

Inverse Melting

Frank H. Stillinger

Department of Chemistry, Princeton University, Princeton, NJ

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The conventional first-order melting process that converts a crystalline solid to isotropic liquid, at constant pressure, requires adding heat to the system. Consequently, the entropy of the liquid phase exceeds that of the crystal with which it coexists. Most cases also involve volume expansion at melting, *i.e.* the liquid is less dense than the crystal. Volume contraction at melting also occurs, though less frequently; the case of ice melting to a more-dense liquid water is the most familiar example.

Inverse melting is a first-order phase change involving the crystal and liquid as well, but with a reversal. In such a case, addition of heat to the liquid, at constant pressure, causes that liquid to freeze into a crystalline solid. As a result of this reversal, the crystal has higher entropy than the isotropic liquid with which it coexists. This is a rare phenomenon, but real-world examples exist. One is ^3He below about 0.3K, and in the 30 bar pressure range. Another is an organic polymer, isotactic Poly(4-methylpentene-1), "P4MP1", with an inverse melting range around 150-200K, and approximately 6 kbar. Our objective (in a collaboration with M.F. Feeney and P.G. Debenedetti at Princeton) has been to develop a classical statistical-mechanical model that exhibits inverse melting. To the best of our knowledge this has not been done heretofore.

The starting point is the conventional form of the so-called Gaussian core model (GCM). This consists of a collection of spherically-symmetric particles that interact in pairs with repelling potentials that are Gaussian functions of distance. That conventional GCM only exhibits ordinary melting, with the liquid higher in entropy than the crystal. In its equilibrium phase diagram this model exhibits both fcc and bcc crystals. Both positive and negative density changes at melting occur, as well as a melting temperature maximum, at which liquid and crystal densities are identical.

In order to transform the GCM to an inverse-melting model, we endow each of the original particles with a simple spectrum of internal states. Each particle has a non-degenerate ground state, and an E -fold degenerate excited state at relative energy $\Delta > 0$. Furthermore, the range of each spherically-symmetric Gaussian repulsion is postulated to depend a bit on the excitation level of the two participating particles. One can suppose either that excitation causes the particles to expand, or to shrink, so far as the Gaussian range is concerned. Both cases lead to inverse melting scenarios if the input parameters (E, Δ, σ) are properly chosen. Our numerical studies have involved separate free energy evaluations for both crystal phases, and for the isotropic fluid. Inverse melting can be made to occur both for the fcc and for the bcc crystals, and with either sign of density change for the latter.

The simple explanation of how inverse melting can exist in this extended GCM is that at coexistence different extents of internal excitation appear for the fluid and the crystal at coexistence. Particle interactions shift the internal excitation equilibrium, with different shifts in liquid and crystal. The crystal manages to possess the higher net entropy because the particles in the periodic lattice have greater internal excitation disorder than those in the translationally-disordered fluid.

No doubt there is a wider range of models that could be shown to display inverse melting. The GCM was an interesting starting point because of its two crystals, and its possibility for both signs of density change during

inverse melting. We hope that the modeling efforts and any insights that might emerge will stimulate synthesis of new materials which will expand the list of real cases showing this counterintuitive phenomenon of inverse melting.