High Pressure Closure of Melting and Freezing Behavior

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Commencing from the triple point at a low temperature and pressure, most commonly encountered substances exhibit melting and freezing behavior that form the boundary curves for two-phase solid and liquid coexistence over a small range of densities [1]. Both the temperature and pressure of solid-liquid equilibria extend to ever increasing values. The density range of two-phase coexistence progressively narrows, but whether the difference eventual becomes zero is unknown. That is, whether or not the melting and freezing curves eventually coincide at extreme values of both temperature and pressure remains unresolved. Experimental measurements at pressures of many gigapascals are challenging, requiring specialized techniques [2]. Molecular simulation [3] arguably provides an ideal computational tool to investigate such phenomena and highly effective algorithms for solid-liquid equilibria have been devised [4]. Nonetheless, a solid-liquid equilibria closure has never been observed using conventional intermolecular potentials [2].

A common feature of many intermolecular potentials, such as the Lennard-Jones potential, is steep repulsion and long-range attractive interaction. Comparison [5] with *ab initio* data consistently indicates that the degree of repulsion is often overestimated, particularly at low intermolecular separation. In this work, we report molecular simulations of solid-liquid equilibria using a relatively soft-repulsion, short attractive-ranged pair potential [6]. We demonstrate the closure of the freezing and melting lines at high pressures and temperature. The nature of the point of closure, which is accompanied by a density inversion of the solid and liquid phases, is examined. The latter is a phenomenon that is usually only observed for water.

References

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