Removing chemical bonding ambiguities in condensed media by steepest-descent quenching

Thomas A. Weber and Frank H. Stillinger

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Motivated by a desire to understand chemical reactivity in condensed phases, we have developed models and have carried out the corresponding molecular dynamics simulations for atomic substances that display covalent bonding. Specific examples are the elements silicon[1] and sulfur.[2,3] In order to capture the main features of the structural chemistry involved in these cases, it has been obligatory to use combinations of two and three atom interactions.

Covalent bonds between pairs of atoms normally are much stronger and shorter than van der Waals noncovalent bonds. Consequently there is no ambiguity in identifying which atom pairs are bonded in a low-temperature crystal; the length ranges for chemically bonded and for nonbonded pairs are clearly separated.

The situation can become less clear under elevated temperature conditions. Vibrational and diffusional motions can reduce or eliminate the distance gap between bonded and nonbonded pairs. Furthermore, vigorous chemical reactions may be underway, frequently breaking and reforming chemical bonds, thereby moving the affected pairs into and across the gap forbidden at low temperatures.

The method of configurational mapping by steepest-descent displacement on the multidimensional potential energy hypersurface has been proposed as a conceptual device to eliminate bonding ambiguity.[2,3] This mapping technique is central to our "inherent structure" approach to condensed phase properties, and has been discussed at length elsewhere.[4,5] In short, it connects any arbitrary atomic configuration (as in a high-temperature fluid, for example) to a mechanically stable packing of the atoms, thereby eliminating all "vibrational" distortion. It is our purpose now to illustrate the fundamental power of this mapping to remove bonding ambiguity, by reporting a demanding and crucial molecular dynamics test that was carried out using our sulfur model.[3]

Figure 1 shows (as a dashed curve) the sulfur–atom pair correlation function evaluated for a well-equilibrated 1000 atom simulation under purposely extreme conditions: the mean temperature is 3.35×10^4 K while the mass density has been kept equal to the melting-point value for pure liquid sulfur, 1.805 g/cm^3. While this pair correlation function shows some weak features at short range, there is no clear separation or distinction between bonded and nonbonded pairs. Many pairs in the system at any given instant are found in transit between the positions of the weak first and second maxima (2.02 and 3.45 Å, respectively).

The final configuration of the high-temperature run was subjected to a steepest-descent quench, where each atom was continuously displaced at a rate proportional to the force it experienced until global mechanical equilibrium obtained. Figure 1 also displays (as a solid curve) the "quench pair
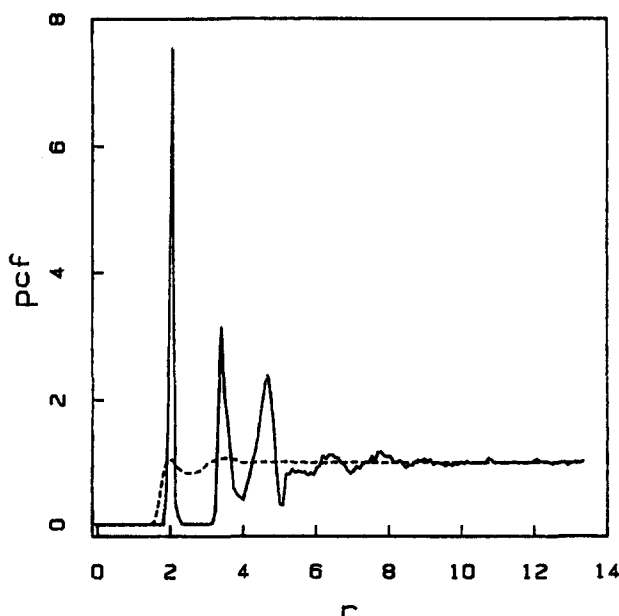

FIG. 1. Pair correlation functions for sulfur in the extreme thermodynamic state 3.35×10^4 K, 1.805 g/cm^3. The dashed curve is the conventional pair correlation function at thermal equilibrium, the solid curve is a quenched pair correlation function obtained by steepest-descent mapping. The horizontal length scale (r) is in angstroms.
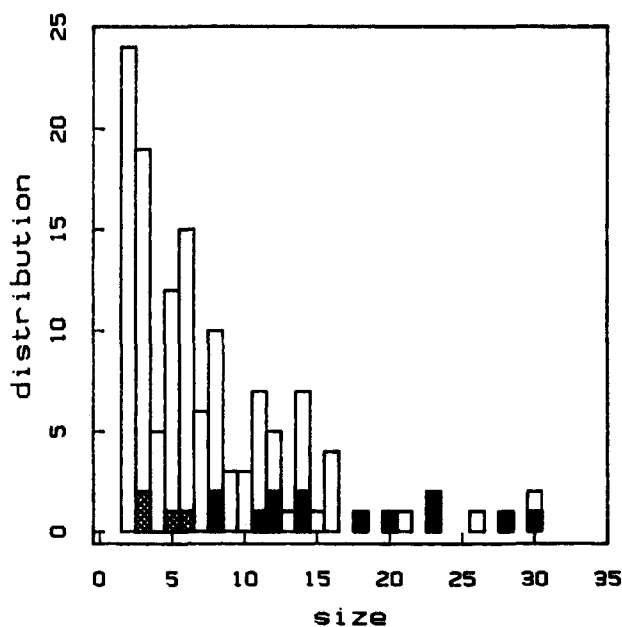

FIG. 2. Size distributions of molecular species S_n present in the quenched configuration. White areas represent chain species, cross-hatched areas are rings, and black areas are branched species.

correlation function" for the resulting stable arrangement of the 1000 sulfur atoms. Its first peak is very narrow and entirely isolated from all remaining pairs. Specifically, no atom pairs whatsoever are found in the interval between 2.36 and 3.03 Å which lies between the first and second peaks. The sharp first peak incorporates precisely and unambiguously 874 covalent bonds. These bonds connect the atoms into a variety of chain, ring, and branched structures ranging in size from S_2 to S_{30}. Figure 2 shows the size distributions for these fragment types in the potential minimum obtained.

The stable low-temperature form of sulfur involves S_8 rings, and that property is reproduced by our model.[3] The deepest potential minima therefore would display 1000 covalent bonds. That only 874 exist in the packing created in our test indicates that a rather high-lying relative minimum is involved. We estimate that it is located approximately 0.16 eV/atom above the absolute minimum.

The steepest-descent mapping protocol for identifying molecular species clearly passes the extreme test imposed. Consequently we believe as a general procedure it has wide theoretical applicability beyond the specific case of sulfur. As another example (again with pair and triplet potentials) it should be possible to model dense-phase reactions of I_2 and Cl_2 to form ICl, the rates and chemical equilibria for which should be accessible through molecular dynamics simulation. At high temperature and pressure it would be unclear from low-order atomic distribution functions how many reactant and product species were present, until steepest-descent reduction to potential minima removed the ambiguity.

Likewise, it would be instructive to apply this method to simulations of ion pairing equilibria in aqueous electrolytes, and of proton transfer reactions (acid-base association, dissociation, and neutralization), provided suitable model potentials for these cases were available. In each of these cases as well, it is unlikely that conventional atomic distribution functions could unambiguously provide the relevant species concentrations.

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[5] F. H. Stillinger and T. A. Weber, Phys. Rev. A 28, 2408 (1983).