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The latent heat of vaporization of supercritical fluids DANIEL BANUTI, MURALIKRISHNA RAJU, Stanford University, JEAN-PIERRE HICKEY, University of Waterloo, MATTHIAS IHME, Stanford University — The enthalpy of vaporization is the energy required to overcome intermolecular attractive forces and to expand the fluid volume against the ambient pressure when transforming a liquid into a gas. It diminishes for rising pressure until it vanishes at the critical point. Counterintuitively, we show that a latent heat is in fact also required to heat a supercritical fluid from a liquid to a gaseous state. Unlike its subcritical counterpart, the supercritical pseudoboiling transition is spread over a finite temperature range. Thus, in addition to overcoming intermolecular attractive forces, added energy simultaneously heats the fluid. Then, considering a transition from a liquid to an ideal gas state, we demonstrate that the required enthalpy is invariant to changes in pressure for $0 < p < 3p_{\mathrm{cr}}$. This means that the classical pressure-dependent latent heat is merely the equilibrium part of the phase transition. The reduction at higher pressures is compensated by an increase in a nonequilibrium latent heat required to overcome residual intermolecular forces in the real fluid vapor during heating. At supercritical pressures, all of the transition occurs at non-equilibrium; for $p \to 0$, all of the transition occurs at equilibrium.

Daniel Banuti
Stanford University

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