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Gas-liquid phase coexistence in quasi-two-dimensional Stockmayer fluids: A molecular dynamics study

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The Maxwell construction together with molecular dynamics simulation is used to study the gas-liquid phase coexistence of quasi-two-dimensional Stockmayer fluids. The phase coexistence curves and corresponding critical points under different dipole strength are obtained, and the critical properties are calculated. We investigate the dependence of the critical point and critical properties on the dipole strength. When the dipole strength is increased, the abrupt disappearance of the gas-liquid phase coexistence in quasi-two-dimensional Stockmayer fluids is not found. However, if the dipole strength is large enough, it does lead to the formation of very long reversible chains which makes the relaxation of the system very slow and the observation of phase coexistence rather difficult or even impossible. © 2011 American Institute of Physics. [doi:10.1063/1.3521393]

I. INTRODUCTION

Dipolar fluids have remained an outstanding interest to researchers in the fields of soft matter physics such as liquid crystals, colloidal ferrofluids, and polymers. Among those studies of dipolar fluids, there are mainly three models in theory and computer simulations: the dipolar hard sphere model, the dipolar soft sphere model, and the Stockmayer model. Dipolar fluids may lead to complex structure, e.g., the formation of reversible chains, which in turn influences the phase behavior of the whole system.^{1–10} Until now there are still some debates and open questions among the topics about the phase behavior and structure in dipolar fluids (e.g., Refs. 11–13), and it has presented considerable challenges to soft matter physics.

In Stockmayer fluids, the particles interact via a normal 12–6 Lennard-Jones potential plus a dipole-dipole potential. Because of the existence of attractive interaction, the Stockmayer fluids can have a gas-liquid (GL) phase transition. In 1993, van Leeuwen and Smit used Gibbs ensemble Monte Carlo (GEMC) technique to study the GL phase behavior of three-dimensional (3D) Stockmayer fluids. They concluded, based on the simulation work, that the GL phase coexistence of the Stockmayer system will disappear when the dipole-dipole interaction becomes dominant, and they attributed it to the formation of a nose-to-tail chain.¹⁴ A different conclusion was reached by Dudowicz, Freed, and Douglas when they mapped the Stockmayer system onto their Flory–Huggins type lattice model. They found that the GL phase coexistence of the Stockmayer system should occur for all dipole strengths.¹⁵ In the later molecular dynamics (MD) simulations by Bartke and Hentschke, the evidence of an abrupt disappearance of the GL critical point in the Stockmayer system was not observed.^{16,17}

Previously people have obtained a significant progress in the research on 3D dipolar fluids. However, the two-

dimensional (2D) dipolar fluids have recently received much attention because many systems can be modeled as 2D system. Furthermore, the 2D dipolar system is more directly relevant to common experimental situations than those on bulk systems, because the structural characterization of highly aggregated ferrofluids in experiments is largely carried out on thin films or monolayers.^{18–21} In the present work we focus on the GL phase coexistence and critical properties in quasi-2D Stockmayer system, where the particles are confined in a plane but the orientation of their dipoles can be freely rotated in 3D space. To our best knowledge, very few studies of the GL phase coexistence in 2D Stockmayer system are found. For instance, Gao and Zeng *et al.* ever employed GEMC to study the GL phase coexistence of quasi-2D Stockmayer fluids,²² but they only gave the phase coexistence curve under a few variants of dipole strength, which probably may be due to the computational difficulties. Therefore, the issue as to whether or not the GL phase coexistence of quasi-2D Stockmayer system disappears as the dipole-dipole interaction becomes more and more dominant is still open.

In this paper, we apply the Maxwell construction approach together with MD simulation to investigate the GL phase coexistence of quasi-2D Stockmayer fluids. The full GL phase coexistence curves under different dipole strengths are reported. The critical points are derived and the corresponding critical properties are calculated so as to explore how the dipole strength affects the GL phase coexistence and the critical points of quasi-2D Stockmayer fluids. In addition, we attempt to answer the question as to whether there is an abrupt disappearance of GL phase coexistence in quasi-2D Stockmayer fluids.

II. MODEL AND SIMULATION METHODOLOGY

The interacting potential in Stockmayer system is given by adding a dipole-dipole interaction term to the normal

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12-6 Lennard-Jones potential, which can be written as

$$U_{SM} = U_{LJ} + U_{DD}. \quad (1)$$

The normal 12-6 Lennard-Jones potential is defined as

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2)$$

where r_{ij} is the pair distance between i th particle and j th particle. The parameter ϵ governs the strength of the interaction and σ defines a length scale. For convenience, the reduced units are used in the simulation, where ϵ , σ , and the mass of Lennard-Jones particle m are chosen as basic units.

The second part in Eq. (1) is the dipole-dipole interacting potential expressed as,

$$U_{DD} = \frac{\mu^2}{r_{ij}^3} \left(\mathbf{s}_i \cdot \mathbf{s}_j - \frac{3}{r_{ij}^2} (\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij}) \right), \quad (3)$$

where μ is the dipole moment $\mathbf{s}_i$ and $\mathbf{s}_j$ are unit vectors of the dipole moment of i th and j th particle, respectively. Note that the positions of the particles are confined in a 2D plane while the dipoles of the particles can be freely rotated in a 3D space.

The Lennard-Jones interaction is a short-range interaction, so it can be calculated using the truncation method. Here we take the cutoff distance as half of simulation box length, i.e., $r_{\text{cut}} = L/2$. As conventionally adopted, a correction for the truncation of the thermodynamic quantities calculation is made by adding a tail contribution, namely the so-called long-range correction. In the Maxwell construction method, attention is mainly paid to the pressure. The corresponding long-range correction of the pressure for Lennard-Jones part is

$$\begin{aligned} P^{\text{tail}} &= \frac{1}{2} \int_{r_{\text{cut}}}^{\infty} 2\pi r \rho^2 dr \frac{1}{2} \mathbf{r} \cdot \mathbf{f}(\mathbf{r}) \\ &= \pi \rho^2 \epsilon \sigma^6 \left(\frac{12\sigma^6}{5r_{\text{cut}}^{10}} - \frac{3}{r_{\text{cut}}^4} \right). \end{aligned} \quad (4)$$

Note that the long-range correction of 2D Lennard-Jones system is different from that of 3D.^{23,24}

The dipole-dipole interaction is a long-range one, which can be calculated via Ewald summation method.²⁵ Since $\mathbf{r}_{ij}$ is within 2D plane and the orientation of the dipole is in 3D space, U_{DD} in Eq. (3) can be written as

$$U_{DD} = \frac{\mu^2}{r_{ij}^3} \left(\mathbf{s}_{is} \cdot \mathbf{s}_{js} - \frac{3}{r_{ij}^2} (\mathbf{s}_{is} \cdot \mathbf{r}_{ij})(\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) \right) + \frac{\mu^2}{r_{ij}^3} s_{iz} s_{jz}, \quad (5)$$

where $\mathbf{s}_{is}$ and $\mathbf{s}_{js}$ are the 2D-plane components of the dipole moment of i th and j th particle, respectively. s_{iz} and s_{jz} are the z components of the dipole moment of i th and j th particle. With such division, U_{DD} is separated into two parts. The Ewald sum of the first part in Eq. (5), i.e., the in-2D-plane part is

$$\begin{aligned} V_s &= \frac{\mu^2}{2} \sum_{i=1}^N \sum_{j=1}^N \left[\sum_{n=0}^{\infty} (\mathbf{s}_{is} \cdot \mathbf{s}_{js} a_1(|\mathbf{r}_{ij} + \mathbf{n}|) \right. \\ &\quad \left. - (\mathbf{s}_{is} \cdot \mathbf{r}_{ij})(\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) a_2(|\mathbf{r}_{ij} + \mathbf{n}|) \right. \\ &\quad \left. + \frac{4\pi^2}{L^3} \sum_{n \neq 0} (\mathbf{s}_{is} \cdot \mathbf{n})(\mathbf{s}_{js} \cdot \mathbf{n}) E(n) \exp\left(-\frac{2\pi i}{L} \mathbf{n} \cdot \mathbf{r}_{ij}\right) \right] \\ &\quad - \frac{2\alpha^3 \mu^2}{3\sqrt{\pi}} \sum_{j=1}^N s_{js}^2, \end{aligned} \quad (6)$$

where

$$\begin{aligned} a_n(r) &= \begin{cases} \frac{\text{erfc}(\alpha r)}{r^3} + \frac{2\alpha \exp(-\alpha^2 r^2)}{\sqrt{\pi} r^2} & n = 1 \\ -\frac{1}{r} \frac{d}{dr} a_{n-1}(r) & n > 1 \end{cases} \\ E(n) &= \frac{1}{n} \text{erfc}\left(\frac{\pi n}{\alpha L}\right). \end{aligned} \quad (7)$$

The Ewald sum of the second part in Eq. (5) is

$$\begin{aligned} V_z &= \frac{\mu^2}{2} \sum_{i=1}^N \sum_{j=1}^N \left[\sum_{n=0}^{\infty} s_{iz} s_{jz} a_1(|\mathbf{r}_{ij} + \mathbf{n}|) \right. \\ &\quad \left. + \frac{2\pi}{L^2} \sum_{n \neq 0} s_{iz} s_{jz} \left(\frac{2\alpha}{\sqrt{\pi}} \exp\left(-\frac{\pi^2 n^2}{\alpha^2 L^2}\right) \right. \right. \\ &\quad \left. \left. - \frac{2\pi n}{L} \text{erfc}\left(\frac{\pi n}{\alpha L}\right) \right) \exp\left(-\frac{2\pi i}{L} \mathbf{n} \cdot \mathbf{r}_{ij}\right) \right] \\ &\quad + \frac{2\alpha \mu^2 \sqrt{\pi}}{L^2} \sum_{i=1}^N \sum_{j=1}^N s_{iz} s_{jz} - \frac{2\alpha^3 \mu^2}{3\sqrt{\pi}} \sum_{j=1}^N s_{jz}^2. \end{aligned} \quad (8)$$

Here $\text{erfc}(x)$ is the complementary error function.²⁶ $\mathbf{n} = n_x \hat{i} + n_y \hat{j}$, $n_x, n_y = 0, \pm 1, \pm 2, \dots$. The prime in Eqs. (6) and (8) means the $i = j$ term for $n = 0$ is excluded.

The Ewald sums include a parameter α whose value must be determined to satisfy the desired numerical accuracy. The parameter α is chosen to ensure the terms of order $\exp(-\alpha^2 L^2)$ are negligible [note that for $x \gg 1$, $\text{erfc}(x) \sim \exp(-x^2)$], so Eqs. (6) and (8) become,

$$\begin{aligned} V_s &= \mu^2 \sum_{1 \leq i < j \leq N} ((\mathbf{s}_{is} \cdot \mathbf{s}_{js}) a_1(r_{ij}) \\ &\quad - (\mathbf{s}_{is} \cdot \mathbf{r}_{ij})(\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) a_2(r_{ij})) \\ &\quad + \frac{2\pi^2 \mu^2}{L^3} \sum_{n \neq 0} [E(n)(C(\mathbf{n})^2 + S(\mathbf{n})^2)] \\ &\quad - \frac{2\alpha^3 \mu^2}{3\sqrt{\pi}} \sum_{j=1}^N s_{js}^2, \end{aligned} \quad (9)$$

and

$$\begin{aligned} V_z &= \mu^2 \sum_{1 \leq i < j \leq N} s_{iz} s_{jz} a_1(r_{ij}) \\ &\quad + \frac{\pi \mu^2}{L^2} \sum_{n \neq 0} \left[\left(\frac{2\alpha}{\sqrt{\pi}} \exp\left(-\frac{\pi^2 n^2}{\alpha^2 L^2}\right) \right. \right. \end{aligned}$$

$$\begin{aligned}
& - \frac{2\pi n}{L} \operatorname{erfc}\left(\frac{\pi n}{\alpha L}\right) \left(S_z(\mathbf{n})^2 + C_z(\mathbf{n})^2 \right) \Big] \\
& + \frac{2\alpha\mu^2\sqrt{\pi}}{L^2} \left| \sum_{j=1}^N s_{jz} \right|^2 - \frac{2\alpha^3\mu^2}{3\sqrt{\pi}} \sum_{j=1}^N s_{jz}^2, \quad (10)
\end{aligned}$$

where

$$\begin{aligned}
C(\mathbf{n}) &= \sum_{j=1}^N (\mathbf{n} \cdot \mathbf{s}_{js}) \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_j\right), \\
S(\mathbf{n}) &= \sum_{j=1}^N (\mathbf{n} \cdot \mathbf{s}_{js}) \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_j\right), \\
C_z(\mathbf{n}) &= \sum_{j=1}^N s_{jz} \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_j\right), \\
S_z(\mathbf{n}) &= \sum_{j=1}^N s_{jz} \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_j\right). \quad (11)
\end{aligned}$$

Imposing a cutoff on the real-space sum at r_c (here r_c is taken as $r_c = L/2$) leads to an error of order $\exp(-\alpha^2 r_c^2)$. Truncating the Fourier space sum at n_c produces an error of order $\exp(-\pi^2 n_c^2 / (\alpha^2 L^2))$. Therefore, to obtain similarly sized errors in both the real and Fourier contributions to U_{DD} , we may simply set $n_c = \alpha^2 r_c L / \pi$.

The motion of particles includes the translation and the rotation of the dipoles. The equation of motion for translation is driven by the force produced by normal Lennard-Jones interactions and the force produced by the dipole-dipole interactions. The former has been used many times previously and is very familiar to researchers. The latter is obtained by evaluating $-\nabla_{\mathbf{r}_i} U_{DD}$ and consists of a sum over all particles inside the cutoff range (including the truncation range in Fourier space). From Eqs. (9) and (10), we may get the dipole contribution to the force on i th particle

$$\begin{aligned}
\mathbf{f}_{Di} &= \mu^2 \sum_{j \neq i} [((\mathbf{s}_i \cdot \mathbf{s}_j) a_2(r_{ij}) - (\mathbf{s}_{is} \cdot \mathbf{r}_{ij})(\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) a_3(r_{ij})) \mathbf{r}_{ij} \\
& + ((\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) \mathbf{s}_{is} + (\mathbf{s}_{is} \cdot \mathbf{r}_{ij}) \mathbf{s}_{js}) a_2(r_{ij})] \\
& + \frac{4\pi^2\mu^2}{L^3} \sum_{n \neq 0} \left[\frac{2\pi}{L} E(n) (\mathbf{n} \cdot \mathbf{s}_{is}) \right. \\
& \times \left(C(\mathbf{n}) \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) - S(\mathbf{n}) \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) \right) \\
& + \left(\frac{2\alpha}{\sqrt{\pi}} \exp\left(-\frac{\pi^2 n^2}{\alpha^2 L^2}\right) - \frac{2\pi n}{L} \operatorname{erfc}\left(\frac{\pi n}{\alpha L}\right) \right) s_z \\
& \times \left(C_z(\mathbf{n}) \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) - S_z(\mathbf{n}) \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) \right) \Big] \mathbf{n}. \quad (12)
\end{aligned}$$

The rotation equation of the dipole vector is the same as that of the linear rigid molecule, i.e.,

$$\ddot{\mathbf{s}}_i = I^{-1} \mathbf{g}_i - (I^{-1} (\mathbf{s}_i \cdot \mathbf{g}_i) + \dot{\mathbf{s}}_i^2) \mathbf{s}_i. \quad (13)$$

I is taken as the moment of inertia of a homogeneous sphere of mass, i.e., $I = m\sigma^2/10 = 0.1$ in reduced units. $\mathbf{g}_i = -\nabla_{\mathbf{s}_i} U_{DD}$ can be obtained from Eqs. (9) and (10);

$$\begin{aligned}
\mathbf{g}_{is} &= \mu^2 \sum_{j \neq i} [-a_1(r_{ij}) \mathbf{s}_{js} + (\mathbf{s}_{js} \cdot \mathbf{r}_{ij}) a_2(r_{ij}) \mathbf{r}_{ij}] \\
& - \frac{4\pi^2\mu^2}{L^3} \sum_{n \neq 0} \left[C(\mathbf{n}) \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) \right. \\
& + S(\mathbf{n}) \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) \Big] E(n) \mathbf{n} + \frac{4\alpha^3\mu^2}{3\sqrt{\pi}} \sum_{j=1}^N \mathbf{s}_{js}, \quad (14)
\end{aligned}$$

and

$$\begin{aligned}
g_{iz} &= \mu^2 \sum_{j \neq i} -a_1(r_{ij}) s_{jz} - \frac{4\pi^2\mu^2}{L^3} \\
& \sum_{n \neq 0} \left[C_z(\mathbf{n}) \cos\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) + S_z(\mathbf{n}) \sin\left(\frac{2\pi}{L} \mathbf{n} \cdot \mathbf{r}_i\right) \right] \\
& \times \left(\frac{2\alpha}{\sqrt{\pi}} \exp\left(-\frac{\pi^2 n^2}{\alpha^2 L^2}\right) - \frac{2\pi n}{L} \operatorname{erfc}\left(\frac{\pi n}{\alpha L}\right) \right) \\
& + \frac{4\alpha^3\mu^2}{3\sqrt{\pi}} \sum_{j=1}^N s_{jz} - \frac{4\alpha\mu^2\sqrt{\pi}}{L^2} \sum_{j=1}^N s_{jz}. \quad (15)
\end{aligned}$$

The MD simulations are performed in NVT ensemble, i.e., the total number of particles N , the temperature T , and the volume of simulation cell V are kept constant. The periodic boundary condition is applied. The equation of particles' motion is integrated using the velocity Verlet algorithm²⁷ with the time step $\delta t = 0.002$, and the constant temperature is controlled via a Berendsen thermostat.²⁸ The GL phase coexistence curves are obtained primarily via Maxwell construction in which a set of NVT simulations are carried out along an isotherm. In the present work, the set of simulations is started from a very dilute gas phase, which goes through a typical NVT process. After that, the simulation cell is compressed to a smaller volume and another NVT simulation begins. Note that the initial configuration of the next simulation is directly from the previous configuration so that it doesn't need to initialize the configuration on lattice and subsequent melting process. By repeating this procedure until a large enough density or a small enough volume needed for Maxwell construction is reached, a lot of data that contain pressure versus volume are obtained. In order to eliminate the effect of hysteresis, the opposite direction of the procedure, i.e., the expansion procedure is started immediately after the compression procedure is finished. Specifically, we fit the isotherm data for which the compressibility is positive using a modified van der Waal's equation of state²⁹

$$P = \frac{Nk_B T}{V - Na_1} + \frac{a_0}{(V - Na_2)(V - Na_3)}, \quad (16)$$

where k_B is Boltzmann's constant and the a_i ($i = 0, 1, 2, 3$) are adjustable parameters. By fitting the data for a series of temperatures, we can yield the GL phase coexistence curve.

FIG. 1. A typical curve of Maxwell construction at $\mu^2 = 3.0$ and $T = 0.9$. The number of particles is $N = 256$. Open circles (squares) represent the results obtained upon compression (expansion) procedure. The solid line is the Maxwell construction fitting using Eq. (16).

Figure 1 is a typical example of Maxwell construction fit. Note that the logarithm is taken on the axis of volume in order to view the plots clearly.

III. RESULTS AND DISCUSSION

It is interesting to compare our results with available literatures. To our best knowledge, there are very few available GL phase coexistence results for quasi-2D Stockmayer fluids. In Table I, we put our results of GL phase coexistence together with the previous data of GEMC in Ref. 22. Note that we only give the corresponding phase coexistence points which appear in Ref. 22 for a comparison. Indeed we have obtained more phase coexistence points under some other dipole

FIG. 2. The curves of the gas-liquid phase coexistence under several typical dipole strengths. From bottom to top: $\mu^2 = 1.0, 2.0, 3.0, 5.0, 7.0$. Open circles (squares) represent our results obtained upon compression (expansion) procedure. Here only error bars of the results obtained upon compression procedure are given. Open triangles represent the results taken from Ref. 22.

strengths and temperatures, but the additional results do not show up in the table. In the case of $\mu^2 = 1.0$, our results are in good agreement with GEMC, especially in the region away from the critical temperature T_c . When the temperature is higher and approaches the critical temperature, the deviation between our results and GEMC becomes larger. As the authors of Ref. 22 did not present more phase coexistence points, such deviation is unknown quantitatively. When the dipole strength is increased, the deviation is also increased significantly.

The GL phase coexistence curve of the quasi-2D Stockmayer system are plotted in Fig. 2 (the data of Ref. 22 are also included). As reported in literatures, the well known scaling

TABLE I. The comparison between our results and Ref. 22 for the gas-liquid phase coexistence under $\mu^2 = 1.0, 2.0, 3.0$. The values in the parentheses indicate the uncertainty in the last digit(s).

T	Data taken from Ref. 22		Present work (compression)		Present work (expansion)	
	ρ_G	ρ_L	ρ_G	ρ_L	ρ_G	ρ_L
$\mu^2 = 1.0$						
0.54	0.0227(9)	0.736(8)	0.0182(12)	0.7468(25)	0.0171(12)	0.7467(30)
0.55	0.035(4)	0.740(6)	0.0259(12)	0.7377(22)	0.0252(12)	0.7380(23)
0.56	0.041(3)	0.723(7)	0.0289(18)	0.7253(29)	0.0281(18)	0.7250(32)
0.57	0.046(5)	0.706(11)	0.0428(30)	0.7154(21)	0.0427(36)	0.7170(23)
0.58	0.057(3)	0.701(13)	0.0505(29)	0.7031(17)	0.0536(30)	0.7039(14)
0.59	0.116(12)	0.642(30)	0.0641(48)	0.6887(25)	0.0641(44)	0.6887(21)
$\mu^2 = 2.0$						
0.72	0.040(4)	0.742(10)	0.0247(13)	0.740(17)	0.0245(13)	0.7410(17)
0.73	0.038(3)	0.717(21)	0.0302(18)	0.7304(18)	0.0295(24)	0.7308(22)
0.74	0.071(4)	0.714(8)	0.0371(28)	0.7168(34)	0.0360(29)	0.7184(34)
0.75	0.069(10)	0.685(22)	0.035(2)	0.7074(24)	0.0353(23)	0.7076(25)
0.76	0.089(15)	0.685(9)	0.0491(31)	0.6979(17)	0.0515(27)	0.6988(12)
0.77	0.207(26)	0.44(7)	0.0571(29)	0.6859(15)	0.0577(37)	0.6824(21)
$\mu^2 = 3.0$						
0.88	0.053(3)	0.755(14)	0.0152(14)	0.7592(23)	0.0156(11)	0.7596(23)
0.89	0.064(5)	0.741(13)	0.0175(16)	0.7513(30)	0.0170(19)	0.7480(43)
0.90	0.073(4)	0.733(16)	0.0160(13)	0.7391(30)	0.0164(14)	0.7419(22)
0.91	0.075(6)	0.721(24)	0.0213(18)	0.7318(24)	0.0209(15)	0.7301(22)
0.92	0.093(5)	0.687(39)	0.0226(33)	0.7191(44)	0.0234(23)	0.7199(28)
0.93	0.158(8)	0.504(28)	0.0277(26)	0.7102(30)	0.0283(24)	0.7102(28)

FIG. 3. The curve of the critical point (T_c and ρ_c) vs the dipole strength μ^2 , respectively. Open circles (squares) represent the results obtained upon compression (expansion) procedure. Here only error bars of the results obtained upon compression procedure are given. The dashed line in the top panel is the linear fitting when $\mu^2 > 3.0$.

relations were usually adopted to estimate the critical temperature T_c and critical density ρ_c ,²⁴

$$\rho_L - \rho_G = A|T - T_c|^\beta \quad (17)$$

and

$$\frac{\rho_L + \rho_G}{2} = \rho_c + B|T - T_c|. \quad (18)$$

Here we take Ising value $\beta = 0.125$ to fit the phase coexistence curve away from T_c so as to achieve the corresponding critical point T_c and ρ_c . The obtained results of the critical point versus μ^2 are plotted in Fig. 3. We should mention that the finite size effect is studied. As the computation cost of Ewald summation in the Stockmayer system with large number of particles is too expensive and the Maxwell construction needs a large amount of simulations, we only perform simulations in the systems with different number of particles for the special case $\mu = 0$, i.e., the normal Lennard-Jones system (it does not need to use Ewald summation). The simulations indicate that the critical temperature is decreased with the increasing of system size, while the critical density does not have a clear tendency due to statistic errors. It can be expected that the case of Stockmayer system has the similar tendency qualitatively.

After the critical points are obtained, we carry out a few more NVT simulations at critical points to calculate the critical properties. In order to reach equilibrium and reduce the statistic uncertainties, the simulations are run in many time steps

FIG. 4. The curve of the critical compressibility factor $\tau_c = P_c/(T_c\rho_c)$ vs the dipole strength μ^2 . The symbol style is the same as Fig. 3.

$2 \times 10^7 \delta t$. The results of critical pressure and critical internal energy are compiled in Table II correspondingly. Moreover, we calculate the critical compressibility factor $\tau_c = P_c/(T_c\rho_c)$ under different dipole strength, which is plotted in Fig. 4. Obviously, the critical compressibility factor decreases with the increasing of the dipole strength.

As is known, the dipolar fluids can form reversible chains or some types of complex structures.¹⁻¹⁰ This has been observed by many authors previously. In Fig. 5, we give some snapshots of critical configuration under a few typical dipole strengths. When the dipole strength is weak, the system is close to 2D Lennard-Jones system so as to form droplets and gas phase region,³⁰ e.g., the case of $\mu^2 = 1.0$ in Fig. 5(a). The particles become nose-to-tail linked and the reversible chains form discernibly as the dipole strength is increased. In order

FIG. 5. The snapshots of the system at the critical points under different dipole strengths. (a) $\mu^2 = 1.0$; (b) $\mu^2 = 3.0$; (c) $\mu^2 = 5.0$; (d) $\mu^2 = 7.0$.

TABLE II. The critical points and some corresponding critical properties for different dipole strength. P_c is the critical pressure and U_c is the critical internal energy. The values in the parentheses indicate the uncertainty in the last digit(s).

μ^2	Compression				Expansion			
	T_c	ρ_c	P_c	U_c	T_c	ρ_c	P_c	U_c
1.0	0.610(1)	0.3723(20)	0.02853(32)	-2.313(3)	0.610(1)	0.3735(21)	0.02865(32)	-2.319(3)
2.0	0.805(2)	0.3718(18)	0.03566(42)	-3.445(4)	0.805(2)	0.3704(28)	0.03611(42)	-3.435(3)
3.0	0.992(4)	0.3470(32)	0.03164(50)	-4.888(4)	0.993(4)	0.3477(32)	0.03106(50)	-4.878(4)
4.0	1.207(3)	0.3304(44)	0.03455(59)	-6.365(5)	1.207(4)	0.3293(30)	0.03487(58)	-6.359(5)
5.0	1.375(8)	0.3304(50)	0.02155(71)	-8.440(6)	1.377(8)	0.3314(43)	0.02033(72)	-8.429(6)
6.0	1.571(8)	0.3010(80)	0.01819(78)	-10.400(7)	1.575(7)	0.3127(43)	0.01749(79)	-10.377(7)
7.0	1.772(8)	0.2919(55)	0.01697(85)	-12.487(7)	1.767(10)	0.2947(77)	0.01588(86)	-12.536(7)
8.0	1.966(9)	0.2696(84)	0.01613(89)	-14.755(8)	1.959(11)	0.2711(82)	0.01625(86)	-14.810(8)

The critical parameters of Ref. 22. P_c and U_c are obtained from our NVT simulations.

μ^2	T_c	ρ_c	P_c	U_c
1.0	0.595	0.378(7)	0.02091(33)	-2.428(2)
2.0	0.775	0.382(11)	0.02226(44)	-3.686(4)
3.0	0.936	0.388(13)	0.00841(57)	-5.434(4)

to show the dependence of chain's formation on the dipole strength, we consider two particles to be neighbors if their distance is less than r_{neigh} . Here r_{neigh} is taken as 1.2 and the average chain length can be calculated via $n_c = N/n$, where n is total number of chains. Although this is a very simple criterion compared with those criteria already used in systematic surveys of dipolar clustering (e.g., Weis and co-workers presented a energy criteria which could distinguish chain formation and compact clusters³¹), we may observe a significant increase of average chain length at critical point with the increment of dipole strength(see Fig. 6).

We define the same order parameter as in Ref. 32 to qualify the structural properties of the system,

$$Q_z = \frac{1}{N} \left\langle \sum_{i=1}^N \frac{1}{2} (3 \cos^2 \theta_i - 1) \right\rangle, \quad (19)$$

where θ_i is the angle between $\mathbf{s}_i$ and z axis. This is a measure of the average out-of-plane tilting of the $\mathbf{s}_i$. Note that $Q_z = 0$ if the particles are non-interacting and $Q_z = -0.5$ if all $\mathbf{s}_i$ are parallel to the x, y plane. Figure 7 shows the curves of Q_z versus ρ for $\mu^2 = 1.0, 3.0, 7.0$ when the temperature is close to the corresponding critical temperature,

FIG. 6. The curve of the average chain length at critical point n_c vs the dipole strength μ^2 . The symbol style is the same as Fig. 3.

i.e., $T = 0.61, 0.992, 1.772$ respectively. At low densities and small dipole strength $Q_z \approx 0$, as expected, the dipole moments are isotropically oriented, because there is little interaction between particles. As the density increases, the growing interaction forces the dipole moments to align into the plane. Such behavior is also observed in Refs. 22 and 32. Especially, when the dipole strength is large enough (e.g., the curve for $\mu^2 = 7.0$ in Fig. 7), Q_z approaches to a significant negative value even in dilute density. This is due to the fact that many particles form the head-to-tail chains [a typical snapshot of chains can be seen in Fig. 5(b)] which also makes the orientation of dipole moment tilt into the plane.

In Ref. 22, the authors did not find the disappearance of GL coexistence when $\mu^2 = 3.0$. For stronger dipole strength, the successful exchange rate in GEMC became extremely low, which prevented from carrying out more simulations. In this paper, we give more phase coexistence curves under different dipole strength from $\mu^2 = 1.0$ to $\mu^2 = 8.0$ (see Figs. 2 and 3). Nevertheless, the open question, i.e., whether the disappearance of GL coexistence in quasi-2D Stockmayer system does happen or not, is still unsettled.

Firstly, let us focus on the phase behavior of the system which has rather large dipole strength $\mu^2 = 8.0$. We

FIG. 7. The curve of the order parameter Q_z vs the density ρ for three typical dipole strengths. From top to bottom, $\mu^2 = 1.0, 3.0, 7.0$. The symbol style is the same as Fig. 1.

FIG. 8. The phase behavior when $\mu^2 = 8.0$. Top: Solid (open) circles represent the calculated order parameter P_1 (P_2) versus the density ρ at $T = 1.8$; The inset shows the simulation snapshot near the transition line $\rho = 0.736$. Bottom: Open circles (squares) represent the results of GL phase coexistence obtained upon compression (expansion) procedure; Solid circles represent the approximate densities for the isotropic to ferroelectric phase transition at the desired temperatures; The dotted line is the estimated ferroelectric phase transition curve.

have investigated the GL phase coexistence curve for this case (see Fig. 8). In the liquid region, it is possible for dipolar fluid to form long-range orientational order, i.e., nematic phase or ferroelectric phase. Such transition from isotropic fluid to anisotropic fluid may interfere with the isotropic GL phase transition resulting in the disappearance of the GL phase coexistence.^{32–36} The possible occurrence of the orientational order is often monitored by calculating the equilibrium first- and second-rank orientational order parameters, $\langle P_1 \rangle$ and $\langle P_2 \rangle$, respectively. As in the previous calculations by other authors,^{37,38} the instantaneous order parameter P_2 is taken to be the largest eigenvalue of the second-rank tensor $\hat{\mathbf{Q}}$ given by

$$\hat{\mathbf{Q}} = \frac{1}{N} \sum_{i=1}^N \frac{1}{2} (3\mathbf{s}_{is}\mathbf{s}_{is} - \hat{\mathbf{I}}). \quad (20)$$

The instantaneous first-rank order parameter P_1 is defined as

$$P_1 = \frac{1}{N} \left| \sum_{i=1}^N \mathbf{s}_{is} \cdot \mathbf{d} \right|, \quad (21)$$

where $\mathbf{d}$ is a unit vector in the direction of the instantaneous eigenvector associated with the largest eigenvalue of $\hat{\mathbf{Q}}$. For isotropic fluids, both $\langle P_1 \rangle$ and $\langle P_2 \rangle$ are zero. For normal non-ferroelectric nematic fluids, $\langle P_1 \rangle = 0$ and $\langle P_2 \rangle \neq 0$. For ferroelectric nematic fluids, both order pa-

rameters are nonzero. As the dipole moments are slightly out-of plane but predominantly in-plane (see Fig. 7), only the 2D-plane components of the dipole orientations are taken.

Using the calculation method described above, three typical temperatures below the critical point $T = 1.8, 1.85, 1.9$ are chosen to study the transition from isotropic to long-range order phase. Via simulations, we get the results of the order parameters P_1 and P_2 , respectively, from lower densities to higher densities. In the top panel of Fig. 8, a typical curve of order parameter P_1 and P_2 versus density and the snapshot of configuration near the transition line ($T = 1.8$ and $\rho = 0.736$) are shown. For a finite number of particles the order parameters are not expected to be exactly zero in the isotropic phase, and the transitions occur when the order parameters increase sharply. The transition from isotropic to normal nematic phase is not found, so only the densities of ferroelectric phase transition are estimated. The results are compiled in Fig. 8. It is clear that the transition from isotropic to long-range orientation order phase does not cause the critical point of GL phase coexistence to vanish abruptly. Certainly the case of Fig. 8 does not mean to work through the whole range of dipole strength, especially much larger dipole strength. It has already been investigated both in theory and simulation that the critical temperature and dipole strength have the scaling relation $T_c \sim \mu^2$ for large μ Refs. 16 and 15 (this can also be seen in Fig. 3), and the ferroelectric transition temperature has the same dependence on the dipole strength at the fixed density ρ according to Debye theory. Moreover, the critical density tends to be lower as the dipole strength becomes larger (see the bottom panel of Fig. 3), which means that the density of liquid phase in GL phase transition shifts to lower. Therefore, the situation for larger dipole moment will be qualitatively the same as the case of $\mu^2 = 8.0$, i.e., the abrupt disappearance of the GL phase coexistence due to being overlapped by the region of ferroelectric phase will not happen.

In 1993, Van Leeuwen and Smit used GEMC to study the GL phase coexistence of 3D Stockmayer system. They found that the GL phase coexistence disappeared abruptly when the dipole strength was above a certain threshold, which was believed to be due to chain formation.¹⁴ A different conclusion was reached by Dudowicz, Freed, and Douglas when they mapped the Stockmayer system onto their Flory-Huggins type lattice model. Their theory implied that the GL phase transition exists for all dipole strengths.¹⁵ The later results of MD simulation by Bartke and Hentschke supported this finding, and in particular they observed the GL phase coexistence for the dipole strength significantly above the threshold proposed previously by van Leeuwen and Smit.^{16,17} In the limit of large μ , the GL transition is anticipated to be driven entirely by dipolar interactions. The observation has been made for 3D Stockmayer fluids in which the ratio $\chi = k_B T_c / (\rho_c \mu^2)$ tends to some universal value ($\chi = 1.53$) as μ tends to infinity.³⁹ Plotting χ using the data in Table II shows that indeed this may be the similar case; using data for $\mu^2 > 3.0$ we may yield $\chi \approx 0.87$. In all, it seems that the chain formation will not lead to the disappearance of GL phase transition in Stockmayer system.

FIG. 9. The snapshots of the system at slightly above the critical temperature for $\mu^2 = 16$. The temperature is $T = 3.55$. Top: $\rho = 0.05$; bottom: $\rho = 0.2$.

As is already pointed out, the scaling relation between the critical temperature and the dipole strength is $T_c \sim \mu^2$ for large μ .^{15,16} Our results shown in Fig. 3, the critical temperature T_c and dipole strength μ^2 do have a linear relation over a wide range of large μ^2 . By fitting the points where $\mu^2 > 3.0$ with a linear function of μ^2 , we can estimate the critical temperatures of the systems with larger dipole strengths. Here we only fit the points obtained through compression procedure in Maxwell construction because the expansion procedure almost get the same results. The final fitting function is found to be $T_c \approx 0.196\mu^2 + 0.407$. When a large enough dipole strength is considered, e.g., $\mu^2 = 16.0$, immediately we can get the corresponding critical temperature about 3.49. Afterwards, we take a slightly larger temperature than the estimated T_c , i.e., $T = 3.55$, and perform the simulations at a moderate density $\rho = 0.2$ and a low density $\rho = 0.05$ in the system with particles number still $N = 256$. The typical configurations in equilibrium at $\rho = 0.2$ and $\rho = 0.05$ are shown, respectively, in Fig. 9. At so large dipole strength, some com-

plex structures are formed including the linear chain, ring chain, and branched chains. From Fig. 9, it can be seen that most of the particles aggregate and there are only a few single particles and chains to contact each other in the system. Furthermore, some longest chains are even across the whole box and can persist for a very long time due to strong dipole-dipole interactions. So this indeed makes the relaxation and equilibrium of the system extremely slow, which causes the simulation rather difficult. Note that a few lower temperatures away from the critical temperature should be used in the procedure of constructing the GL phase coexistence curve, which makes the situation worse. Especially, for GEMC method, the rate of the configuration Monte Carlo sampling in translation and exchanging particles approaches to zero so that the simulation with GEMC method is almost impossible, as already happened in Ref. 14. Finally, we should mention that our observation is in accord with the theoretical result of Dudowicz, Freed, and Douglas, i.e., the polymerization transition for the critical composition under strong dipole strength occurs at a higher temperature than the critical temperature of GL phase transition T_c .¹⁵ Therefore, we can conclude that the GL phase coexistence in the system under strong dipole strength may not be observable via simulation due to the formation of very long chains, although it does exist.

IV. CONCLUSION

In this paper, we use Maxwell construction method together with MD simulation to investigate the GL phase coexistence of quasi-2D Stockmayer fluid. The critical points under different dipole strength are estimated and the corresponding critical properties are given. Meanwhile, our results of GL phase coexistence in quasi-2D Stockmayer system are compared with those of literatures in detail. The critical temperature increases with the increasing of dipole strength and the scaling relation between them is $T_c \sim \mu^2$ at large dipole strength, while the critical density shifts to lower density. Such dependence of critical point on the dipole strength is similar to the case of 3D Stockmayer system. The apparent chains formation is investigated when the dipole-dipole interaction becomes dominant. It is found that larger dipole strength may lead to the formation of longer chains. Furthermore, the dipole moments tend to align into the confined plane, especially, when apparent chains are formed.

Under a strong dipole strength, there is no normal nematic phase transition near liquid region. The possible ferroelectric phase transition which interfaces with the curve of the GL phase coexistence is not expected to make the GL phase transition disappear. However, very large dipole strength will result in the formation of rather long chains and cause it almost impossible to observe the GL phase coexistence via simulation. Therefore the GL phase coexistence under large enough dipole strength is not attainable using normal simulation.

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