

The Intramolecular Pressure and the Extension of the Critical Point's Influence Zone on the Order Parameter

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The critical point affects the coexistence behavior of the vapor-liquid equilibrium densities. The length of the critical influence zone is under debate because for some properties, like shear viscosity, the extension is only a few degrees, while for others, such as the density order parameter, the critical influence zone covers up to hundreds of degrees below the critical temperature. Here we show that, for ethane, the experimental critical influence zone covers a wide zone of tens of degrees (below the critical temperature) down to a transition temperature, at which the apparent critical influence zone vanishes, and the transition temperature can be predicted through a pressure analysis of the coexisting bulk liquid phase, using a simple molecular potential. The liquid phases within the apparent critical influence zone show low densities, making them behave internally like their corresponding vapor phases. Therefore, Molecular Dynamics simulations reveal that the experimentally observed wide extension of the critical influence zone is the result of a vapor-like effect due to low bulk liquid phase densities.