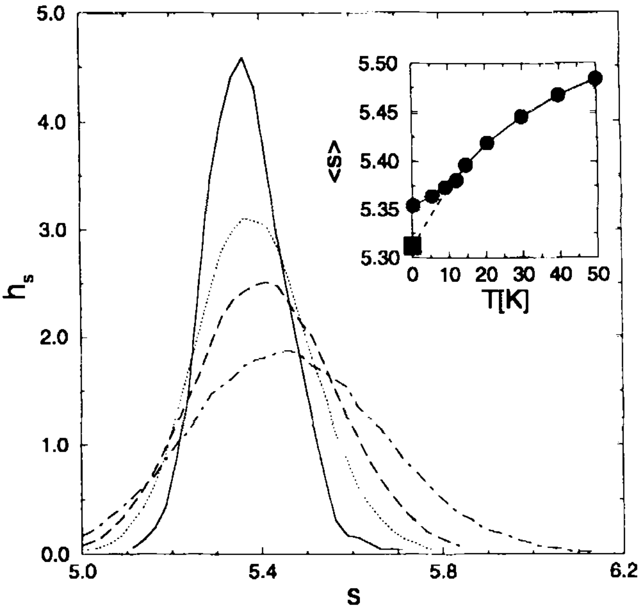


FIGURE 5 Cell surface distribution function:
Solid line 0.3 K; dotted line 9 K; dashed line: 14.5 K; dot-dashed line: 29.7 K.
Inset: mean surface $\langle s \rangle$ as a function of temperature (the full square indicates the surface of a perfect dodecahedron of volume 1; the dashed line is a guide to the eye).

In the liquid phase the f_e's are smoothly and monotonically varying with temperature, converging very slowly towards the values obtained for a random packing (indicated by the arrows) which would be reached for very large temperatures. Around the glass transition temperature a large discontinuity occurs, f_5 dropping sharply while f_4 and f_6 increase drastically. Upon further cooling this trend is reversed and the system recovers it's dodecahedral ordering, f_5 approaching finally 45% when T goes to zero. The origin of this discontinuity remains for now uncertain: is it an intrinsic signature of the glass transition or is it due to crystallization effects which were not noticeable in other physical quantities ? The fact is that the usual signatures of crystallization (sudden increase of the temperature, sharp peaks in the pair distribution function or the structure factor) do not indicate even a partial crystallization of our systems. Therefore if crystallization does indeed occur it would mean that the f_e's are very sensitive indicators for this phenomenon.

If this discontinuity is intrinsic to the glass transition it would mean that the competition between local and long range correlations would be one of the causes of the transition. The loss of long range correlations in the liquid

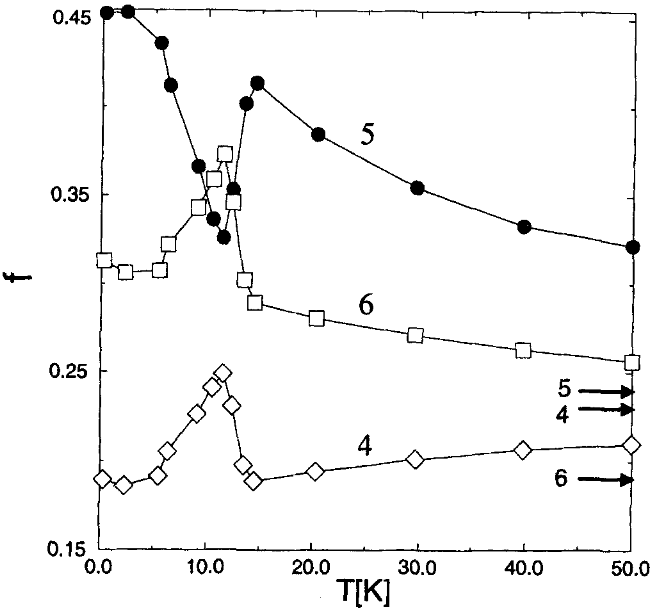


FIGURE 6 Fraction f_v of cell faces having a given number e of edges as a functio of temperature: ◇: $e = 4$; ●: $e = 5$; □: $e = 6$ (the arrows indicate the f_v's for a random packing).

phase (simply due to atomic diffusion) would then be compensated by an increase of the local order (shown by the increase of pentagonal faces), the transition occurring when a given rate of disorder is reached in the system.

To test which explanation is correct, one has to look in closer detail at the structures for which f_5 is very small. Moreover, even if 300 ps represents a tremendous amount of simulation time, it might be necessary to go further and monitor the evolution of the f_e's as a function of time. This is what we intend to do in the near future.

V. CONCLUSIONS

We have presented and discussed the results of a detailed molecular dynamics investigation of the glass transition in a model system. Our aim was first to confront our results with previous studies done with the same potential on glassy systems. In Section II we showed that, concerning the "standard" quantities such as the pair distribution function, the structure factor or the diffusion constant our results are in perfect agreement with the work already done.

In a second step we have combined molecular dynamics and geometrical analysis. The Voronoi tessellation of a 1000-particle system during the simulation has permitted to get a better insight on the evolution of the *local* structure during the glass transition. Our results on the volume and the surface of the Voronoi cells have shown that the transition is reflected in a gel of local density fluctuations below T_g. Upon cooling of the liquid phase the system behaves as if it would like to reach the perfect dodecahedron arrangement. In agreement with a recent theory [22], the glass transition would then occur because the three dimensional space cannot be filled with perfect dodecahedra only.

Moreover a closer analysis of the shape of the Voronoi cells (namely the number of edges of a given face) as a function of temperature has shown a discontinuity around T_g. This quantity appears as a very good tool to investigate precisely the local structure of disordered systems. Nevertheless further investigations are currently under way to see if this discontinuity is an intrinsic signature of the glass transition or if a "hidden" crystallization has taken place in our samples, even though no evidence of that kind of behavior has been found in the usual physical quantities.

Acknowledgements

We would like to thank C. Alba-Simionesco, A. Fuchs and R. Vacher for giving us the opportunity to review part of our work on glasses so far. Part of the numerical calculations were done at CNUSC (Centre National Universitaire Sud de Calcul), Montpellier.

References

[1] Barrat, J. L. and Klein, M. L. (1991). "Molecular dynamics simulations of supercooled liquids near the glass transition", *Annu. Rev. Phys. Chem.*, **42**, 23.

[2] Soules, T. F. (1979). "A molecular dynamic calculation of the structure of sodium silicate glasses", *J. Chem. Phys.*, **71**, 4570; Feuston, B. P. and Garofalini, S. H. (1988). "Empirical three-body potential for vitreous silica", *J. Chem. Phys.*, **89**, 1; Tsuneyuki, S., Tsukada, M., Aoki, H. and Matsui, Y. (1988). "First-principles interatomic potential of silica applied to molecular dynamics", *Phys. Rev. Lett.*, **61**, 869; Jin, W., Vashishta, P., Kalia, R. K. and Rino, J. P. (1993). "Dynamic structure factor and vibrational properties of SiO2 glass", *Phys. Rev. B*, **48**, 9359.

[3] Abraham, F. F. (1980). "An isothermal-isobaric computer simulation of the supercooled-liquid/glass transition region: is the short range order in the amorphous solid fcc?", *J. Chem. Phys.*, **72**, 359; Roux, J. N., Barrat, J. L. and Hansen, J. P. (1989). "Dynamical diagnostics for the glass transition in soft-sphere alloys", *J. Phys. Condens. Matter*, **1**, 7171; Soules, T. F. (1990). "Computer simulation of glass structures", *J. Non-Cryst. Solids*, **123**, 48; Variyar, J. E., Kivelson, D. and Lynden-Bell, R. M. (1992). "Velocity autocorrelation functions of particles and clusters in liquids. A possible criterion for

correlation length of incipient glass formation", *J. Chem. Phys.*, **97**, 8549; Della Valle, R. G. and Andersen, H. C. (1992). "Molecular dynamics simulation of silica liquid and glass", *J. Chem. Phys.*, **97**, 2682; Delaye, J. M. and Limoge, Y. (1993). "Simulation of vacancies in a Lennard-Jones glass", *J. Non-Cryst. Solids*, **156**, 982; Binder, K. (1994). "Monte Carlo simulation of the glass transition of polymer melts", *Prog. Colloid. Polym. Sci.*, **96**, 7; Bembenek, S. D. and Laird, B. B. (1995). "Instantaneous normal modes and the glass transition", *Phys. Rev. Lett.*, **74**, 936.

[4] Laird, B. and Schober, H. (1991). "Localized low-frequency vibrational modes in a simple model glass", *Phys. Rev. Lett.*, **66**, 636.

[5] Hsu, H. C. and Rahman, A. (1979). "Interaction potentials and their effect on crystal nucleation and symmetry", *J. Chem. Phys.*, **71**, 4974; Nosé, S. and Yonezawa, F. (1979). "Isothermal-isobaric computer simulations of melting and crystallization of a Lennard-Jones system", *J. Chem. Phys.*, **84**, 1803; Honeycutt, J. D. and Andersen, H. C. (1987). "Molecular dynamics study of melting and freezing of small Lennard-Jones clusters", *J. Phys. Chem.*, **91**, 4950.

[6] Caprion, D., Jund, P. and Jullien, R. (1996). "Phonons in glasses: numerical simulations and phenomenological theory", *Phys. Rev. Lett.*, **77**, 675.

[7] Gazzillo, D. and Della Valle, R. G. (1993). "An improved representation for the high-density structure of Lennard-Jones systems: from liquid toward glass", *J. Chem. Phys.*, **99**, 6915.

[8] Hoover, W. G., Young, D. A. and Grover, R. (1972). "Thermodynamic properties of the fluid and solid phases for inverse power potentials", *J. Chem. Phys.*, **56**, 2207.

[9] Steinhardt, P. J., Nelson, D. R. and Ronchetti, M. (1983). "Bond-orientational order in liquids and glasses", *Phys. Rev. B*, **28**, 784.

[10] *Gaskell, P. H. (1991). in "Materials Science and Technology"*, **9**, 175 (ed. Cahn, R. W., Hassen, P. and Kramer, E. J.); Rahman, A., Mandell, M. J. and McTague, J. P. (1976). "Molecular dynamics study of an amorphous Lennard-Jones system at low temperature", *J. Chem. Phys.*, **64**, 1564; Waseda, Y., Okazaki, H. and Masumoto, T. (1977). "Current views on the structure and crystallization of metallic glasses", *J. Mater. Sci.*, **12**, 1927.

[11] Finnery, J. (1977). "Modelling the structures of amorphous metals and alloys", *Nature*, **266**, 309.

[12] Wendt, H. R. and Abraham, F. F. (1978). "Empirical criterion for the glass transition region based on Monte Carlo simulations", *Phys. Rev. Lett.*, **41**, 1244.

[13] Schober, H. R. and Laird, B. B. (1991). "Localized low-frequency vibrational modes in glasses", *Phys. Rev. B*, **44**, 6746.

[14] Jund, P., Caprion, D. and Jullien, R. (1997). "Local investigation of the glass transition: molecular dynamics and Voronoi tessellation", *Europhys, Lett.*, **19**, 4106.

[15] Bernal, J. (1964). "The structure of liquids", *Proc. Roy. Soc.*, **A 280**, 299.

[16] Finney, J. "Local structure of disordered hard sphere packings" in *Disorder and granular medai*, p. 35, ed. by Bideau, D. and Hansen, A. (Elsevier Science Publisher, NorthHolland, 1993).

[17] Hoare, M. R. (1978). "Packing models and structural specificity", *J. Non-Cryst. Solids*, **31**, 157.

[18] Sadoc, F. and Mosseri, R. "Icosahedral order, curved space and quasicrystals" in *Aperiodidicity and order 3, Extended icosahedral structures*, p. 163 (Academic Press, New York, 1989); Mosseri, R. and Sadoc, J. F. "Non-crystalline atomic structures: from glasses to quasi-crystal" in *Geometry in condensed matter physics, Directions in Condensed Matter Physics*, **9**, 239, ed. by Sadoc, J. F. (World Scientific, Singapore, 1995).

[19] Rivier, N. "Order and disorder in packings and froths" in *Disorder and granular media*, p. 55, ed. by Bideau, D. and Hansen, A. (Elsevier Science Publishers, North Holland, 1993).

[20] Cusak, N. E. *The Physics of structurally disordered matter: an introduction* (Adam Hilger, Bristol and Philadelphia, 1987)

[21] Jullien, R., Jund, P., Caprion, D. and Quitmann, D. (1996). "Computer investigation of long-range correlations and local order in random packings of spheres", *Phys. Rev., E*, **54**, 6035.

[22] Kivelson, D., Kivelson, S. A., Zhao, X., Nussimov, Z. and Tarjus, G. (1995). "A thermodynamic theory of supercooled liquids", *Physica*, **A21**, 27.