Vapor-liquid phase coexistence of square-well ellipsoids: the empty liquid limit

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AIMS:
- Studying the vapor-liquid coexistence of square-well ellipsoids.
- Studying the trend for large anisotropies of the critical temperature and density.
- Determining the boundaries between mesophases.
- Determining the structure of the vapor-liquid interface.

INTERACTION POTENTIAL

\[ u(r) = \begin{cases} \infty, & r < r_{\text{SW}}, \\ -\sigma_{\text{SW}} \sum_{i} \chi_{i} \left( A_{i}^{+} \right)^{-1}, & r_{\text{SW}} < r < r_{\text{SW}} + \lambda, \\ 0, & r > r_{\text{SW}} + \lambda. \end{cases} \]

Analytical approximation, modified Berne and Pechucas (MBP) [1-3]:

\[ \sigma_{\text{SW}} = \sigma_{0} \left( 1 - \frac{1}{2} \left( A_{+}^{2} + A_{-}^{2} \right) \right)^{-1}, \]

\[ A_{\pm} = \left( \frac{a_{\pm} + b_{\pm}}{1 + \beta_{\pm}} \right)^{2}, \]

Model parameters for a prolate. We introduce \( k = \frac{a_{\pm}}{b_{\pm}} \).

REPLICA EXCHANGE MC [4,5]

We use a temperature expansion of the Canonical ensemble to access the liquid-vapor coexistence:

\[ Q_{\text{LVE}} = \prod_{i=1}^{N} Q_{\text{STP}}, \]

\[ P_{\text{LVE}} = \min \left\{ 1, \exp\left[ \beta \left( U_{\text{L}} - U_{\text{V}} \right) \right] \right\}. \]

In this case prism cells are used where the liquid phase is set as a slice at their centers. Vapor appears at their sides. We consider 800 particles and M=14 replicas.

We use a pressure expansion of the isothermal ensemble [6] to determine the mesophase boundaries.

\[ Q_{\text{rLVE}} = \prod_{i=1}^{N} Q_{\text{STP}}, \]

\[ P_{\text{rLVE}} = \min \left\{ 1, \exp\left[ \beta \left( P_{\text{L}} - P_{\text{V}} \right) \right] \right\}. \]

In this case we set cubic cells with N=220 and M=16 replicas. The use of REMC avoids hysteresis at the mesophase boundaries. REMC and histogram reweighting provide a nice combination to determine phase boundaries.

RESULTS

** Vapor-liquid coexistence: Oblates (k=3, λ=0.25) **

Snapshots showing equilibrated configurations of simulation cells containing 800 oblate particles for high (right) and low (left) λ.

** Vapor-liquid coexistence: Prolates (k=1/3, λ=0.25) **

Snapshots showing equilibrated configurations of simulation cells containing 800 prolate particles for high (right) and low (left) λ.

** The isotropic-nematic transition and more for k=5 and 1/5 **

Radial distribution functions (axial and rotational) 2nd and 4th Legendre polynomials for the different mesophases detected under different thermodynamic conditions. Systems have k=1/5 and k=5 (oblates at the left) and k=1/3 (prolates at the right). The obtained mesophases are isotropic (black), nematic (red dotted), cubatic (blue dotted), and urchin-like (black solid). The isotropic limit was detected. The urchin-like phase was detected. The corresponding order parameter profiles are shown in Fig. 4. The obtained mesophases were detected. The isotropic limit was detected. The urchin-like phase was detected.

** Compressibility factor, Z, isothermal compressibility, λ, potential energy, E, and isothermal compressible, Z, for prolate. The vertical dashed line shows the critical temperature. Examples of the largest detected aggregate for high (oblate) and low (prolate) explored temperatures. Examples of the largest detected aggregate for high (oblate) and low (prolate) explored temperatures. Examples of the largest detected aggregate for high (oblate) and low (prolate) explored temperatures.**

** BIBLIOGRAPHY:**