455a Phase Transitions and Criticality in Small Nanoscale Systems

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Phase transformations in small nanoscale systems, which demonstrate characteristic signatures of 1st order phase transitions, have been extensively documented in experiments and molecular simulations of various systems ranging from molecular clusters to confined fluids. From the positions of statistical mechanics, a rigorous interpretation of these observations represents a fundamental problem. Nanoscale systems are essentially small, finite volume systems, in which the thermodynamic functions are analytical so that the very definition of phase transitions has to be revisited. The concept of the thermodynamic limit is no longer valid, and the statistical ensembles (canonical and grand canonical) are not equivalent. The phase transitions in finite systems are characterized by a convexity anomaly of thermodynamic potentials and van der Waals-type caloric curves and isotherms. We present a rigorous statistical mechanical framework for the description and molecular simulations of phase transitions in small confined systems, which is based on the mesoscopic canonical ensemble (MCE) [1]. The sample system is considered in chemical equilibrium with a finite reservoir of ideal particles called the gauge cell. By varying the gauge cell volume, one can control the level of density fluctuations in the sample system and study the states that are stable in the canonical ensemble yet unstable (or metastable) in the grand canonical ensemble. The method is illustrated on the example of vapor-liquid transition (capillary condensation) in spherical cavities. [1].A.V. Neimark and A. Vishnyakov, J. Chem. Phys., 2005, v. 122, 234108