Nanoconfinement and the Glass Transition: A Cluster Hypothesis

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Received: February 10, 2006

It is suggested that the depression of the glass temperature in nanoconfined liquids and polymers may be explained by an effect of the confinement alone: specifically, confinement by hard walls creates an excluded volume effect that decreases the fraction of molecules organized in clusters. If we think of this fraction as a rough surrogate determining the fictive or structural temperature, then the confined liquid will have a higher fictive temperature than the bulk liquid at the same actual temperature. A computational method already used to study clusters may test the hypothesis.

In a recent comprehensive review,[1] Alcoutlabi and McKenna, after summarizing a range of not too concordant experimental and computational results on the effect of nanoconfinement of molecular liquids and polymers on their glass transition temperatures (or other measures of relaxation times in the highly supercooled range), came to the following conclusions:

It is clear now that there is evidence of a reduced T_g at the nanometer size scale. What is not clear though is whether the T_g reduction is due to an intrinsic size effect, confinement effects, sample preparation, or a combination of these effects.... It remains a challenge to build a widely accepted theoretical model that accounts for the total panoply of experimental and computational results.

As they point out, there is no universally accepted explanation of the phenomena.

I would like to offer here a qualitative hypothesis to account for a lowering of T_g in nanoconfined systems and a possible computational procedure for testing it. The hypothesis is that formation of clusters, which in the supercooled liquid has been invoked to account for the dramatic slowing down of relaxation processes near T_g,[2,3] is inhibited by nanoconfinement on a length scale comparable to cluster dimensions. It seems reasonable that, if the particles are in a box with hard walls, the development of clusters will be hindered and the fraction of molecules in clusters must be smaller. For simplicity, let us imagine spherical clusters, whose number and mean radius (r) are temperature dependent in the bulk liquid. Hard walls create an excluded volume for such clusters, reducing their volume fraction relative to the volume fraction in the bulk liquid. As an example, consider a liquid confined in a cubical hard box of side s nanometers. There can be no clusters of radius r nanometers with their centers within a distance r from any wall of the box. This implies a reduction of the volume fraction of clusters that makes the structure of the confined liquid resemble that of the bulk liquid at a higher temperature. Of course, the cluster size distribution, not just the volume fraction, may be altered by the presence of the walls, so that the correspondence to a higher temperature state of the bulk liquid may not be exact.

The fraction of the volume of the box available to clusters of radius r is easily calculated to be $(s - 2r)^3/s^3 = [1 - (2r/s)]^3$. The fraction of the volume available to clusters of size 0.5 nm in a box of side s equal to 10 nm is thus 0.73; if the side of the box is 5 nm, the fraction falls to 0.51, and to 0.22 in a box of side 2.5 nm. It is obvious that the available volume fraction falls rapidly to zero as the size of the box is decreased, reaching zero when the cluster diameter equals s. It is tempting though premature to suggest that this rapid vanishing of the volume fraction is related to the reported marked dependence of the decrease of T_g on the diameter (h) of the nanopore, often expressed as being proportional to $1/h$.

A computational approach to testing the hypothesis is suggested by papers by Dzugutov et al.[2] and by Doye et al.,[3] which describe the formation of clusters of nanometer dimensions in a supercooled monatomic liquid. These authors used modified interatomic potentials that minimize the formation of crystalline order. The number of particles studied was 16 000. In addition to molecular dynamics calculations of the diffusion constant and its temperature dependence, the formation of extended domains of icosahedral order was studied. The atomic configurations were found by steepest descent minimization of instantaneous configurations of equilibrium liquids. Members of a cluster were identified first by finding 13-atom icosahedra of nearest neighbors and then finding those other icosahedra that shared at least three atoms with the reference one.[3] The clusters so found were extended in space rather than compact, and given a nearest neighbor distance of the order of a tenth of a nanometer, they had longest dimensions of the order of several nanometers. Dzugutov et al. calculated the number of molecules bound in clusters as a function of temperature.[2]

A test of this hypothesis is therefore to compare the fraction of molecules in clusters under periodic boundary conditions with the fraction with hard walls. It is of course not necessary to follow the choices by Dzugutov et al.[2] or Doye et al.[3] of the

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J. Phys. Chem. B, Vol. 110, No. 20, 2006 **9773**

particular potential functions, or the particular criteria that determine which atoms are in the cluster.

References and Notes

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