Reply to "Comment on 'Equilibrium polymerization and gas-liquid critical behavior in the Stockmayer fluid'"

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In their Comment, Ivanov, Kantorovich, and Camp [Phys. Rev. E. **77**, 013501 (2008)] analyze molecular dynamics simulation data on the gas-liquid critical point of the Stockmayer fluid obtained recently by the authors. Based on this analysis they conclude that vapor-liquid phase separation may occur in purely dipolar systems. In this reply we argue that the existing data for the Stockmayer fluid as well as a related system are consistent with the nonexistence of vapor-liquid phase separation in purely dipolar systems.

In Ref. [1] we discuss the implications of the mapping that exists between the Stockmayer (St) fluid, for which the gas-liquid (GL) phase coexistence has been studied via molecular dynamics simulation in Refs. [1,2], and a second model consisting of a Lennard-Jones (LJ) potential with adjustable dispersion attraction in addition to the same dipole-dipole term as in the St fluid. The latter model was studied via Gibbs-ensemble Monte Carlo simulation by van Leeuwen and Smit [3]. The St potential is given by

$$\frac{U_{\mathrm{St}}(r_{\mathrm{St}},\mu_{\mathrm{St}})}{T_{\mathrm{St}}} = \frac{4}{T_{\mathrm{St}}}\left(\frac{1}{r_{\mathrm{St}}^{12}} - \frac{1}{r_{\mathrm{St}}^{6}}\right) - \frac{\mu_{\mathrm{St}}^{2}}{T_{\mathrm{St}}r_{\mathrm{St}}^{3}}f, \quad (1)$$

where f is simply a function of the relative orientation of two interacting dipoles. The quantities r_{St}, μ_{St}, and T_{St} refer to interparticle separation, magnitude of the dipole moment, and temperature, respectively. The other potential, here denoted as vLS, is

$$\frac{U_{\mathrm{vLS}}(r_{\mathrm{vLS}},\mu_{\mathrm{vLS}})}{T_{\mathrm{vLS}}} = \frac{4}{T_{\mathrm{vLS}}}\left(\frac{1}{r_{\mathrm{vLS}}^{12}} - \lambda\frac{1}{r_{\mathrm{vLS}}^{6}}\right) - \frac{\mu_{\mathrm{vLS}}^{2}}{T_{\mathrm{vLS}}r_{\mathrm{vLS}}^{3}}f, \quad (2)$$

where λ is a parameter. Notice that the vLS potential includes the dipolar soft sphere (DSS) potential in the limit $\lambda \to 0$. Based on the GL phase behavior of this model for a series of λ one may attempt the extrapolation of the critical parameters to the DSS limit. The same holds true for the St fluid, because, as was already pointed out by others (cf. Sec. 2 in Ref. [4]), the two formulas for U/T may be converted into each other via the relations $T_{\mathrm{St}} = \lambda^{-2}T_{\mathrm{vLS}}$, $\rho_{\mathrm{St}} = \lambda^{-1/2}\rho_{\mathrm{vLS}}$, and $\mu_{\mathrm{St}} = \lambda^{-3/4}\mu_{\mathrm{vLS}}$. Notice that $\exp[-U/T]$ determines configurational averages in the *NVT* ensemble.

Figure 1 shows GL critical temperatures, $T_{c,\mathrm{St}}$, plotted vs μ_{St}^{2} obtained via computer simulation by different groups. Here the hollow squares are the data from van Leeuwen and

Smit [3] converted via the above relations (using $\mu_{\mathrm{vLS}}=2$). The most striking feature perhaps is the apparent linear dependence of $T_{c,\mathrm{St}}$ on μ_{St}^{2}, which is found by all groups who have studied dipole strengths above $\mu_{\mathrm{St}}^{2} \approx 4$ (see also Fig. 1 in the Comment by Ivanov *et al.* [7]).

Figure 2 shows the same data converted via the above relations to $T_{c,\mathrm{vLS}}$ vs λ (upper panel) as well as the corresponding critical densities (taken from Fig. 3 in Ref. [2]) analogously converted to, $\rho_{c,\mathrm{vLS}}$ vs λ (bottom panel). The solid line in the upper panel is obtained by inserting the straight line fit from Fig. 1, $T_{c,\mathrm{St}} = m\mu_{\mathrm{St}}^{2} + b$ (with $m \approx 0.2587$ and $b \approx 1.0006$; including only data for $\mu_{\mathrm{St}}^{2} \geq 4$ in the fit) into $T_{c,\mathrm{vLS}} = \lambda^{2}T_{c,\mathrm{St}}$, i.e., $T_{c,\mathrm{vLS}} = \lambda^{2}(m\lambda^{-3/2}\mu_{\mathrm{vLS}}^{2} + b) = \lambda^{1/2}m\mu_{\mathrm{vLS}}^{2} + \lambda^{2}b$. This result is shown as a solid line in the upper panel of Fig. 2. Notice that the agreement with the simulation data is excellent for $\lambda < 1$. For $\lambda > 1$ the deviation is expected, because this case corresponds to $\mu_{\mathrm{St}}^{2} < 4$ in Fig. 1, where the dependence of $T_{c,\mathrm{St}}$ on μ_{St}^{2} is not linear. Notice also that $T_{c,\mathrm{vLS}} \sim \lambda^{1/2} \to 0$ for $\lambda \to 0$ or $\mu_{\mathrm{St}}^{2} \to \infty$ (at fixed
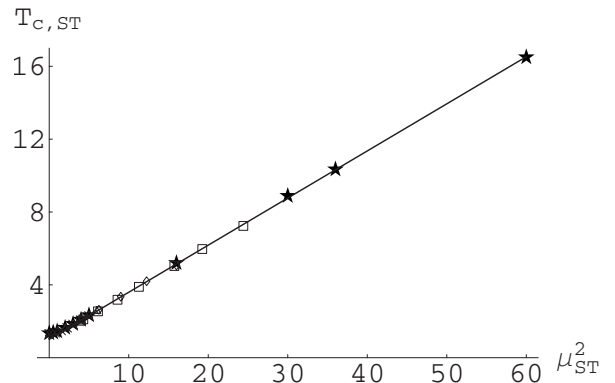

FIG. 1. Gas-liquid critical temperature $T_{c,\mathrm{St}}$ of the Stockmayer fluid vs dipole strength μ_{St}^{2}. Symbols indicate computer simulation results (stars: this group; the value at $\mu_{\mathrm{St}}^{2}=60$ is new and was not included in Ref. [1]; the method of computation, however, is the same as described previously); hollow squares: Ref. [3]; hollow diamonds: Ref. [4]; hollow triangles: Ref. [5]; crosses: Ref. [6]).
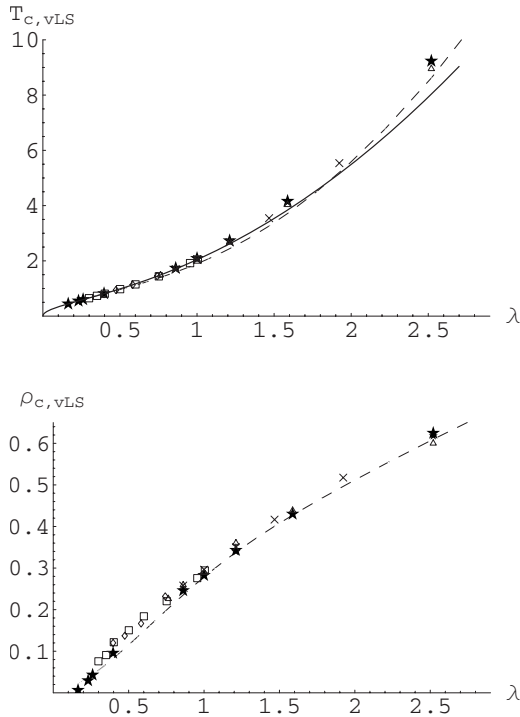
FIG. 2. Top: Gas-liquid critical temperature $T_{c,\mathrm{vLS}}$ of the vLS fluid vs λ. Symbols indicate computer simulation results (stars: this group; note that $T_{c,\mathrm{St}} \approx 16.5$ and $\rho_{c,\mathrm{St}} \approx 0.025$ at $\mu_{\mathrm{St}}^2 = 60$); hollow squares: Ref. [3]; hollow diamonds: Ref. [4]; hollow triangles: Ref. [5]; crosses: Ref. [6]). The solid line corresponds to the linear approximation of $T_{c,\mathrm{St}}$ shown in the previous figure. The dashed line is the result obtained via the lattice theory developed in Ref. [2], where the same result is shown in Fig. 3 (top panel). Bottom: Gas-liquid critical density, $\rho_{c,\mathrm{vLS}}$, of the vLS fluid vs λ. Symbol types correspond to those in the upper panel. The dashed line is the result obtained via the lattice theory developed in Ref. [2], where this result, but as $\rho_{c,\mathrm{St}}$ vs μ_{St}^2, is shown in Fig. 3 (bottom panel).

μ_{vLS}). Thus according to the scaling argument presented here, there should be no finite GL critical temperature in the DSS system.

The dashed line included in the upper panel of Fig. 2 is our lattice theory according to Fig. 3 in Ref. [2] mapped to the vLS system via the above relations. The dashed line in the bottom panel of Fig. 2 shows the analogous mapping of the lattice theory for the critical density. Notice that here we use the relation $\rho_{\mathrm{vLS}} = \lambda^{1/2} \rho_{\mathrm{St}}$. Thus because the simulations yield a monotonous decrease of $\rho_{c,\mathrm{St}}$ with increasing μ_{St}^2, we do expect that $\rho_{c,\mathrm{vLS}}$ vanishes for small λ. The lattice theory in fact yields $\rho_{c,\mathrm{vLS}} \to 0$ for $\lambda \to 0$.

Therefore we conclude that in the DSS limit a vanishing GL critical temperature and a simultaneously vanishing GL critical density is consistent with the simulation data obtained thus far for the St and vLS models. In principle of course there may be other types of phases and phase transitions intervening before the limit is reached, which are not included at present (cf. the Conclusion section of Ref. [1]). However, direct simulations of the DSS system under conditions for which the dipolar hard sphere (DHS) system was investigated (cf. below) did not reveal evidence for GL phase separation [8]. We remark that recently Ganzenmüller and Camp have used extensive computer simulations to study vapor-liquid coexistence in fluids of charged hard dumbbells [9]. In the limit of vanishing dumbbell length and constant dipole moment this system approaches the limit of dipolar hard spheres. The analysis of the DHS limit lead the authors to conclude that this system should indeed show GL phase separation (see also Ref. [10]). We note that the DHS interaction differs from the system discussed here due to the distinct length scale of the repulsive interaction which the above power law repulsion does not possess. Overall therefore the question whether or not purely dipolar attraction may lead to GL phase separation to us appears to be unsettled.

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