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Algorithms and Interaction Potentials
phase density, surface tension and carbon dioxide

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Abstract

This thesis is an amalgamation of articles (Papers I–V) by the author.

We present a perturbation algorithm to calculate the phase density, and thus the partition function including its temperature dependence. It works for Hamiltonians that are not too dissimilar, for which an extra degree of freedom interpolating between the two is defined so that microcanonical sampling allows the calculation of the ratio between the phase densities at any energy. The method is illustrated on a number of problems of different dimensionalities. In Paper I, we consider an anharmonic Einstein crystal, the square-well tetradecamer, and liquid gold. In addition, we consider the one-dimensional rotor and the low-dimensional ideal gas in a homogeneous external field, two Hamiltonians that display a phase transition at well-defined critical energies.

We consider the interaction of linear molecules and discuss two coarse-grained pair potentials for their description. In Paper III, one of these potentials has been parametrized for the vapor-liquid envelope of carbon dioxide using two adjustables obtaining good agreement, but for a detailed description of the carbon dioxide dimer and trimer structures, such coarse-graining fails. As reported in Paper IV, conventional all-atom force field descriptions also fail in describing the experimental second and third virial coefficients but an all-atom description with coarse-grained, single-site anisotropic three-body dispersion and single-site electrostatic induction manages to reproduce them. In addition, we note that this simple anisotropic three-body dispersion correction is essential for predicting the correct relative stability of the experimental trimer conformations when combined with a literature parametrization of the dimer *ab initio* potential energy surface.

We present a simple method for calculating the surface tension with respect to vacuum from cluster simulations, by relating the scalar pressure to the infinitesimal isothermal pressure-volume work and equating it with the expression from classical nucleation theory. We then discuss the effect of molecular polarization on the surface tension using this method, as well as study its effect on the second and third virial coefficients of the fluid of polarizable Stockmayer molecules. The surface tension increases with polarizability, but so does its rate of decrease with temperature. The Tolman length is found positive and largely insensitive to temperature but increases non-linearly with increasing molecular polarizability.

We discuss the semi-empirical calculation of the crystal-water surface tension of the pharmaceutical bicalutamide as reported in Paper V and provide a slight modification of the procedure.