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Final Technical Report

Covering the Period 12/1/90 to 8/31/93

by

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This report summarizes the principal conclusions of the work carried out under Grant DE-FG02-87ER13714 during the period 12/1/90 to 8/31/93. Details can be found in the relevant publications. The research addressed the following main topics (see publications list below for other topics):

i) Computational and theoretical studies of molecular interactions in supercritical mixtures.

ii) Supercooled liquids, network fluids, and glasses.

iii) Fast algorithms for the simulation of large systems on a vector processor.

Computational and Theoretical Studies of Molecular Interactions in Supercritical Mixtures

We proposed the now widely-used classification scheme of dilute supercritical mixtures into attractive, weakly attractive, and repulsive (Debenedetti and Mohamed, 1989). The attractive/repulsive criteria are quite useful, as they allow the quick and easy selection of model systems for computer simulations or integral equation calculations. We developed mathematical criteria for the prediction of the attractive or repulsive character of a given mixture for three mixture models: van der Waals, Panayiotou-Vera lattice gas, and perturbed hard chain (Petsche and Debenedetti, 1991). These criteria are expressed in terms of differences in size, interaction energy, or chain length between the solute and the solvent (Figure 1). In an attractive supercritical mixture, the solute's partial molar volume and enthalpy are large and negative, diverging to minus infinity in at the solvent's critical point, in the limit of infinite dilution. The microstructure around solute molecules is solvent-rich with respect to the bulk, and the solute-solvent distribution function decays to unity from above. All actual or proposed applications of supercritical mixtures involve attractive systems. In general, attractive behavior results when a large solute molecule, having a relatively large characteristic interaction energy is dissolved in a solvent with smaller, more weakly interacting molecules. This corresponds to a non-volatile solute (e.g., pyrene) dissolved in a lighter solvent (e.g., carbon dioxide).

We performed the first direct comparison between fluorescence spectroscopy and molecular dynamics investigations of the local molecular environment surrounding non-volatile solutes in supercritical solvents (Knutson et al., 1992). The simulations showed that the solvent enrichment around solute molecules is more pronounced (local-to-bulk density ratio of 1.7 averaged over two solvation shells) at substantially sub-critical densities (less than $\rho_c/3$ at a reduced temperature of 1.02). Good agreement was obtained between the local density augmentation determined by simulations and experiments (Figure 2), a rather surprising result in light of the very simple pair potentials used in the simulations. In earlier work (e.g., Debenedetti, 1987) we did not distinguish clearly the local environment surrounding solute molecules in supercritical mixtures from near-critical effects. McGuigan and Monson (1990), and Levelt-Sengers (1991) have shown that local density enhancements are unrelated to (or, more precisely, only very mildly related to) near-criticality. The simulations and experiments of Knutson et al. (1992), which show local effects becoming more pronounced at substantially sub-critical densities, substantiate this view.

We derived new exact relations for the solute-solute pair correlation function integrals at infinite dilution, and applied these expressions to supercritical systems (Debenedetti and Chialvo, 1992). The new expression relates the integral of the solute-solute pair correlation function to the solvent's compressibility, a long-ranged quantity, and the integral of the solute-solvent direct correlation function, a short-ranged quantity. We showed that near the solvent's critical point the solute-solute pair correlation function integral diverges to plus infinity, regardless of the attractive or repulsive character of the system. This means that the solute-solute distribution function decays to unity from above.

We performed a molecular dynamics investigation of the distribution of solute molecules around each other in model attractive and repulsive supercritical mixtures (Chialvo and Debenedetti, 1992a). This study confirmed the theoretical predictions as to the fact that such distribution functions always decay to unity from above (Figure 3). The simulations also revealed very large first peaks in the solute-solute distribution functions at sub-critical density. However, the integral of the distribution functions showed no evidence of solute-solute aggregation. In the attractive case, the very high first peak and other interesting structural features (such as a first valley where the distribution function was still as high as 6) corresponded at most to a dimer. In related and very recent work we have studied solute-solute collision dynamics in attractive supercritical mixtures and found no evidence of enhanced collision frequency in the compressible region (Corti and Debenedetti, 1993a).

We used integral equations to study molecular distributions in supercritical mixtures (Tom and Debenedetti, 1993). For attractive systems, we found the solvent enrichment around the solute to be more pronounced at reduced densities between 0.5 and 0.8. For repulsive systems, we found solvent depletion around the solute to be particularly pronounced in the solvent's compressible regime, including the formation of remarkable correlation holes. We also quantified the extent of the local region around a solute molecules that is important for solubility (Figure 4). This was done by calculating the solute's fugacity coefficient as a function of a variable distance cutoff, beyond which the mixture was assumed to be uniform. For attractive systems, this solvation region was found to range from 3 to 5 solvent diameters over the reduced density range 0.5 to 2, with a mild maximum at near-critical conditions.

Supercooled Liquids, Network Liquids, and Glasses

Most liquids, when supercooled, show no anomalies or peculiarities in their thermodynamic properties. However, water, heavy water, and some liquid metals show anomalous increases in their response functions (isothermal compressibility, isobaric heat capacity) when supercooled. Microscopically, this means that density and enthalpy fluctuations play a dominant role in the thermodynamics of these fluids. In the particular case of water and heavy water, where extensive and careful measurements in the supercooled region have been made, power-law fits of the data appear to suggest a low-temperature divergence of the response functions. Were this actually to be the case, it would imply the existence of a thermodynamic limit of stability (spinodal curve) for the supercooled liquid. This viewpoint (Speedy, 1982; Debenedetti and D'Antonio, 1988) is known as the stability limit conjecture. A recent study of supercooled water (Poole et al., 1992) suggests an entirely different picture, in which the anomalies of the response functions are a consequence of a metastable first-order phase transition between two forms of amorphous ice terminating at a metastable critical point. Thus, the general question of the stability (or loss thereof) of fluctuation-dominated supercooled liquids remains very much an open one.

In earlier work (D'Antonio and Debenedetti, 1987; Debenedetti and D'Antonio, 1988), we showed, using thermodynamic consistency arguments, that a necessary condition for loss of stability upon supercooling is that the liquid have a negative thermal expansion coefficient in some region of the phase diagram. We then showed that there is a class of spherically symmetric potentials (which we called core-softened), that can give rise to negative thermal expansion. In a core-softened potential, there exists a range of

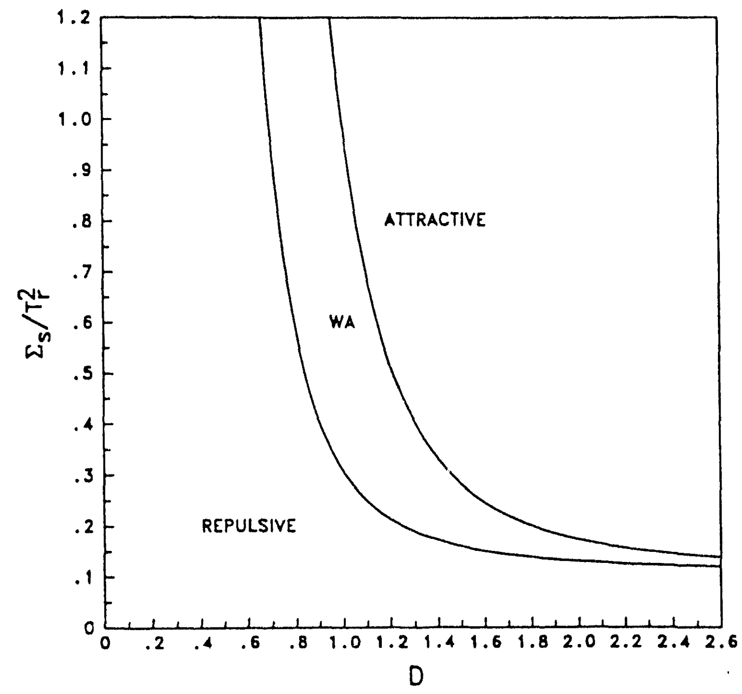

Figure 1: Boundaries between the attractive, weakly attractive, and repulsive regimes along the solvent's critical isochore for the van der Waals mixture. Σs is the ratio of solute-to-solvent energy per unit volume (ε/σ^3). D is the ratio of solute-to-solvent diameters. (Petsche and Debenedetti, 1991).

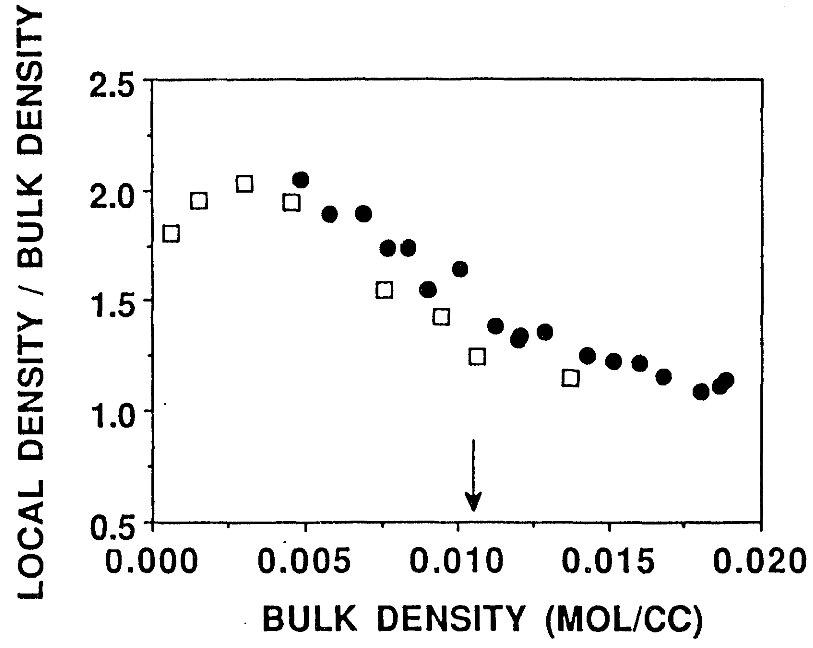

Figure 2: Comparison between fluorescence spectrocopy measurement (dots) and computer simulation calculation (squares) of local density enhancements of supercritical carbon dioxide around dilute pyrene, at a reduced temperature of 1.02. In the simulations, the local density was calculated in the first solvation shell. The Lennard-Jones potential was used to simulate the pyrene-carbon dioxide binary. The arrow indicates the critical density of carbon dioxide. Note the maximum local effect at sub-critical density. (Knutson et al., 1992).

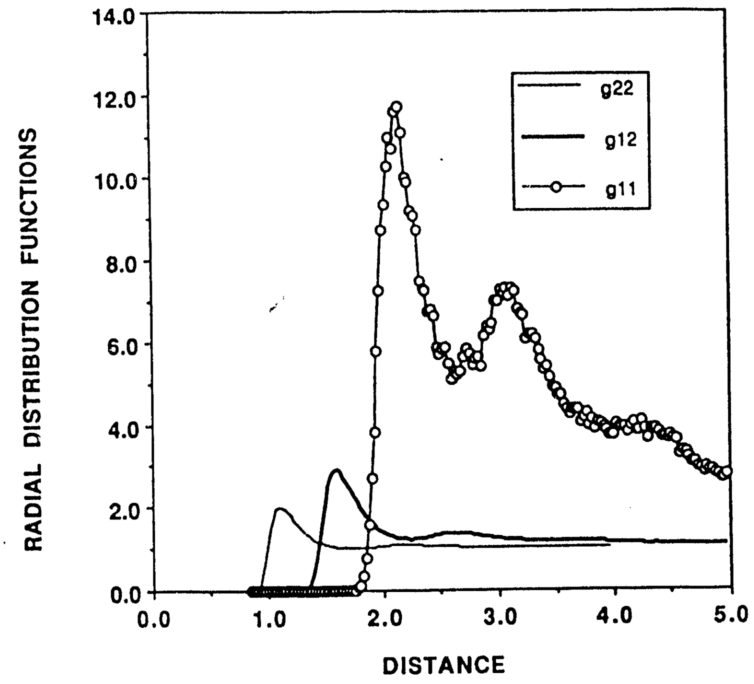

Figure 3: Solute-solute (11), solute-solvent (12), and solvent-solvent (22) pair correlation functions for an attractive Lennard-Jones binary at solvent reduced density and temperature of 0.8 and 1.07. (Chialvo and Debenedetti, 1992).

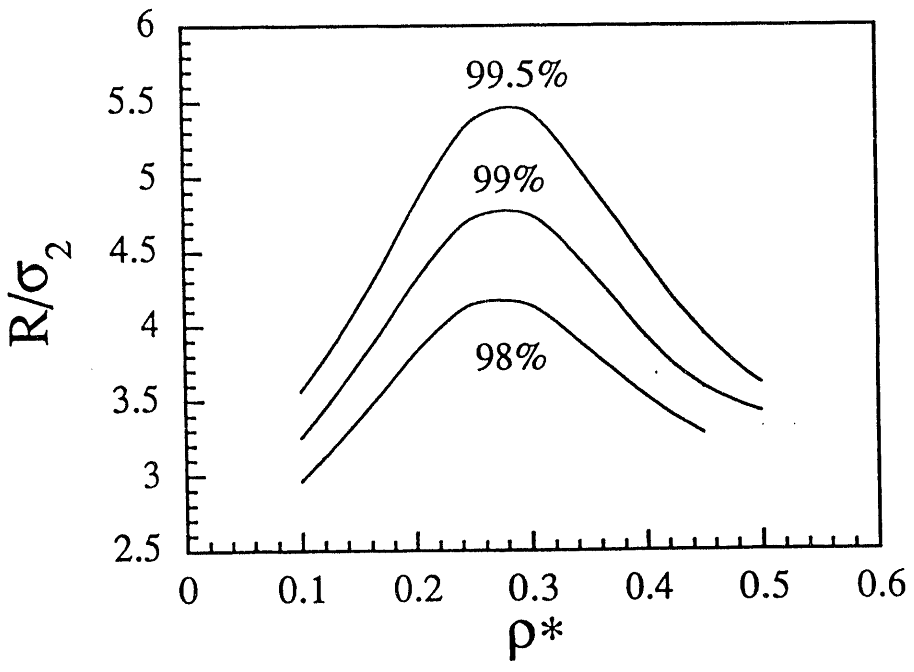

Figure 4: Density dependence of the cutoff distance (beyond which the mixture is assumed to be homogeneous) needed to obtain 98, 99, and 99.5% of the asymptotic solute fugacity coefficient. Lennard-Jones representation of the naphthalene-carbon dioxide binary at solute mole fraction of 10^{-9} and solvent reduced temperature of 1.07. (Tom and Debenedetti, 1993).

intermolecular separations within which the repulsive force between two molecules does not increase monotonically as their distance decreases. A simple lattice version of this model (a lattice gas with nearest neighbor attraction and next-nearest neighbor repulsion) indeed showed density anomalies an a continuous stability boundary with a retracing spinodal (Figure 5) and tensile strength maximum (Debenedetti et al., 1991), just as has been postulated for water in the stability limit conjecture (Speedy, 1982; Debenedetti and D'Antonio, 1988). More recently, we used the cluster variation method to solve a lattice model that combines core-softening and directional bonding (Borick and Debenedetti, 1993). Both of these features can cause negative thermal expansion because they can stabilize ground states (states with the lowest energy) of low density. While the model yielded some water-like features (negatively-sloped melting curve), the resulting density anomalies included prominent density minima, and bore little resemblance with thermal expansion in water. This suggests that more than the mere superposition of spherically symmetric and directional features capable of causing negative thermal expansion (core-softening, tetrahedral coordination) is required to model a negatively-sloped density maxima locus with no density minima, such as exists in water, heavy water and silica.

Recently (Chakravarthi et al., 1993), we have shown that when core-softened, generalized van der Waals fluids display density anomalies that differ in a fundamental way from those seen in nature: water, silica, and heavy water become normal (i.e., their thermal expansion coefficient becomes positive) when compressed, whereas core-softened van der Waals fluids become anomalous upon compression. This is an important negative result, as it suggests which aspects of density anomalies are peculiar to network systems, and which are not.

We have used the tethering technique, a basic component of the nucleation simulations described in this proposal, to study the entropy of the crystal, fluid, and glassy phases of a tetravalent network model (Speedy and Debenedetti, 1993). Angell (1990) has proposed a useful classification of glass-forming liquids into strong and fragile. The former are tetrahedrally coordinated and their viscosity show Arrhenius behavior in the supercooled regime. Fragile (molecular) liquids lack such tetrahedral coordination, and their viscosities deviate markedly from Arrhenius behavior. Angell (1990) has argued, plausibly, that strong liquids have fewer potential energy minima than fragile ones because the latter, lacking bonding constraints, can sample more inherent structures (Stillinger and Weber, 1984). Our work (Speedy and Debenedetti, 1993) suggests that, at least for hard-core fluids, the extra constraints, not the extra freedom, increases the number of available

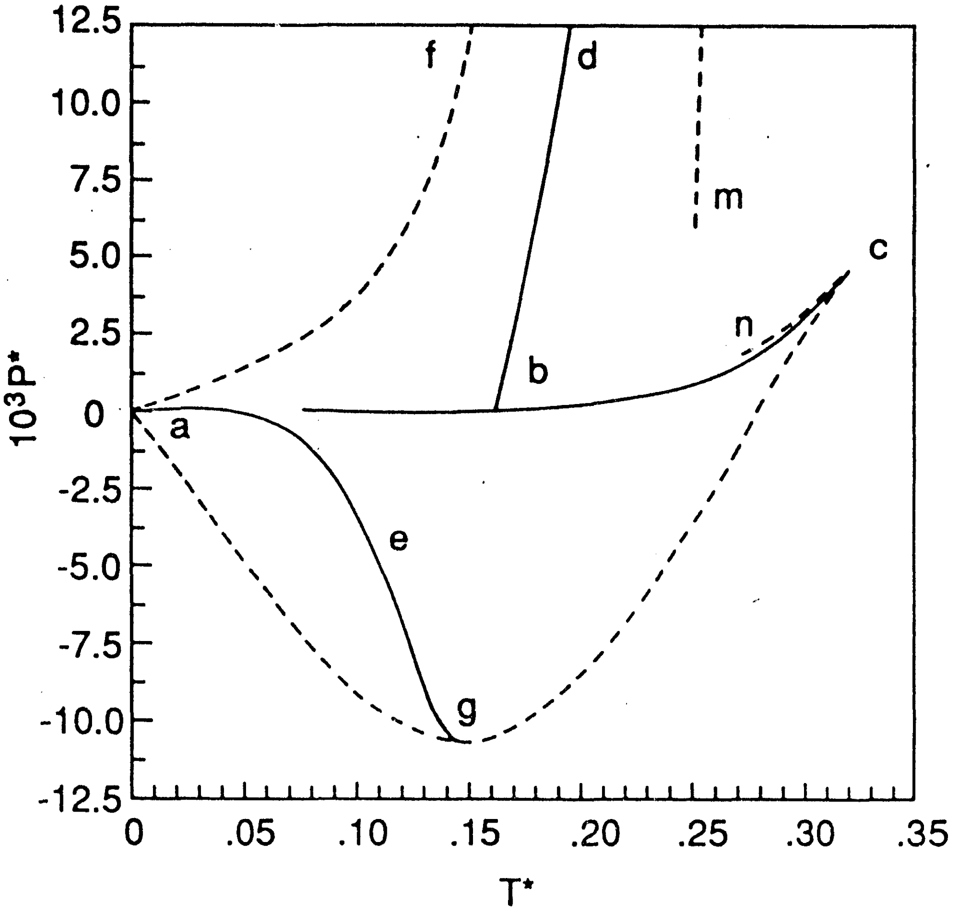

Figure 5: Re-entrant spinodal (cga) in a lattice model with nearest-neighbor attraction and next-nearest-neighbor repulsion. aeg is the locus of density maxima, bd and bc are binodal lines, and the dotted lines are stability limits. (Debenedetti et al., 1991).

Refereed Publications related to Grant DE-FG02-87ER13714; period 12/1/90 to 8/31/93

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