

Effect of the Attractive Interactions in a Simple Molecular Model

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We present a computer simulation investigation of a simple molecular model (HGOSW) consisting of elongated molecules with superimposed square-well attractive interactions [1]. The repulsive pair interactions are represented by a hard Gaussian overlap (HGO) model, which is similar (but not equal) to a model of hard molecules with ellipsoidal shape. In the absence of attractive interactions, the HGOSW model reduces to the purely repulsive HGO model. On the other hand, the HGOSW model reduces to the standard square-well model appropriate for spherically symmetric interactions when the anisotropy parameter is set equal to $k=1$. For sufficiently elongated molecules, the HGO model is known to exhibit an orientationally ordered (nematic) phase before crystallization [2]. When the attractive interactions are explicitly considered, the HGOSW model exhibits, in addition to the nematic phase, a smectic A phase where the molecules are arranged in layers with no positional in-layer order [3,4].

In this communication we present the results of a thorough study of the phase behaviour of the HGOSW model for model parameters $k=5$ (molecular anisotropy) and $l=1.5$ (range of the attractive interactions). Depending on the temperature and pressure, the observed sequence of phases is isotropic-nematic-smectic-solid. From a global analysis we first bracket the approximate location of several triple points in the phase diagrams beyond which the liquid crystal (nematic or smectic) phases are no longer stable. The coexistence lines are determined from a combination of different simulation techniques that involve the calculation of the free energy (or chemical potential) of all the phases: thermodynamic integration, Einstein-crystal method, and Gibbs-Duhem integration. Our main conclusions are: (1) the attractive interactions are largely responsible for the stabilization of the smectic phase. (2) The nematic-to-smectic transition is continuous at high temperature and first order at low temperatures. According to this, the model exhibits a tricritical point. (3) The smectic-like ordering turns unstable at sufficiently high temperature, where the repulsive interactions are expected to dominate over the attractions.

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