[6]L. Spitzer and R. Härm, Phys. Rev. 89, 977 (1953).
[7]F. L. Hinton and R. D. Hazeltine, Rev. Mod. Phys. 48, 239 (1976); see also N. K. Winsor, W. H. Miner, and I. B. Bernstein, in Proceedings of the Annual Control Fusion Theory Meeting, Gatlinburg, Tennessee, 26–28 April 1978 (unpublished).
[8]M. D. Kruskal and I. B. Bernstein, Princeton University Report No. MATT-Q-20, 1962 (unpublished).
[9]J. A. Krommes, R. G. Kleva, and C. Oberman, Princeton University Report No. PPPL-1389, 1978 (unpublished).
[10]K. Molvig and S. P. Hirshman, Massachusetts Institute of Technology Plasma Fusion Center Research Report No. PFC/RR-78-7 (unpublished).
[11]M. Gaudreau *et al.*, Phys. Rev. Lett. 39, 1266 (1977).
[12]J. D. Callen, private communication.

## Empirical Criterion for the Glass Transition Region Based on Monte Carlo Simulations

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We propose a new empirical criterion using the pair distribution function for specifying the supercooled-liquid/amorphous phase boundary.

Modeling techniques and computer simulations as applied to noncrystalline solids have developed into a very active and rewarding area of research, and generally seek to reproduce the salient features of the experimentally determined "pair distribution function" (hereafter designated PDF) obtained from radiation diffraction techniques.[1-3] Tools for the theoretical analysis of the amorphous state include hard- and soft-sphere packing,[1] molecular dynamics,[2] and, very recently,[4] the Monte Carlo method[5] for a canonical ensemble (temperature $T$, volume $V$, and number of atoms $N$ are fixed).

However, the onset of the glass transition region, as a function of *both* temperature and pressure, has heretofore not received significant attention. By employing the isothermal-isobaric Monte Carlo method of classical statistical mechanics,[1,2] we are presently investigating whether there exist unique, or distinctive, structural and thermodynamic features associated with the {supercooled-liquid $\rightarrow$ glass} transition region reached by abruptly cooling and/or compressing an equilibrated simple liquid.

The $(N, P, T)$ Monte Carlo procedure used in this study has been described by McDonald.[6] The interatomic force law was arbitrarily taken to be Lennard-Jones 12-6 with $(\epsilon, \sigma)$ denoting the well-depth and size parameters, respectively. In order to simulate the bulk, the standard periodic boundary conditions were imposed with respect to translations parallel to the faces of the computational cube composed of 108 atoms. In each simulation "experiment," we started with the last fluid configuration of a well-equilibrated fluid state at reduced temperature $T^* = kT/\epsilon = 1.0$ and reduced pressure $P^* = P\sigma^2/\epsilon = 1.0$. Then we abruptly quench and/or compress the system to a new $(P^*, T^*)$ by simply setting the pressure and temperature in the Monte Carlo procedure to the new desired values.[7] After "equilibrating" the system through $2\times10^5$ Monte Carlo moves with a 50% acceptance ratio, $6\times10^5$ further moves were performed to obtain the enthalpy $H$, the average density $\langle\rho\rangle$, the PDF $g(r)$, and other quantities. Experiments were simulated for constant $P^* = 1$ and various $0.1 \leq T^* < 1.0$, constant $T^* = 1.0$ and various $1 < P^* \leq 20$, and various combinations of $1 < P^* \leq 9$ and $0.6 \leq T^* < 1$.

As illustrated in Fig. 1, the PDF's generally show the features expected. In the supercooled-liquid state, two smooth peaks exist: a first prominent peak and a second smaller peak, corresponding to the first and second coordination shells of an atom in the liquid, respectively. As the instantaneous temperature quenches probe deeper into the metastable region, the first peak becomes more pronounced in magnitude and narrower in width, the first minimum decreases in magnitude, and the second peak gradually flattens in shape with an eventual "bimodal splitting" at very low temperatures ($P^* = 1.0$, $T^* \leq 0.4$). Clearly, the development of the split second peak indicates an amorphous atomic packing,[1-3] this being the principal structural feature in the experimental PDF of amorphous materials that previous theoretical models have attempted to describe. However, the second-peak flattening preceding the fully developed splitting may be the "signature" that the glass transition region has been reached.

The evident problem is to formulate a quantitative criterion for specifying the boundary between the supercooled-liquid region and the amorphous region. Kinetically, the dramatic change in viscosity has been identified as such a signature.[2] We now describe a *structural* feature of the PDF which suggests a quantitative criterion for identifying the amorphous phase. We define an empirical parameter

$$\mathcal{R} = g_{\min}/g_{\max}, \tag{1}$$

where $g_{\min}$ and $g_{\max}$ are the magnitudes of the first minimum and first maximum of the PDF. In Fig. 2, $\mathcal{R}$ is plotted versus the sequence of ($P^*$, $T^*$) states which were achieved by abruptly quenching, crunching, and crushing the ($P^*=1$, $T^*=1$) liquid state.[8] We make special note of the fact that the dependence of $\mathcal{R}$ over significant portions of the liquid branch and amorphous branch of the ($P^*$, $T^*$) state variables is linear, the slopes of the two branches are different, and linear extrapolation of the respective branches intersect at $\mathcal{R}_a \cong 0.14$ for all three cases. This value of $\mathcal{R}_a$ correlates reasonably well with the flattening of the second peak in the PDF. Therefore, *our criterion for the onset of the amorphous state by rapidly quenching and/or compressing a liquid is that the structure parameter $\mathcal{R}$ of the PDF [Eq. (1)] equals*

$$\mathcal{R}_a \cong 0.14. \tag{2}$$

A possible hypothesis for this striking feature is the packing saturation of the first shell of nearest neighbor atoms. Unfortunately, present statistics of the PDF's does not allow us to test this hypothesis or establish other trends. Experimental verification of our finding is presently being contemplated.[9]

We make a further important observation. Using this criterion and employing the Weeks-Chandler-Anderson liquid-state perturbation theory,[10] we have calculated the equivalent hard-sphere fluid packing fraction $\eta = \frac{1}{6}\pi\rho d^3$ of the supercooled liquid at the supercooled-liquid/amorphous phase boundary. We find for our three cases that $\eta_a$

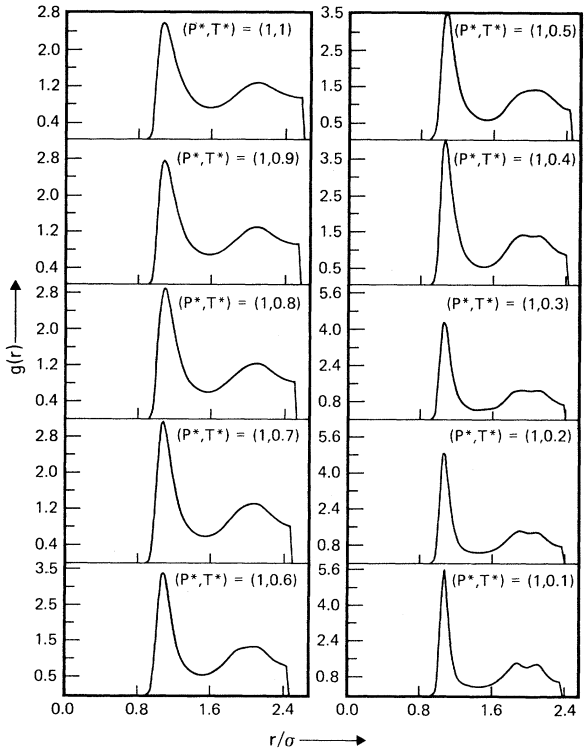


FIG. 1. The pair distribution function $g(r)$ as a function of radial distance $r$ for the sequence of temperature quenches ($P^*=1$, $T^*$) from ($P^*=1$, $T^*=1$).

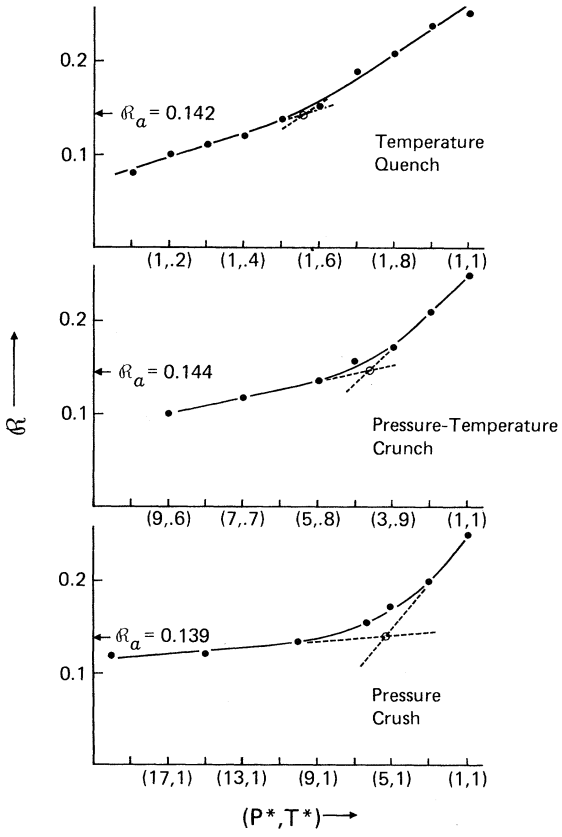


FIG. 2. The ratio of the PDF's first minimum to first maximum $\mathcal{R}$ as a function of the sequence of ($P^*$,$T^*$) states achieved by abruptly quenching, crunching, and crushing the ($P^*=1$, $T^*=1$) liquid state.

$=0.534-0.55$. Using $\eta_a$ and liquid-state perturbation theory, we may generate the phase boundary in the entire ($P^*$, $T^*$) plane for the Lennard-Jones 12-6 fluid *or another chosen fluid described by a different interatomic potential.*

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[1]J. L. Finney, Nature (London) 266, 309 (1977).
[2]A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. 64, 1564 (1976).
[3]Y. Waseda, H. Okazaki, and T. Masumoto, J. Mater. Sci. 12, 1927 (1977).
[4]F. F. Abraham, N.-H. Tsai, and G. M. Pound (to be published).
[5]W. W. Wood, in *Physics of Simple Fluids*, edited by H. N. V. Temperley, G. S. Rushbrooke, and J. S. Rowlinson (North-Holland, Amsterdam 1968), Chap. 5.
[6]I. R. McDonald, Mol. Phys. 23, 41 (1972).
[7]If we were to attempt to ascertain the effect of finite quench rates on the simulation results, we must use the molecular-dynamics simulation method. However, because of the short time available for a molecular-dynamics run ($\sim 10^{-10}$ sec), it would be presently impossible to simulate even the fastest laboratory quench rates ($\sim 10^{8}$ °C/sec). It is our opinion that the same general amorphous-structure features reported in this study exist at the laboratory quench rates.
[8]We thank J. A. Barker, IBM Research Laboratory, San Jose, for this novel terminology, in particular his observation that a crunch = crush + quench.
[9]A. Bienenstock, private communication.
[10]J. D. Weeks, D. Chandler, and H. C. Anderson, J. Chem. Phys. 54, 5237 (1971).

## Segregation Effects in Cu-Implanted Si after Laser-Pulse Melting

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Cu-implanted Si crystals were irradiated with $Q$-switched ruby-laser single pulses. After irradiation with energy density in excess of 1.0 J/cm$^2$, the Cu atoms accumulate at the sample surface. Thermal annealing in the 500–800°C range casues a migration of Cu inside the specimen, in agreement with diffusion coefficient and solid solubility values. The results indicate the formation of a liquid layer induced by laser irradiation. The solid-liquid interface movement during freezing qualitatively justifies the observed surface accumulation.

High-power laser pulses were used recently to anneal out the damage in ion-implanted semiconductors.[1-6] The transition of an amorphous layer to a single-crystal structure was ascribed to the laser-induced melting of the surface layer.[7,8] Liquid phase epitaxial growth on the underlying single-crystal substrate occurs during the subsequent freezing. Changes in the ion-implanted profiles were also accounted for by a liquid formation.[7] The time involved in the $Q$-switched laser irradiation ($\sim 10^{-7}$–$10^{-8}$ s) cannot in fact allow detectable atom migration in the solid phase with the usual activation energies.

These effects could be also interpreted in terms of ionization-enhanced diffusion.[9] The high density of absorbed photons with energy greater than the band gap produces a large amount of broken bonds between nearest-neighbor atoms or non-equilibrium hole-electron pairs which can enhance the mobility of a defect. The observed growth rates and impurity diffusion coefficients could be then described in terms of kinetic processes in a solid medium with suitable low values of the activation energies, without invoking any liquid formation.

In the present work we show that $Q$-switched ruby laser pulses with power densities higher than 20 MW/cm$^2$ and 50-ns duration induce liquid formation in ion-implanted Si.

Silicon single crystals, 300 $\mu$m thick and $\langle 100 \rangle$ oriented, were implanted at room temperature with 70-keV $Cu^+$ to a fluence $2 \times 10^{15}$ ions/cm$^2$. After implantation some samples were irradiated with pulsing ruby laser ($\lambda = 0.694$ $\mu$m) in the energy density range between 1.0 and 3.0 J/cm$^2$. Other samples were thermally annealed, under vacuum condition ($\sim 10^{-5}$ Torr), in the temperature range 500–850°C for isochronal steps of 30 min. MeV He particles scattered at 102° away from the beam incidence were used to analyze in depth the Cu distribution. The energy-to-depth conversion was obtained using stopping cross sec-

 