Computer simulations of structure and transport in glasses and supercooled liquids

Peter H Poole

In terms of developments in the study of glasses and glass-forming liquids via computer simulation, during 1997 and early 1998, notable advances have been made in the quantification of dynamical heterogeneities in supercooled liquids; in particular several studies have identified a growing dynamical length scale as the glass transition is approached. New insights into the origins of 'polyamorphism' have been obtained from simulations of water and silica. Most significantly, a connection between equilibrium relaxation and inherent structures of liquids has been identified that suggests an underlying static origin for the glass transition.

Address
Department of Applied Mathematics, University of Western Ontario; London, Ontario N6A 5B7, Canada

Abbreviations
IS   inherent structure
MD   molecular dynamics
T_g glass transition temperature
VDOS   vibrational density-of-states

Introduction

Historically, computer simulations have perhaps had their largest impact on the fundamentals of materials science in the study of amorphous systems, especially the liquid state. The complexity of the microscopic structure and dynamics of liquids, and the glasses formed from them at low temperature, lends itself to a computational, rather than an analytic theoretical treatment [1]. Most realistic simulation techniques, for example, molecular dynamics (MD) simulations [2], are still limited to studying relatively small numbers of molecules (typically 10^3 atoms), and short overall physical times scales (typically 10^{-8} s). Despite these limitations, simulations in the last few years have proven themselves capable of reproducing many of the liquid properties characteristic of the approach to the glass transition temperature, T_g. Also, improvements in computational models and techniques have established the ability to accurately reproduce and study the structure of at least some important glassy materials at a temperature, T far below T_g.

This review will report on recent advances that have occurred in the computer simulation of glasses, and of the liquids from which glasses are prepared. The focus will be exclusively on research published during 1997 and the first few months of 1998. A remarkable number of notable works have been published during this period, and the concise format of the present review does not permit a just accounting of all of them. I have therefore identified a few major topics on which to report, and ask the reader to excuse the bias that such a choice necessarily implies.

Simulation investigations of dynamical heterogeneity

In an effort to understand the strongly nonexponential relaxation behavior observed universally for liquids approaching the glass transition, much discussion over the past few years has focused on the question of 'dynamical heterogeneity' [3]. Though the term is used to mean different things by different researchers, the underlying question is often expressed as: can nonexponential relaxation be understood as a superposition of simpler, exponential relaxation processes, each with a different characteristic relaxation time; or, is nonexponential behavior intrinsic to the relaxation process even at the level of individual particles and/or short time scales?

Experimental efforts to address this question are reviewed in another article in this issue [4]. However, it is not surprising that computer simulations are also being used to elucidate this question. The detailed single particle trajectories generated in a MD simulation can provide information on microscopic relaxation that is presently impossible to extract from an experiment. The results of the past year have been a number of new, potentially important insights.

Heuer, Spiess and co-workers [5–8] frame their studies of dynamical heterogeneity in the following way: if a subset of a liquid system is relaxing at a particular rate at a particular time, to what extent is that same subset still relaxing at that rate at a later time? A system in which local relaxation rates do not vary with time is termed homogeneous, whereas variation of the rate over time is defined as a heterogeneous relaxation. A formal definition of the multitime correlation function associated with this concept leads to a quantification of a 'rate distribution' and 'rate memory' for the system. This approach is in part motivated by the fact that such multitime correlation functions can be related to those measured in multidimensional NMR experiments [5]. Hence a strength of this work is that it can be applied both to simulation and experimental results on an (approximately) equal basis. The multitime correlation functions have been used to study relaxation in several systems, including simulated polymers modeled via a bond fluctuation model [6]. The formalism has also been applied to the experimental results of the relaxation of

polystyrene [7]. These particular studies suggest that, for polymers, the system is dominated by homogeneous relaxation at high T, but that this becomes increasingly heterogeneous as T decreases toward T_g.

One of the motivating factors for the original discussions of dynamical heterogeneity was to attempt to identify a dynamically-defined length scale in glassforming liquids, and to test if this length increases (and perhaps diverges) as T approaches T_g [3,9]. To address this question, Kob et al. [10] evaluated from MD simulations the distribution, P(r), of values of individual particle displacements, r, in a glass-forming liquid. P(r) is found as a function of the time over which r is measured, and at several different T. The model liquid used is the same two-component Lennard–Jones mixture that was used to such good effect by Kob and Anderson [11] to perform simulation tests of mode-coupling theory which began in 1994. In the limit of both short and long times, P(r) follows a Gaussian distribution, but substantial deviations from a Gaussian are found at intermediate times, approximately corresponding to the latter part of the beta relaxation regime, the time scale on which individual particles cease to be localized by surrounding particles. Furthermore, the deviations from Gaussian behavior increase as T decreases. These authors then identified the particles with the largest values of r in a given time interval, and examined their spatial correlation. It was found that these 'most mobile' particles are grouped into clusters which grow in size as T decreases. By extending this simulation series, Donati et al. [12] were able characterize the detailed morphology of these correlated groups of mobile particles. Rather than being compact clusters, the most mobile particles form highly ramified 'stringlike' groups in which their is a clear tendency for one mobile particle to move into the space vacated by a mobile nearest neighbor. These simulations demonstrate that the dynamics of individual particles becomes increasingly spatially heterogeneous on approaching T_g. However, it has yet to be determined if the length associated with this spatial heterogeneity might diverge, or if the effect is common to other liquids.

In this regard of the results in [10] and [12], it is useful to note the studies of Yamamoto and Onuki [13,14] who examined a two-dimensional soft-sphere liquid in the supercooled regime, via a MD simulation. As part of this work, the spatial arrangement of 'broken bonds' was determined. That is, a broken bond is located when two particles, initially nearest-neighbors, are separated by a distance greater than a chosen threshold distance after some time. The broken bonds so located are clearly spatially correlated. Indeed, some of the 'clusters' have a stringlike character reminiscent of the groups of mobile particles discussed in [12], and here too the size of the clusters grows as T decreases.

Also addressing the issue of length scales in glassforming liquids is a simulation of a dense polymer melt by Weber

et al. [15]. In their study, the motivation was to explain the long range correlations implied for certain liquids by the excess light scattering observed experimentally at small wave numbers [16]. Weber et al. [15] showed that excess scattering, found in their simulated polymer melt could be accounted for as being due to the buildup of substantial local nematic order of chain segments as T decreased. From this finding they conclude that the associated excess scattering "is not directly connected with the glass transition in the system". However, it is noted that other authors would take a different view, specifically that the onset and growth of local order may in some systems be crucial to understanding the nature of relaxation near the glass transition. To the extent that these locally ordered structural regions occur in an equilibrium liquid, they have the potential to strongly influence the relaxation behavior in the bulk. An example of this was found in a recent work by Hurley and Harrowell [17]. They examined, in MD simulations of a two-dimensional soft sphere liquid, the relaxation of that contribution to the density-density correlation function due to locally crystal-like structural fluctuations. They found that it is the relaxation of these crystal-like regions that indeed dominates the long-time behavior of the full correlation function.

Network-forming liquids and glasses

Next attention is given to recent developments in the study of structure and transport in network-forming liquids and glasses, in particular water (H_2O) and silica (SiO_2). For both of these substances, whether in liquid, crystal, or glass form, the local molecular structure is dominated at ambient pressure by tetrahedral arrangements of atoms. Such an open, structured framework gives these materials uncommon properties as glassformers.

The development of MD simulation potentials for silica has a rich history. In the past decade, a considerable number of studies have employed the potentials that were developed by Tsuneyuki et al. [18] and van Beest et al. [19]. However, as computational power has increased, it is now possible to conduct systematic studies in which the behavior of numerous model potentials can be compared. Exploiting this opportunity, Hemmati and Angell [20] carried out an extensive assessment of the ability of a variety of model potentials (including those in [18] and [19]) to reproduce the IR spectra of silica glass. Although the models studied predicted similar structural properties, such as the pair correlation function, g(r), the IR spectra for each are quite different from each other and from experimental results, highlighting the sensitivity of vibrational properties to the shape of the interaction potential used. Studies such as this are crucial to the future improvement of potential models, and are to be encouraged.

General interest continues to be focused on the origin of low-frequency contributions to the vibrational density-of-states (VDOS), known as the 'boson peak'. The boson peak is particularly prominent in silica glass; indeed, a prominent boson peak has been, in general, associated

with 'strong' glassformers, of which silica is the archetype. Following up on evidence presented by Angell [21], Guillot and Guissani [22] performed detailed MD simulations of both silica liquid and glass in order to directly study the relationship between the boson peak and the 'strength' of a glassformer. This is possible within a simulation study of a single substance because, as pointed out in [21], the relative strength or fragility of a glassforming liquid is not a fixed material property, but will also, in general, depend on the thermodynamic state of the substance. In the case of silica, it is argued that as the tetrahedral network that dominates the ambient pressure liquid and glass is destroyed under pressure, so too will the strong liquid behavior that has its origin in the network structure of the system. The results of Guillot and Guissani confirm this picture: they have been able to reproduce the boson peak in simulated silica glass at ambient pressure, and have observed that it is reduced in intensity for silica glasses of higher density.

Guillot and Guissani [22] also carried out a MD simulation in which all the atoms of an amorphous silica framework were held fixed except for the atoms of one SiO_4 tetrahedra. During the run, they evaluated the VDOS due to this one vibrating tetrahedral unit. This process was then repeated for all the other tetrahedral units and the results averaged. In this way they identified the contribution to the VDOS due to vibrational modes internal to SiO_4 tetrahedra alone, and found no contribution in the frequency region where the boson peak occurs. This demonstrates that the excitations contributing to the boson peak should involve collective vibrations of groups of SiO_4 units. A related result is described in a particularly clear paper by Taraskin and Elliott [23]. Among other things, they show that the vibrational properties of bulk amorphous SiO_2 are well represented by the vibrational properties of a small cluster of atoms within the amorphous solid network, so long as the cluster contains an integral number of tetrahedral units.

Also receiving attention in the past year has been the importance of five-fold coordinated Si atoms (SiO_5 units) to understanding the structure of crystalline and glassy SiO_2, and transport in liquid SiO_2 and related silicate melts. Simulations of silicate melts have long predicted that the self-diffusion coefficient, D, would first increase with increasing pressure, P, and only at higher P begin to decrease, as is expected for a 'simple' liquid [24]. Such anomalous behavior can be understood by the crossover in the liquid structure from four-fold coordinated Si atoms (SiO_4 units) to six-fold coordinated Si atoms (SiO_6 units) under pressure. Between these two energetically favored states occurs the (seemingly) disfavored SiO_5 state, which acts as the relevant local structure facilitating atomic motion. Hence D is maximal at densities that maximize the fraction of SiO_5 units in the liquid. Experimental investigation of the behavior of D for aluminosilicate melts under pressure has recently been successfully carried out for pressures up to 15 GPa, and has confirmed the importance of

SiO_5 units for understanding the transport properties of silicate melts [25]. However, in the past year, two simulation discoveries have added new insights on the importance of local SiO_5 units to our understanding of the bulk behavior of SiO_2.

First, Badro et al. [26] have given a full account of their 1996 discovery of a metastable crystal (the 'penta phase') composed solely of five-fold coordinated Si atoms. The result is a significant one, because it shows that an arrangement of SiO_5 units alone can generate a thermodynamically stable state. It also emphasizes the fact that local SiO_5 arrangements of atoms are energetically stable. Hence, though certainly not so favored energetically as SiO_4 or SiO_6 units, SiO_5 units do not necessarily occur in the liquid and glass structure only as unstable transient structures; at least occasionally, their appearance in an amorphous system may be energetically driven.

Second, Wentzcovitch et al. [27] have used MD simulations to clarify the precise mechanism by which alpha-quartz undergoes pressure-induced amorphization. Previous experimental studies had reported the appearance of a previously unknown crystal phase immediately prior to amorphization. However, the detailed properties of this new but transient phase could not be determined. Wentzcovitch et al. [27] were able to observe a new crystal phase prior to amorphization, and further — due to the precise control of the thermodynamic state possible in a simulation — were able to study its structure at leisure. They found a structure consisting partly of SiO_5 and SiO_6 units. Though the geometry of the SiO_5 unit was different than that found for the 'penta phase' by Badro et al. [26], once again, it is seen that the formation of SiO_5 units may be (however weakly) an energetically driven phenomenon.

For water, one of the (many) areas of active research in recent years has focused on understanding the behavior of glassy water [28]. In particular, glassy water prepared at ambient P transforms abruptly upon compression into a much denser glass [29]. Such behavior is reminiscent of that observed in the shock compression of SiO_2 glass. However, the phenomenon is more pronounced with water than with SiO_2. For water, the sudden densification of the glass under pressure is sufficiently dramatic so as to be described in the first experimental account as an 'apparently first order phase transition' from one glass form to another, a phenomenon now referred to as 'polyamorphism' [29]. In 1992, evidence developed from MD simulations of supercooled liquid water was used to propose that the observed glass-to-glass transition was a sub-T_g manifestation of a first-order liquid–liquid phase transition [30]. This phase transition of the liquid was predicted to terminate in a critical point located at a temperature less than the homogeneous nucleation temperature for the formation of ice.

Though thermodynamically permitted, the occurrence of a liquid–liquid phase transition remains controversial. Such

a transition has not been directly observed experimentally for any substance, although indirect evidence does exist for a wide range of materials [31]. In simulation, direct observation of behavior characteristic of a liquid–liquid phase transition has been found in MD studies of molten Si [32–34], a tetrahedral liquid, and in a lattice model of a network-forming liquid [35]. However, for water no direct simulation evidence was in existence until the recent report by Harrington et al. [36]. By carrying out extensive, large-scale MD simulations of the ST2 model of water (in a constant volume ensemble), they showed that this model liquid, at sufficiently low T but still in equilibrium, exhibits a phase separated state in which a region of high density liquid coexists with a region of low density liquid. This study also identified metastable liquid states occurring in the vicinity of the transition, a crucial hallmark distinguishing a first-order transition from higher order continuous transitions.

Another possibility for explaining the abrupt glass-to-glass transition observed experimentally for amorphous solid water is that, rather than a fully developed liquid–liquid phase transition, there is instead a rapid but continuous variation of the density as a function P [37]. Though less extreme than a phase transition, this scenario still requires there to be an interval of densities in which the isothermal compressibility is quite large compared to that at lower or higher density. Regardless of the outcome in the case of water, this latter scenario is probably more appropriate to explaining the behavior of silica glass under compression. In this regard, Poole et al. [38] have shown through MD simulations that an SiO_2-like liquid has behavior that mirrors much of that found for ST2 water, except that no explicit liquid–liquid phase transition is indicated, either by direct observation, or extrapolation.

One possible conclusion that might be drawn from these studies is that water, Si and SiO_2 exhibit properties that are different realizations of an underlying family of behaviors for tetrahedral-network-forming substances. At one extreme lies the possibility of an explicit liquid–liquid phase transition, at the other, merely a 'soft region' in the mechanical behavior of the system under compression. Indeed, the observation of energetically stable SiO_5 units of the kind discussed above is consistent with the idea that for SiO_2 glass, densities in the 'soft region' remain at least marginally stable thermodynamically. Glassy water on the other hand may well not have access to such stabilizing intermediate-coordination structures (stable crystals containing five-fold coordinate water molecules are not known) and so has a greater tendency towards exhibiting a thermodynamic instability.

Potential energy 'landscapes' of amorphous systems

Particularly exciting developments in the past year are associated with the use of 'inherent structures' in simulations to analyze the properties of liquids and glasses. An inherent structure (IS) is the configuration of a system of atoms obtained by carrying out a steepest-descent minimization (with respect to particle coordinates) of the total potential energy of the system, starting from an equilibrium configuration [39]. An IS is therefore the structure of the system at a local minimum of the potential energy considered as a function of all phase space coordinates (often called the 'potential energy landscape'), and corresponds to the structure of the system that would be obtained in the limit of an infinitely fast quench to T = 0.

Though the concept of the IS was introduced in the early 1980s, its use in practice is hampered by the enormous complexity of the multidimensional potential energy function, which in any realistic simulation of a bulk system has thousands of independent variables. Despite this complexity, many qualitative discussions of the behavior of glasses and supercooled liquids assume that the potential energy landscape has certain properties that have never been directly observed. Motivated by such discussions, Heuer [40] has made an imaginative attempt to formally visualize this landscape, via a procedure that maps the multidimensional surface into one dimension. Though the mapping is not necessarily a unique one, it has the virtue of being quantitative, and thus should be used to sharpen the discussion of the implications of the structure of the landscape for understanding liquids and glasses.

Important insights into the general nature of the liquid state are described in a series of papers by Sastry and co-workers [41–43]. Among a number of interesting results, they show how an analysis of the void spaces occurring in the IS for a liquid can be used to elucidate the behavior of metastable liquids, and characterize the decay of metastable states. While the work described in [41–43] focuses on the metastability of superheated liquids, it has great potential to also clarify the structural and mechanical properties of glasses, due to the above mentioned relation between an IS and a rapidly quenched glass. Indeed, Tanaka [44] has used information on the IS of water to clarify the possible structure of the high and low density liquid phases which were discussed in the previous section.

Most significantly, Sastry et al. [45] have evaluated E_{IS}, the average energy of the IS for a model glassforming liquid (a Lennard–Jones mixture) along an isochore as a function of T. At a high T, E_{IS} is relatively T-independent, but as T decreases below a certain value, E_{IS} begins to decrease rather dramatically, compared to the high T behavior. Notably, this crossover in the T-dependence of E_{IS} coincides with the crossover from exponential to nonexponential behavior of the relaxation of the equilibrium liquid from which the ISs are obtained. The appearance and growth of nonexponential relaxation is widely held to be the harbinger of an approaching glass transition. The fact that the crossover in the relaxation behavior is associated with a crossover in the behavior of a static property such as E_{IS} is (in my view) one of the first pieces of clear evidence

supporting the controversial possibility that the glass transition might be formally related to thermodynamic behavior, rather than being just a kinetically determined phenomenon. If the result proves to be a generic one, common to a wide range of glassforming liquids, it has the potential to radically change how we think about the glass transition.

Other developments

Even given the limited scope of this review, there are several other works that have been published in past year that merit attention by the reader. Important among these are simulation tests of the mode-coupling theory, for a diatomic molecular liquid [46], for a dense polymer melt [47], and for the Lennard–Jones binary mixture [48]. Sciortino and co-workers [49,50] have presented a proposal for a 'semi-schematic' mode-coupling model to describe relaxation in molecular liquids, and have tested this in some extremely long time scale MD simulations of water. This group has also continued careful simulation studies of other dynamical properties of supercooled water [51,52].

Conclusions

The past eighteen months have generated a number of important new results on the nature of glasses and glass-forming liquids. Studies of dynamical heterogeneity in supercooled liquids have progressed substantially. There are now numerous quantitative ways to monitor such heterogeneity in simulation, a few of which can also be related to experimental observables. The challenge now is to determine which approaches are most useful, in particular as a means to developing and refining predictive theories of the glass transition. The question of the possible existence of a diverging length scale at T_g is particularly important. Experiments and simulations of confined liquids would be useful in this regard. Also, simulations of thermodynamic and structural properties of glasses are likely to benefit significantly from studies employing inherent structure calculations. Finally, as discussed above, the connection between inherent structures and equilibrium liquid dynamics is particularly exciting, and is certain to be an area of vigorous research in the future.

References

1. Hanson J-P, McDonald IR: *Theory of Simple Liquids, 2nd edn.* New York: Academic Press; 1986.

2. Allen MP, Tildesley DJ: *Computer Simulation of Liquids.* Oxford: Oxford University Press;1989.

3. Richert R: **Origin of dispersion in dipolar relaxations of glasses.** *Chem Phys Lett* 1993, 216:223-227.

4. Böhmer R: **Nanoscale heterogeneity of glassforming liquids.** *Curr Opin Solid State Mater Sci* 1998, 3:378-385.

5. Heuer A: **Information content of multitime correlation functions for the interpretation of structural relaxation in glass-forming systems.** *Phys Rev E* 1997, 56:730-740.

6. Heuer A, Okun K: **Heterogeneous and homogeneous dynamics in a simulated polymer melt: analysis of multi-time correlation functions.** *J Chem Phys* 1997, 106:6176-6186.

7. Kuebler SC, Heuer A, Spiess HW: **Glass transition of polymers:**

8. Heuer A, Tracht U, Spiess HW: **Dynamic heterogeneities and cooperativity in a lattice model glass.** *J Chem Phys* 1997, 107:3813-3820.

9. Ediger MD, Angell CA, Nagel SR: **Supercooled liquids and glasses.** *J Chem Phys* 1996, 100:13200-13218.

10. Kob W, Donati C, Plimpton SJ, Poole PH, Glotzer SC: **Dynamical heterogeneities in a supercooled Lennard–Jones liquid.** *Phys Rev Lett* 1997, 79:2827-2830.

11. Kob W, Andersen HC: **Scaling behavior in the beta relaxation regime of a supercooled Lennard–Jones mixture.** *Phys Rev Lett* 1994, 73:1376-1379.

12. Donati C, Douglas JF, Kob W, Plimpton SJ, Poole PH, Glotzer SC: **Stringlike cooperative motion in a supercooled liquid.** *Phys Rev Lett* 1998, 80:2338-2341.

13. Yamamoto R, Onuki A: **Nonlinear rheology of a highly supercooled liquid.** *Europhys Lett* 1997, 40:61-66.

14. Yamamoto R, Onuki A: **Kinetic heterogeneities in a highly supercooled liquid.** *J Phys Soc Jpn* 1997, 66:2545-2548.

15. Weber A, Paul K, Kob W, Binder K: **Small-angle excess scattering: glassy freezing or local orientational ordering?** *Phys Rev Lett* 1997, 78:2136-2139.

16. Fischer EW, Donth E, Steffen W: **Temperature dependence of characteristic length for glass transition.** *Phys Rev Lett* 1992, 68:2344-2346.

17. Hurley MM, Harrowell P: **Resolving the structural relaxation of a two-dimensional liquid using apertured cross correlation functions.** *J Chem Phys* 1997, 107:8586-8593.

18. Tsuneyuki S, Tsukada M, Aoki M, Matsui Y: **First-principles interatomic potential of silica applied to molecular dynamics.** *Phys Rev Lett* 1988, 61:869-872.

19. van Beest BWH, Kramer GJ, van Santen RA: **Force fields for silicas and aluminophosphates based on ab initio calculations.** *Phys Rev Lett* 1990, 64:1955-1958.

20. Hemmati M, Angell CA: **IR absorption of silicate glasses studied by ion dynamics computer simulation. I. IR spectra of SiO$_2$ glass in the rigid ion model approximation.** *J Non-Cryst Solids* 1997, 217:236-249.

21. Angell CA: **Formation of glasses from liquids and biopolymers.** *Science* 1995, 267:1924-1935.

22. Guillot B, Guissani Y: **Boson peak and high frequency modes in amorphous silica.** *Phys Rev Lett* 1997, 78:2401-2404.

23. Taraskin SN, Elliott SR: **Nature of vibrational excitations in vitreous silica.** *Phys Rev B* 1997, 56:8605-8622.

24. *Structure, Dynamics and Properties of Silicate Melts* (Reviews in Mineralogy, volume 32). Edited by Stebbins JF, McMillan PF, Dingwell DB. Washington: Mineralogical Society of America; 1995.

25. Poe BT, McMillan PF, Rubie DC, Chakraborty S, Yarger J, Diefenbacher J: **Silicon and oxygen self-diffusivities in silicate liquids measured to 15 gigapascals and 2800 kelvin.** *Science* 1997, 276:1245-1248.

26. Badro J, Teter DM, Downs RT, Gillet P, Hemley RJ, Barrat JL: **Theoretical study of a five-coordinated silica polymorph.** *Phys Rev B* 1997, 56:5797-5806.

27. Wentzcovitch RM, da Silva C, Chelikowsky JR, Binggeli N: **A new phase and pressure induced amorphization in silica.** *Phys Rev Lett* 1998, 80:2149-2152.

28. Debenedetti PG: *Metastable Liquids.* Princeton: Princeton University Press; 1997.

29. Mishima O, Calvert LD, Whalley E: **An apparently first-order transition between two amorphous phases of ice induced by pressure.** *Nature* 1985, 314:76-78.

30. Poole PH, Sciortino F, Essmann U, Stanley HE: **Phase behaviour of metastable water.** *Nature* 1992, 360:324-328.

31. Poole PH, Grande T, Angell CA, McMillan PF: **Polymorphic phase transitions in liquids and glasses.** *Science* 1997, 275:322-323.

memory effects in structural relaxation of polystyrene. *Phys Rev E* 1997, 56:741-749.

32. Ludke WD, Landman U: **Preparation and melting of silicon by molecular-dynamics simulations.** *Phys Rev B* 1988, **37**:4656-4663.

33. Ludke WD, Landman U: **Preparation, structure, dynamics and energetics of amorphous silicon: a molecular-dynamics study.** *Phys Rev B* 1989, **40**:1164-1174.

34. Angell CA, Borick S, Grabow M: **Glass transitions and first order liquid-metal-to-semiconductor transitions in 4-5-6 covalent systems.** *J Non-Cryst Solids* 1996, **205-207**:463-471.

35. Roberts CJ, Panagiotopoulos, Debenedetti PG: **Liquid–liquid immiscibility in pure fluids: polyamorphism in simulations of a network-forming fluid.** *Phys Rev Lett* 1996, **77**:4386-4389.

36. Harrington S, Zhang R, Poole PH, Sciortino F, Stanley HE: **Liquid–liquid phase transition: evidence from simulations.** *Phys Rev Lett* 1997, **78**:2409-2412.

37. Sastry S, Debenedetti PG, Sciortino F, Stanley HE: **Singularity-free interpretation of the thermodynamics of supercooled water.** *Phys Rev E* 1996, **53**:6144-6154.

38. Poole PH, Hemmati M, Angell CA: **Comparison of thermodynamic properties of simulated liquid silica and water.** *Phys Rev Lett* 1997, **79**:2281-2284.

39. Stillinger FH, Weber TA: **Packing structures and transitions in liquids and solids.** *Science* 1984, **225**:983-989.

40. Heuer A: **Properties of a glass-forming system as derived from its potential energy landscape.** *Phys Rev Lett* 1997, **78**:4051-4054.

41. Sastry S, Corti DS, Debenedetti PG, Stillinger FH: **Statistical geometry of particle packings. I. Algorithm for exact determination of connectivity, volume, and surface areas of void space in monodisperse and polydisperse sphere packings.** *Phys Rev E* 1997, **56**:5524-5532.

42. Sastry S, Debenedetti PG, Stillinger FH: **Statistical geometry of**

43. DS Corti, Debenedetti PG, Sastry S, Stillinger FH: **Constraints, metastability, and inherent structures in liquids.** *Phys Rev E* 1997, **55**:5522-5534.

44. Tanaka H: **Fluctuation of local order and connectivity of water molecules in two phases of supercooled water.** *Phys Rev Lett* 1998, **80**:113-116.

45. Sastry S, Debenedetti PG, Stillinger FH: **Identification of potential energy landscape signatures of distinct dynamical regimes in a glass forming liquid.** *Nature* 1998, **393**:554-557.

46. Kammerer S, Kob W, Schilling R: **Dynamics of the rotational degrees of freedom in a supercooled liquid of diatomic molecules.** *Phys Rev E* 1997, **56**:5450-5461.

47. Bennemann C, Paul W, Binder K, Dunweg B: **Molecular dynamics simulations of thermal glass transition in polymer melts: alpha relaxation behavior.** *Phys Rev E* 1998, **57**:843-851.

48. Nauroth M, Kob W: **Quantitative test of the mode-coupling theory of the ideal glass transition for a binary Lennard–Jones system.** *Phys Rev E* 1997, **55**:657-667.

49. Fabbian L, Sciortino F, Tartaglia P: **Mode coupling for non-spherical molecules: a semischematic model applied to simulated water.** *Phil Mag B* 1998, **77**:499-505.

50. Fabbian L, Sciortino F, Thiery F, Tartaglia P: **Semischematic model for the center-of-mass dynamics in supercooled molecular liquids.** *Phys Rev E* 1998, **57**:1485-1488.

51. Chen SH, Gallo P, Sciortino F, Tartaglia P: **Molecular-dynamics study of incoherent quasielastic neutron-scattering spectra of supercooled water.** *Phys Rev E* 1997, **56**:4231-4243.

52. Sciortino F, Tartaglia P: **Harmonic dynamics in supercooled liquids: the case of water.** *Phys Rev Lett* 1997, **78**:2385-2388.

particle packings. II. "Weak spots" in liquids.** *Phys Rev E* 1997, **56**:5533-5543.