

Supercooling of liquids, as described by the Enskog–Vlasov kinetic equation

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A model combining Enskog’s collision integral for dense fluids with a Vlasov-style description of the van der Waals force is applied to supercooling. First, the spinodal temperature T_s is calculated, at which a liquid becomes unstable to small perturbations and transitions to solid. In particular, it turns out that isochoric cooling allows one to reach a lower temperature than isobaric cooling. Second, the surface tension of a supercooled liquid–vapor interface is shown to diverge at T_s . The singularity is caused by an oscillatory region emerging on the liquid side of the interface as $T \rightarrow T_s$; it develops because the liquid approaches instability, and the interface starts radiating (so far, evanescent) waves. At $T = T_s$, the waves cease to be evanescent and the oscillatory region extends to infinity – hence, the singularity of the surface tension. Since this effect has a clear physical interpretation, it should occur regardless of the model and approximations under which it was obtained. This and the other results of the paper are illustrated using argon and several other fluids.