

Calculations of Virial Coefficients and Free Energies

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In the gas phase and supercritical region, thermodynamic properties of substances may be most efficiently calculated from a virial expansion of the pressure in powers of the density. The N 'th virial coefficient B_N that occurs in this expansion is calculated from the intermolecular potential for clusters containing 2 to N molecules. The computational cost of a direct calculation of B_N scales worse than factorially with N , and the feasibility limit of direct calculations is $N=8-10$, which can be insufficient in the supercritical region. The author recently devised a new method of calculation which scales only exponentially with N , making calculations up to $N=15$ possible. The method appears to be numerically stable, and can be applied without extra cost to non-pair-additive potential energy functions. In the liquid phase, free energies relative to the ideal gas reference are more difficult to calculate. Promising results have been obtained for realistic molecular models using nested sampling (also known as energy partitioning), which calculates the density of states directly relative to the ideal gas. This allows the free energy to be calculated as a function of temperature from a single simulation. The nested sampling method can be used to calculate thermodynamics of liquid mixing and of the liquid-gas phase transition, and recent work has enabled the calculation of free energies for solids, and thermodynamic properties of solid-liquid equilibria.