Comment on “Equilibrium polymerization and gas-liquid critical behavior in the Stockmayer fluid”

A. O. Ivanov* and S. S. Kantorovich

Department of Mathematical Physics, Ural State University, 51 Lenin Avenue, Ekaterinburg 620083, Russia

Philip J. Camp

School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom

(Received 25 April 2007; published 4 January 2008)

In a recent paper [Phys. Rev. E 75, 011506 (2007)] Hentschke et al. presented new results on the vapor-liquid transition in the Stockmayer fluid. In this Comment, we analyze the data further and demonstrate that at high dipole strength, the isotropic attractive part of the Stockmayer potential is negligible compared to the thermal energy at the vapor-liquid critical point. The results therefore suggest that the transition is largely driven by the dipolar interactions.

DOI: 10.1103/PhysRevE.77.013501

Hentschke, Bartke, and Pesth [1] have recently presented a theoretical model of chain formation in the Stockmayer fluid at high dipolar strengths, and have described the zero-field vapor-liquid critical behavior. The Stockmayer (Lennard-Jones plus dipole-dipole) pair potential is

\[ u(r) = 4\epsilon \left[ \frac{(\sigma/r)^6}{(\sigma/r)^12} - \frac{1}{2} \left( \frac{\sigma/r}{6} \right)^6 \right] + \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5}, \]

where \( \epsilon \) is the isotropic well depth, \( \sigma \) is the range parameter, \( \mu_i \) is the dipole moment on particle \( i \), and \( r \) is the length of the interparticle separation vector \( r \). Reduced quantities are defined as follows: \( T^* = k_B T/\epsilon \) is the reduced temperature; \( (\mu^*)^2 = \mu^2/\epsilon \sigma^3 \) is the characteristic dipolar energy; \( \lambda = (\mu^*)^2/T^* \) is the dipolar coupling constant; \( \rho = N\sigma^3/V \) is the reduced number density of \( N \) particles in a volume \( V \).

One of the most significant findings presented in the Conclusion of Ref. [1] is that, “...[the authors] do not find evidence, in either simulation or theory, for an abrupt disappearance of the gas-liquid critical point found to occur in earlier simulation work.” This result seems to be of principal importance because it has often been claimed that in dipolar fluids the condensation can only take place in the presence of additional isotropic attractions. The results obtained in Ref. [1] together with the analysis presented below indicate that the vapor-liquid phase transition might be found not only in the Stockmayer fluid but also in dipolar soft-sphere or hard-sphere systems.

Dudowicz, Freed, and Douglas [2] summarized the simulation results on the vapor-liquid critical point obtained in the late 1980s and early 1990s [3–7] and showed that the reduced critical temperature \( T_c^* \) increases linearly with increasing \( (\mu^*)^2 \) in the range \( (\mu^*)^2 \geq 2 \). The largest dipolar energy investigated in those simulations was \( (\mu^*)^2 = 24 \) and the corresponding critical temperature was \( T_c^* = 7 \) [5]. Hentschke, Bartke, and Pesth [1] have presented some new simulation points in the range 16 \( \leq (\mu^*)^2 \leq 36 \). In Fig. 1 we plot the inverse critical temperature \( 1/T_c^* \) and the inverse critical coupling constant \( 1/\lambda_c \) against dipolar energy \( (\mu^*)^2 \). A linear fit to the relation \( 1/T_c^* = A + B(\mu^*)^2 \) in the range \( (\mu^*)^2 \geq 10 \) gives \( A = 0.98 \pm 0.05 \) and \( B = 0.259 \pm 0.002 \); hence \( 1/\lambda_c = B + \lambda_c/(\mu^*)^2 \) (essentially identical to a fit presented in Ref. [7]). The curves are shown in Fig. 1. As \( (\mu^*)^2 \to \infty \), \( T_c^* \) remains proportional to \( (\mu^*)^2 \), but \( \lambda_c \) approaches a limiting value of 3.86. Therefore the condensation of the Stockmayer fluid occurs at finite values of the dipolar coupling constant even though the Lennard-Jones well depth \( \epsilon \) is insignificant compared to both the dipolar energy and the thermal energy at the critical point.

An important point (also mentioned by Hentschke, Bartke, and Pesth [1]) is that in the strongly dipolar regime, the Lennard-Jones attraction is negligible in the vicinity of the critical point and therefore it cannot play a dominant role. In other words, in strongly dipolar systems with \( (\mu^*)^2 \gg 1 \), the Lennard-Jones potential renders the particles as simply “very soft” spheres. A key question then arises: “What provides the driving force for the condensation of strongly dipolar Stock-

![FIG. 1. (Color online) Inverse critical temperature $1/T_c^*$ (filled symbols) and inverse critical coupling constant $1/\lambda_c$ (open symbols) against dipolar energy $(\mu^*)^2$. Points are simulation results: black circles Ref. [3]; red squares Ref. [4]; green diamonds Ref. [5]; blue up triangles Ref. [6]; black left triangles Ref. [7]; red down triangles Ref. [1]. The lines show the functions $1/T_c^* = 1/(0.98 + 0.259(\mu^*)^2)$ and $1/\lambda_c = 0.259 + 0.98/(\mu^*)^2$ fitted to the data with $(\mu^*)^2 \geq 10.$](image-url)
FIG. 2. (Color online) The inverse effective critical coupling constant $1/\lambda_e$ (filled symbols) and effective critical density $\rho_e^*$ (open symbols) against dipolar energy $(\mu^*)^2$. Points are simulation results from Fig. 1, scaled by the effective hard-sphere diameter (see text). The solid line shows the function $1/\lambda_e=0.177+1.47/(\mu^*)^2$ fitted to the data with $(\mu^*)^2 \approx 10$.

The answer is that cohesive interactions must arise predominantly from interactions between the dipoles. So, we cannot but blame the dipolar interactions for giving rise to a vapor-liquid phase transition. This conclusion seems to be of principal nature since the widespread opinion is that the noncentral dipole-dipole interaction alone does not result in condensation, but only drives chain formation at low concentration and ferroelectric ordering at high concentration; for a recent review see Ref. [8]. To our knowledge the only (recent) exceptions are simulations of dipolar hard particles in Refs. [9,10] (to be discussed below).

Now let us discuss the critical density $\rho_e^*$. Simulations predict a decrease in $\rho_e^*$ with increasing $(\mu^*)^2$ (see Fig. 3 in Ref. [1], and Fig. 2 in Ref. [2]). For large values of $(\mu^*)^2 \approx 20–36$ the critical density lies in the region $\rho_e^* \approx 0.1–0.2$. The dispersion of simulation points and the simulation uncertainties are both rather large, and one cannot say for sure what the asymptotic value is in the limit $(\mu^*)^2 \rightarrow \infty$. However, it is worth commenting that the theoretical models developed in Refs. [1,2] show a tendency to approach a value in the region of $\rho_e^* \approx 0.15$.

A mapping is now sought between the critical parameters for the dipolar hard-sphere fluid, and those for the Stockmayer fluid at high dipolar strength. Near the critical point of the Stockmayer fluid in the strongly dipolar regime, the interparticle repulsion in the Stockmayer fluid is very soft and the particles may approach closer than the range $\sigma$. In other words, the effective hard-core diameter $\sigma_e$ of the softened repulsion will be smaller than $\sigma$. Therefore the effective critical dipolar coupling constant $\lambda_e=\mu^2/k_BT\sigma_e^2=\lambda_e(\sigma/\sigma_e)^2$ will be larger than the asymptotic value of $\lambda_e \approx 3.86$ obtained above. For the purposes of illustration, the effective hard-sphere diameter is estimated using the Barker-Henderson formula [11] for the repulsive part of the Weeks-Chandler-Andersen partition of the Lennard-Jones potential, which is

$$u_R(r) = \begin{cases} 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \epsilon & r \leq 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma. \end{cases}$$

The attractive part is bounded from below by $-\epsilon$, and so this perturbation is insignificant in the limit $(\mu^*)^2 \rightarrow \infty$. The Barker-Henderson formula is

$$\sigma_e = \int_{0}^{\infty} \{ 1 - \exp[ -u_R(r)/k_BT ] \} dr. \tag{3}$$

Figure 2 shows $1/\lambda_e$ as a function of $(\mu^*)^2$; fitting a function $1/\lambda_e= B_e+ A_e/ (\mu^*)^2$ gives $A_e=1.47\pm0.04$ and $B_e=0.177\pm0.003$. The limiting value $B_e$ is rather close to the corresponding values of 0.16 [9] and 0.153 [10] for dipolar hard particles. The effective critical density $\rho_e=\rho_e(\sigma_e/\sigma)^3$ is also shown in Fig. 2; a limiting value in the region of 0.1 seems reasonable. This is in accord with simulations of hard dipolar particles for which the corresponding critical density is approximately 0.1 [9,10].

In conclusion, the simulation data obtained by Hentschke, Bartke, and Pesth [1], which agree perfectly with previous results for the Stockmayer fluid, appear to approach the dipolar soft-sphere limit (with no isotropic attractions) which can, in turn, be mapped onto a system of dipolar hard spheres with some effective particle diameter. In the latter systems the condensation can only take place because of the dipole-dipole interactions. Therefore this analysis lends weight to the possibility of vapor-liquid phase separation in purely dipolar systems.

The work was supported by INTAS Grant No. 03-51-6064, DFG-RBRF Joint Grants No. HO 1108/12-1 and No. 06-02-04019. S.S.K. acknowledges support from the CRDF and President of Russian Federation Grant No. MK-4836.2006.2.