Is There an Ideal Quenching Rate for an Ideal Glass?

Philippe Jund, Didier Caprion, and Rémi Jullien
Laboratoire des Verres, Université Montpellier 2, Place E. Bataillon Case 069, 34095 Montpellier, France

(Received 27 March 1997)

Using classical molecular dynamics simulations combined with the Voronoï tessellation we study, at very low temperature, the local structure in a model glass as a function of the quenching rate and the relaxation time. The critical quenching rate below which crystallization effects become important is detected by the geometrical analysis. In fact we show that this rate can be viewed as an *ideal* cooling rate since the study as a function of the aging time reveals a maximum stability of the glass structures quenched at that rate. [S0031-9007(97)03499-6]

PACS numbers: 61.43.Fs, 61.43.Bn, 81.40.Gh

In the past several years, with the help of computer modeling and the rapid increase of the computing speed, a great body of work has been dedicated to the study of the relaxation effects in glasses. The investigation of these effects demands a tremendous amount of computer time and only parallel computing has permitted one to achieve longer aging times or lower quenching rates of the samples. These studies have shown that for both model systems [1] or more realistic systems [2], properties like the glass density or the glass transition temperature depend on the cooling rate. However, this dependence is shown to be small; therefore a large range of cooling rates has to be explored. Of course the knowledge of the "critical" cooling rate below which crystallization effects become dominant is crucial in the study of amorphous systems in order to have reliable results. In computer simulations one way of determination of this critical rate is the use of the Voronoï tessellation which has been widely used to study the "structure" of various liquid or amorphous states [3–5]. The Voronoï cell is an extension of the Wigner-Seitz cell for disordered systems and gives information on the local structure around every single particle of the system.

In this study we present the results of a classical molecular dynamics simulation performed on a model soft-sphere glass. We focus on the influence of the quenching rate and the subsequent relaxation time on the local structure of the samples. Similarly to what has been done in a Lennard-Jones system [4] or in liquid sodium [5] we detect through the Voronoï cell statistics, the critical cooling rate below which crystallization takes place. Furthermore the study of the evolution of the local structure in the glass phase as a function of the aging time shows a tendency towards crystallization which *increases* with increasing cooling rates while this tendency is quasi-inexistent for the glass samples quenched with the critical cooling rate. Therefore we suggest that for a given glass, there exists an ideal quenching rate for which the structural stability is stronger than for the same glass quenched differently. In an attempt to explain this behavior we analyze the local volume fluctuations as a function of the quenching rate. With increasing rates these fluctuations increase (especially when they are measured just after the quench) and therefore crystal "germs" are more likely to exist in the glass samples. This may explain why a stronger tendency towards crystallization is observed at high quenching rates.

We perform molecular dynamics simulations on microcanonical systems of $N = 1000$ soft spheres interacting via the inverse sixth power potential defined by Laird and Schober [6]:

$$U(r) = \epsilon\left(\frac{\sigma}{r}\right)^6 + Ar^4 + B\,. \qquad (1)$$

To simplify the simulations the potential is cut off at $r/\sigma = 3.0$ and A and B are chosen so that the potential and the force are equal to zero at the cutoff. Similarly to previous calculations [7] we use a rigid cubic box of edge length L, with periodic boundary conditions at a constant density $(N/L^3)\sigma^3 = 1$. The equations of motion are integrated using the fourth order Runge-Kutta algorithm with a time step $\Delta t = 10$ fs. The values of Lennard-Jones argon are chosen for ϵ, σ and the mass of the particles in order to give results in conventional units (of course no attempt is made to simulate real argon). The low temperature configurations are obtained by quenching well equilibrated initial liquid samples at about 50 K (well above the melting temperature which is about 23 K [8]). After full equilibration, these liquid samples are cooled down to $T = 0$ K at quenching rates equal to 10^{13}, 7.5×10^{12}, 5.0×10^{12}, 2.5×10^{12}, 10^{12}, 7.5×10^{11}, 2.5×10^{11}, and 10^{11} K/s by removing the corresponding amount of energy from the total energy of the system at each iteration. After the quench the samples are relaxed during 60 000 time steps and simultaneously the Voronoï tessellation is performed using an efficient algorithm which has been detailed elsewhere [9]. This permits us to follow the evolution of the local structure during the aging process through the characteristics of the Voronoï cells. A good indicator of the degree of randomness (or on the other hand the degree of crystallization) is the fraction f_5 of pentagonal cell faces: in a soft sphere system a large value of f_5 is a sign of strong icosahedral local order characteristic of a glass phase, while on the contrary crystal nucleation is shown by a small value of f_5. All the other cell characteristics (surface, volume, length of the edges, number of faces) have been calculated as well but since they all give basically the same kind of information here we focus on the evolution of f_5 and the standard deviation σ_v of the cell-volume distribution which describes the local density fluctuations. Finally in order to improve the statistics of the results we use ten independent high temperature samples for each quenching rate for a total simulation time of five million time steps which were run on an IBM/SP2 parallel computer.

In Fig. 1 the time evolution of f_5 for one sample quenched at 10^{13} K/s (which is the fastest rate considered in this study), is represented. As can be seen, just after the quench the value of f_5 is relatively large and corresponds to nearly 50% of all the cell faces. This is typical of an amorphous state as illustrated in Fig. 2(a) which is a snapshot of the structure at the beginning of the relaxation period. With increasing time f_5 decreases sharply after 23 000 time steps and finally oscillates around 0.1 which means that approximately 10% only of the cell faces have five edges. This is typical of crystallized or partially crystallized systems. The crystalline character of this particular sample can be verified in Fig. 2(b) which is a snapshot of the structure after 35 000 time steps: the crystallographic planes can be clearly seen in this figure. This result shows that f_5 is an excellent and very sensitive tool to measure the local order and/or disorder of our samples.

The curve at the top of Fig. 3 represents the variation of f_5 as a function of the quenching rate directly after the quench (only 4000 relaxation steps have been allowed). It is important to note that these values have been obtained by averaging over ten samples. For quenching rates between 10^{13} and 10^{12} K/s the quantity f_5 is approximately constant around 0.45, a value typical of a glassy state. Below 10^{12} K/s it drops tremendously which is the signature of crystallization. This shows that the critical cooling rate which separates the crystal-forming rates and the glass-forming rates is around 10^{12} K/s for our model glass. This value is comparable to the one found previously in Lennard-Jones argon [4]. Once this critical cooling rate has been determined a problem of interest is the evolution of the glass samples as a function of the relaxation time after the quench. The results are reported in Fig. 3 for five different aging times: 4000, 8000, 15 000, 35 000, and 60 000 time steps. Of course for the quenching rates below the critical rate (for which most of the samples have already crystallized after the quench) the decrease of f_5 during the relaxation period must be very small which is indeed the case. The results obtained for faster quenching rates (between 10^{12} and 10^{13} K/s), i.e., in the glass-forming range, are more surprising: it appears that the faster the rate, the higher the propensity to crystallize with increasing aging time. Indeed, for example, at 10^{13} K/s six samples have crystallized after 60 000 time steps while only three have crystallized at 5.0×10^{12} K/s. Eventually after an infinite amount of relaxation time all the systems will crystallize but the results reported in Fig. 3 show that the samples rapidly quenched crystallize faster than the ones cooled down more slowly. Even more it seems that this crystallization time exhibits a strong maximum (diverges?) for the samples quenched at the critical quenching rate since in the aging period studied here no sample quenched at 10^{12} K/s showed any sign of crystallization. If this result can be extrapolated to other glasses it means that for a given glass type, an ideal cooling rate exists for which the structural stability is much stronger than for the same glass quenched faster. Our results show that this *ideal* quenching rate is equal or close to the *critical* rate separating glass and crystal-forming quenching rates (of course in realistic glasses this ideal quenching rate is

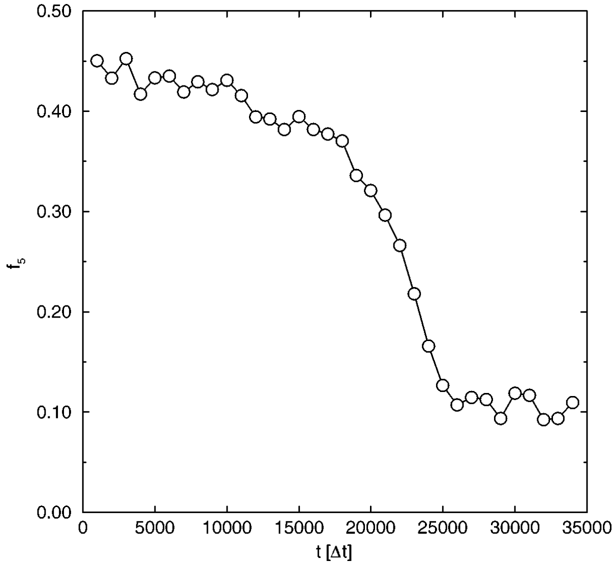

FIG. 1. Time evolution of the fraction of pentagonal faces, f_5, showing the crystallization of a sample quenched at 10^{13} K/sK/s.

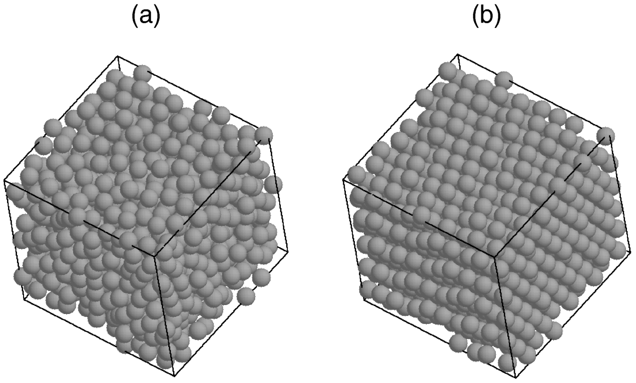

FIG. 2. (a) Snapshot of the structure directly after the quench (glass phase); (b) snapshot of the structure 35 000 time steps after the quench (crystal phase).

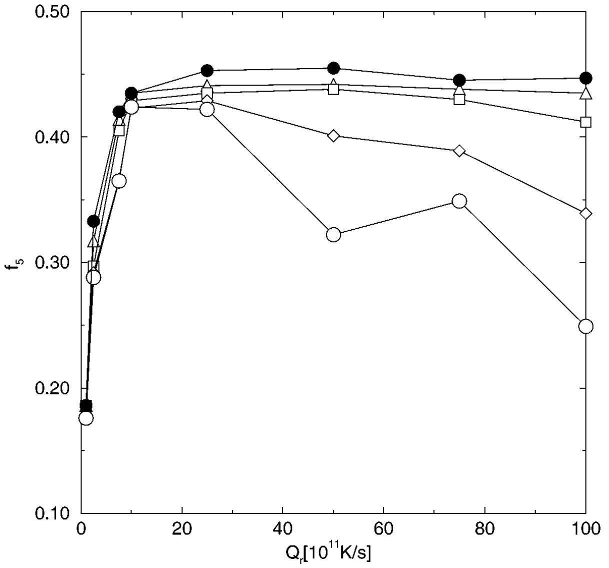

FIG. 3. f_5 as a function of the quenching rates after (●) 4000 time steps, (△) 8000 time steps, (□) 15 000 time steps, (◇) 35000 time steps, and (○) 60 000 time steps.

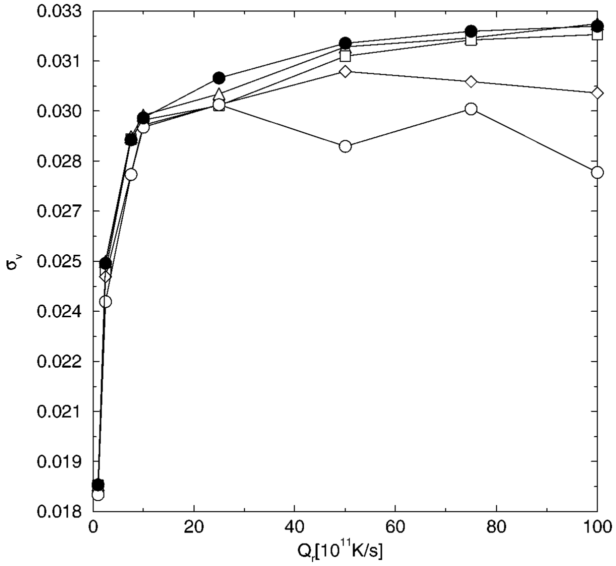

FIG. 4. Standard deviation σ_v of the cell-volume distribution as a function of the quenching rates after (●) 4000 time steps, (△) 8000 time steps, (□) 15 000 time steps, (◇) 35 000 time steps, and (○) 60000 time steps.

several orders of magnitude smaller than the one found in our model glass). On the other hand our results imply also that an ultrafast quench of a given glass leads to a lesser stability of its structure. Of course due to the relative limited number of samples studied at each quenching rate, statistical errors can bias the results reported in Fig. 3. This can be seen, for example, in the curve obtained after an aging of 60 000 time steps in which the decrease of f_5 with increasing quenching rates is not continuous. Nevertheless these statistical errors do not modify significantly the general results discussed above. In an attempt to understand the increased propensity towards crystallization with increasing quenching rate we report in Fig. 4 the variation of the standard deviation σ_v of the Voronoï cell-volume distribution as a function of the quenching rate for the different aging times (of course due to our particular choice of the density, the average cell volume is always equal to unity). This is a quantity of physical interest since it measures the amplitude of the local density fluctuations. As a general trend it follows the variation of f_5 shown in Fig. 3 which means that σ_v is also a good quantity to detect order (a small value of σ_v being a sign of crystallization) with one major difference: in the glass phase with increasing quenching rates σ_v increases while f_5 remains constant (this is particularly visible for small aging times). This is expected since the faster the quenching rate, the more the high local density fluctuations present in the liquid are frozen out in the amorphous state. Consequently if the views concerning crystal nucleation based on the growth of crystal germs [10] are correct it is coherent to think that the higher the local density fluctuations, the higher the probability of finding such germs. In other words, in the samples in which the volume distribution is more widespread, the probability of finding local arrangements close to the crystal one is higher. This could explain why the samples quenched faster (with a broader volume distribution) show a more pronounced tendency towards crystallization as time goes by. Of course this explanation is very rough since it does not take into account the ability of the existent germs to grow. Further investigations are needed to confirm this hypothesis.

In conclusion, in this Letter we have presented results concerning the evolution of the local structure in a model glass as a function of the quenching rate and the aging time. These results have been obtained from molecular dynamics simulations combined with the Voronoï tessellation. Using the Voronoï cell characteristics we have found the critical cooling rate separating glass forming and crystal forming rates to be around 10^{12} K/s. In the glass phase our results show that the crystallization rate increases with increasing quenching rates, while it is very small at 10^{12} K/s. This indicates that glasses quenched at the critical cooling rate have the highest structural stability. In that sense the critical rate can be viewed as an ideal rate. A confirmation of these results could come from experimental liquids cooled down with rates much larger than the critical quenching rate: the subsequent glass phases should evolve towards a crystalline state much faster than glasses obtained after “softer” quenches. This behavior is more likely to be observed in the so-called “fragile” glasses which are better described by our model system in which the barriers to atomic movements are small compared to the ones existing in the more common “strong” glasses.

Even though it seems that our results point towards the existence of an ideal quenching rate, its microscopic origin remains to be elucidated. Which characteristics of the glass structure drive its behavior? How does it depend on these characteristics? This will be the topic of further studies.

We thank J. Pelous for helpful discussions. Part of the numerical calculations were done at CNUSC (Centre National Universitaire Sud de Calcul), Montpellier.

[1] J.R. Fox and H.C. Andersen, J. Phys. Chem. **88**, 4019 (1984); H. Miyagawa and Y. Hiwatari, Phys. Rev. A **40**, 6007 (1989); S.K. Lai and M.S. Lin, J. Non-Cryst. Solids **117/118**, 907 (1990); K. Vollmayr, W. Kob, and K. Binder, Europhys. Lett. **32**, 715 (1995); K. Vollmayr, W. Kob, and K. Binder, J. Chem. Phys. **105**, 4714 (1996).

[2] J. Baschnagel, K. Binder, and H.P. Wittmann, J. Phys. Condens. Matter **5**, 1597 (1993); K. Vollmayr, W. Kob, and K. Binder, Phys. Rev. B **54**, 157 808 (1996).

[3] H.C. Hsu and A. Rahman, J. Chem. Phys. **71**, 4974 (1979); P.J. Steinhardt, D.R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983); V.P. Voloshin, N.N. Medvedev, and Y.I. Naberukhin, J. Struct. Chem. **26**, 376 (1985); H. Jónsson and H.C. Andersen, Phys. Rev. Lett. **60**, 2295 (1988); J.C. Gil Montoro and J.L.F. Abascal, J. Phys. Chem. **97**, 4211 (1993); P. Jund, D. Caprion, and R. Jullien, Europhys. Lett. **37**, 547 (1997).

[4] S. Nosé and F. Yonezawa, J. Chem. Phys. **84**, 1803 (1986).

[5] M.S. Watanabe and K. Tsumuraya, J. Chem. Phys. **87**, 4891 (1987).

[6] B. Laird and H. Schober, Phys. Rev. Lett. **66**, 636 (1991).

[7] D. Caprion, P. Jund, and R. Jullien, Phys. Rev. Lett. **77**, 675 (1996).

[8] W.G. Hoover, D.A. Young, and R. Grover, J. Chem. Phys. **56**, 2207 (1972).

[9] P. Jund, D. Caprion, and R. Jullien, Mol. Sim. (to be published).

[10] G.W. Scherer, in *Glasses and Amorphous Materials*, edited by R.W. Cahn, P. Haasen, and E.J. Kramer (VCH, Weinheim, 1991).