Phase Diagram of Hard Ellipsoids Revisited

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A system of hard ellipsoids of revolution (HER) is a very valuable model for studying colloidal liquid crystals. The exact location of the phase boundaries is therefore an interesting matter. In their seminal work, Frenkel and Mulder [1] partially addressed this issue. They studied the phase diagram of the HER model for small elongations k ($1/3 < k < 3$) and located the different phase transitions from a computation of the free energy of all of the phases. Four phases are identified: isotropic liquid (I), nematic (N), plastic solid (P), and orientationally ordered solid (S). Camp et al. [2] later studied the I-N transition for larger molecular elongations ($5< k <20$) using the Gibbs-Duhem integration technique. Although the phase diagram of the HER model is partially known, some questions still remain unanswered. Firstly, it is necessary to establish the boundaries of the solid phases for large elongations, thus completing the work carried out by Frenkel and Mulder, and Camp et al. Secondly, it would be interesting to perform a full free-energy analysis of the relative stability of different crystalline structures. Though a crystalline structure with ABC stacking is expected to be the most stable structure, recent studies [3] suggest that a simple monoclinic structure may actually be the thermodynamically stable crystalline structure at the melting transition. We address these issues in this communication and revisit the phase diagram of the HER model for molecular elongations $1 < k < 10$ using different simulation techniques, such as thermodynamic integration, Einstein crystal method, and Gibbs-Duhem integration. Our results are compared with those obtained for a closely related molecular model: the hard Gaussian overlap [4,5].

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