

COMPUTER SIMULATIONS OF POLAR LIQUIDS IN AN EXTERNAL ELECTRIC FIELD

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1. Introduction

The computer is known as an electronic calculating machine, which has been developed to solve the difficult calculations involved in the development of nuclear weapons and in cryptography. Before the computer simulation was introduced as one important research method in materials science, the precise material structures, properties and their relationships are investigated only through time-consuming and expensive experiments. On the other hand, one can only go through employing a theory that provides an approximate description of the available material that predict the properties of a molecular substance. Because of the complexity of some systems, such approximations are unavoidable. With sufficient information about the intermolecular interactions, theories can estimate the observed or deliver desired properties. Unfortunately, our knowledge of the intermolecular Interactions fairly limited. Essentially, computer simulations allow us to obtain exact results for a given model system. We can then compare the results with those from the experiment and/or compare the analytical results of the theory[1].

In nature, polarizability is a fundamental property of all atoms and molecules. The point polarizability can affect macroscopic properties of the material, e.g. the dielectric constant and critical parameters, by the induced dipole moment. The additional polarizability on the point dipole makes the model even more complicated, but also more realistic. Although some simulation works have been previously performed, polarizable models for polar liquids are still challenging. This is due to the difficulty mentioned the simulation[2, 3].

For many years, chemists and physicists have studied the phase behavior of dipolar liquids[4-6], since dipolar liquids are very good model systems for ferrofluid. Ferrofluid are liquids that react to external fields. Because of the controllability of their viscosity, thermal conductivity by means of external fields, such liquids have very extensive technical applications. In the aerospace sector, attempts have also been made to apply some special properties of these materials. In medicine, for example, Ferrofluides are used for cancer detection by the so-called magnetic resonance spectroscopy, or by modifying the upper part which attached the active ingredients for cancer treatment.

Because of their large proportion in nature and the important role in the biological world, the new functions of the macromolecular materials have more and more scientists Interest in the field of soft matter. On the one hand, scientists use experimental methods to understand the structure and the dynamic properties of liquids. On the other hand, theorists try to Construct models to describe and explain the behavior of the liquids.

There is another very interesting question, whether the DD interaction alone, i.e. without further contribution to the attraction force between the particles, leading to the g-l coexistence. In the last twenty years, the absence of a g-l critical point in systems consisting of particles only with DD interaction without further attraction potential, claimed in a series of theoretical works[7]. This conclusion is consistent with the results from some computer simulations for dipolar systems[8, 9]. On the other hand, other researchers got the opposite result by the exact investigations. Apart from the practical applications, many seemingly simple model systems became important both theoretically and by means of computer simulation studies, with the complicated and difficult phase behaviour by the addition of the DD interaction to the simple short-range one, potential should be introduced into the systems.

We focus on Shifts of the critical points, i.e. T_c and ρ_c , in the modeled dipolar ones Liquids because of the presence of external electric fields. There are some research papers, which, through simulations, show the dependency between the Shift in the gas-liquid (g-l) critical parameter of a dipolar liquid and the external electric field[10-12].

In the present work, we focus exclusively on the analysis, using computer simulation, of one molecular models of the dipolar liquid under continuous flow of external electric fields. This model will be represented by the so-called dipole soft sphere potential (DSS potential)[11, 13]. We will compare our results to other results obtained using two different models. This first model is so called Stockmayer liquid (ST liquid), which is responsible for the entire changing effect between two particles in the liquid by the Lennard-Jones potential plus describes a dipole-dipole (DD) interaction. The second model, the polarizable one Stockmayer particle (pST particle), is a variation of ST particle. The pST particle has an additional polarizability on the dipole. We run our investigation results through simulations using the molecular dynamics (MD) method for ST liquids. The after-effects of the external electric fields was investigated in details.

2. Simulation method

The first step in a scientific investigation using simulations is to select a suitable model for the simulation system or construct it yourself. The model should have all or at least most of the properties of the one being studied systems. This is possibly the most important part of the whole investigation. For research on the polar system in an external electric field, we adopt the mostly used model from the literature, namely the DSS model. Such model can represent the real liquids very well. In order to examine the field for the polar system, we also introduced different external electric fields into our system.

The DD interaction has no radial symmetry and is a long-range interaction. The Interactions between the pST particles are almost the same as those in the ST model after the effect of the additional induced dipole moment in the pST model on the total system has added. The formulation of the electrical interaction in the DSS model is the same as in the ST model. The difference between ST and DSS model refers to the radially symmetrical part is limited. The radially symmetric potential of the DSS model is modelled by turning off the attractive term of the LJ potential and only the repulsive term is retained. The effect of the external field on the polar system or on its Phase separations is studied. The g-l phase separation of an ST system

without external field has already been examined. The shift in the critical parameters of a polar system due to an external electric (or magnetic) field theoretically discussed by many research groups, but there are only a few Investigations with computer simulations [30-34]. Most works [7, 13, 14] investigate the ST system in an external field \vec{E}^∞ (or \vec{H}^∞) with the Ewald summation method [15]. With this method, however, the dielectric structure of the system cannot be examined in detail. Furthermore, in this work, the DSS systems examined in an additional field \vec{E}^{ext} . The \vec{E}^{ext} leads to an inverse shift of the critical parameters against the shift direction in field \vec{E}^∞ . The differences between the two electric fields \vec{E}^∞ and \vec{E}^{ext} will be analysed.

The interactions of the particles in DDs model consist of radially symmetric and electrical parts. The radially symmetrical Interaction describes the van der Waals (vdW) energy that the repulsive and/or attractive potentials between the unbound atoms. Then we consider the electrical part of the models, which results in the embedded dipole.

The vdW equation describes the deviations of real gases from ideal gases. The vdW energy should be positive and very large if the distance between two particles becomes very small. It also has a slightly negative minimum when both touch the particles just barely. For large distances between two particles, the attractive forces predominate. As the distance increases, the vdW energy approaches the zero. For the realization, the LJ potential is a popular function [16]:

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

which meets these general requirements and independent of the orientations of the particles, where $r_{ij} = r_i - r_j$ denotes the distance between the particles i and j. The σ is the distance at which the LJ potential has a zero and ϵ is the absolute value of the minimum energy. The LJ potential describes well the interaction of two uncharged and weakly interacting atoms that are not covalent chemical bond.

The electrical interactions in this model are calculated as follows. The embedded Dipole consists of two parts. On the one hand from a fixed dipole moment $\vec{\mu}_i$ and on the other hand from an induced dipole moment \vec{p}_i . The total dipole moment of a particle can through:

$$\vec{m}_i = \vec{\mu}_i + \vec{p}_i = \vec{\mu}_i + \alpha \vec{E}_i$$

where α is the polarizability and \vec{E}_i is the local electric field of the i-th particle. For DSS models, the polarizability $\alpha = 0$ simply applies. The dipole moment is given in units of $\sqrt{4\pi\epsilon_0\epsilon\sigma^3}$, where ϵ_0 is the permittivity of the vacuum. Then, the electrostatic potential at location r_i can be due to the surrounding dipoles according to Einstein's summation:

$$\varphi_D(\vec{r}_i) = \frac{\vec{r}_{ij} \cdot \vec{m}_i}{r_{ij}^3}$$

3. Results and discussion

Because of the absence of the attractive term in the SP, the DSS system is already lower in density in the liquid phase. Therefore, we provide for all simulations $r_{cut} = 9.5 \text{ \AA}$. But the

particle number ($N = 900$) still remains the same as in other models. Figure 1 consists of a series of simulation snapshots representing the configurations with the low and high densities on the phase separation lines near T_c . The two snapshots below are for the case in the field with $E^{(\infty)} = 0.5$. The structures are similar to the corresponding representations by [7, 17, 18] for $H^* = 1.0$, or $E^{(\infty)} \approx 0.22$, if the field strength is transferred to our system. If the field strength is reduced, one can observe the decrease in the degree of orientation. On the lower density, the shorter chains or linear aggregates appear. If the field strength is further reduced, close to the limit with $E = 0$, one obtains the monomers of the pST particle, small rings or loops become in the vicinity. Since the coexistence curves of the DSS liquid in the weak field even without a field are very flat near T_c , as shown in the literature, we find that at slightly higher temperature one can observe more and larger loops in a background, which are dominated by the monomers. Instead of linear aggregates, the loops appear at small field strengths and low aggregate counts because the energy gain of an additional reversible bond outweighs the entropy loss as explained in detail in Ref. [7]).

Figure 2 shows the values of the average aggregate size $\langle L \rangle$ as a function of the $E^{(\infty)}$ field at the respective critical density and temperature of the DSS liquid. There is a distinct and expected increase in $\langle L \rangle$ when the $E^{(\infty)}$ field strength is reduced. The average aggregate size increases, however apparently in the limit with $E^{(\infty)} \approx 0$, it is not divergent. We investigated if two particles are neighbors to each other in the same aggregate, using a distance criterion. Two dipoles are neighbors if and only if their distance is less than r_0 . Even though the value of the distance r_0 affects the result of $\langle L \rangle$, as shown in Figure 2, the general conclusions, within a reasonable range, do not depend on r_0 . If r_0 is too small, no neighboring particles are found. For too large r_0 , especially in the case close to $\rho^{-1/3}$, the distinction between the aggregates is lost. Here we use $r_0 = 2.0$. We must emphasize that $\langle L \rangle$ encloses the monomers, i.e., $\langle L \rangle = 1$. Moreover, the numbers of rings and chains are comparable in the vicinity of $E^{(\infty)}$.

In Figure 3, the mean numbers $\langle n \rangle$ of monomers, chains, and rings plotted as functions of the $E^{(\infty)}$ field. The mean numbers of monomers and chains are almost the same everywhere. They increase very quickly when the field strength is weak and slowly converge to a constant for a strong field. Conversely, the mean number of rings decreases first, apparently also converging towards one lower constant.

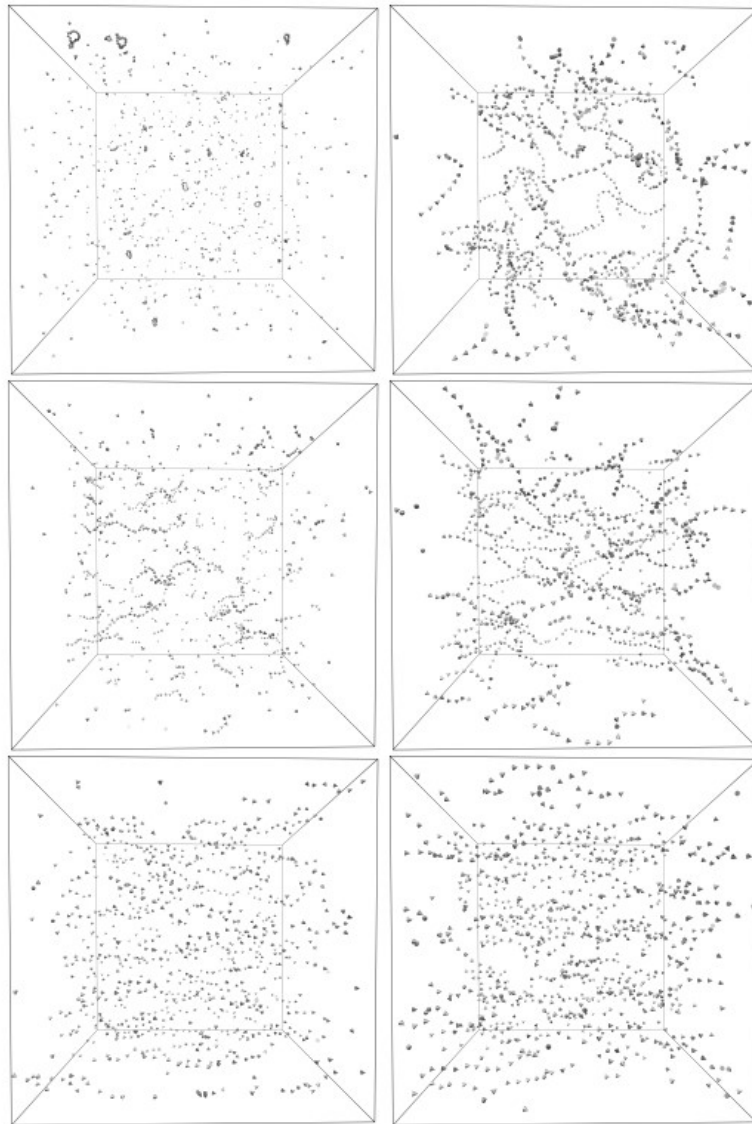


Figure 1. Simulation snapshots along the coexistence curves of the DSS Liquid near the respective critical temperatures. Upper Images: $E^{(\infty)} = 0.005$, $T = 0.064$, $\rho = 0.0001219$ (left), $\rho = 0.01218$ (to the right); middle images: $E^{(\infty)} = 0.05$, $T = 0.076$, $\rho = 0.00157$ (left), $\rho = 0.00954$ (right); lower images: $E^{(\infty)} = 0.5$, $T = 0.114$, $\rho = 0.0129$ (left), $\rho = 0.0202$ (right).

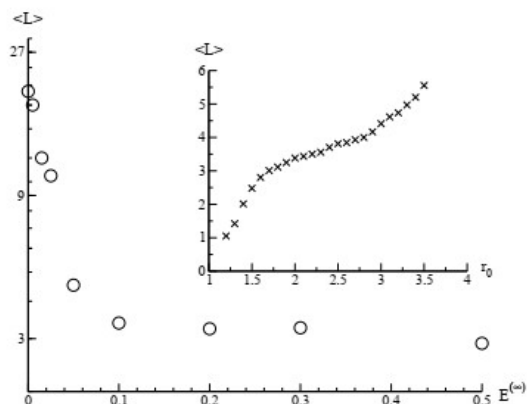


Figure 2. Average aggregate sizes $\langle L \rangle$ of the DSS fluid as function of the $E^{(\infty)}$ field at the critical points. Inset: $\langle L \rangle$ against r_0 in field $E^{(\infty)} = 0.1$.

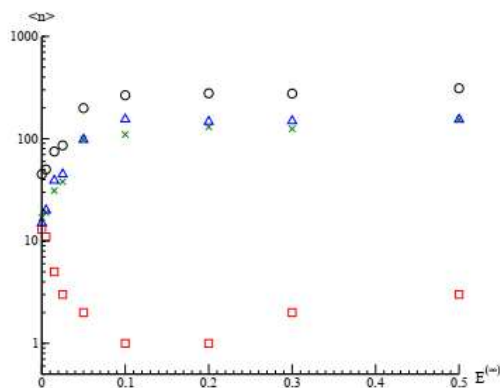


Figure 3. Average number of different aggregates $\langle n \rangle$ in the DSS system as a function of the $E^{(\infty)}$ field at the critical points. Circles: Total number of all aggregates; squares: number of rings; triangles: number of chains; Crosses: number of monomers.

3.1. g-l phase coexistence in the DSS liquid

We use the NVT ensemble and use the Maxwell construction to determine the critical parameters of the DSS system with $\mu = 1.0$. In the work of Stevens and Grest [8] the g-l phase coexistence of the DSS liquid in an outer magnetic field is presented. Therefore, we decide to calculate the isotherms of the DSS liquid in the fields $E^{(\infty)} = 0.5$ and 0.05 . The results are shown in Figure 4. Clearly, one can see here at low temperatures the vdW loops. The loops disappear again at high temperatures, like it is expected. The lowest magnetic field in the work of Stevens and Grest [8] is $H = 0.25$, which corresponds to $E^{(\infty)} \approx 0.0543$ in our research. We continue to try to simulate the system without an external field. The left image in Figure 5 shows the isotherms of the DSS liquid in the absence of the external field. Despite relatively large scattering, the vdW loops are still recognizable at low temperatures, i.e., there is indeed the g-l phase coexistence in the DSS system with no external field. As shown in this figure, the loop disappears at $T = 0.064$. With the help of the Maxwell construction, we determine the phase diagram in the right image of Figure 5 of the DSS liquid in the absence of the outer field. The hat shape is not like at the ST feet. The region for the gas phase is quite narrow. Therefore the

Phase coexistence in this case very difficult to detect. Moreover, The critical temperature and Densities are $T_c = 0.0631$ and $\rho_c = 0.0033$. with changing of the extended $E^{(\infty)}$ field strength, the hat shape of the phase diagram of the DSS fluid gradually changes to the shape of the ST-Systems, namely the area of the pure gas phase is getting bigger and bigger. We presents this Change process in Figure6.

This can be explained as the external electric field shifts theoretical parameters in different directions depending on how the field is used. In Table 1, we list the critical parameters from our simulations. The illustration in figure 7 presents the critical temperature T_c and the critical density ρ_c as function the external field strength. In the case for $E=E^{(\infty)}$, we get a monotonically decreasing Function for T_c . This is qualitatively identical to the corresponding results of the ST and pST systems, which have already been explained in different references []. However, the difference in the much lower value of T_c is due to the lack of attraction between the particles. In addition, the quadratic rule for the increase in T_c , which results from the LL theory [18], is no longer valid for smaller field strengths than that in the ST system. Figure 7 contain the changes of the critical parameters ΔT_c and $\Delta \rho_c$ according to the $E^{(\infty)}$ field strengths. one should note that the mean field theory which has been used by other research groups, cannot be applies any more in such case.

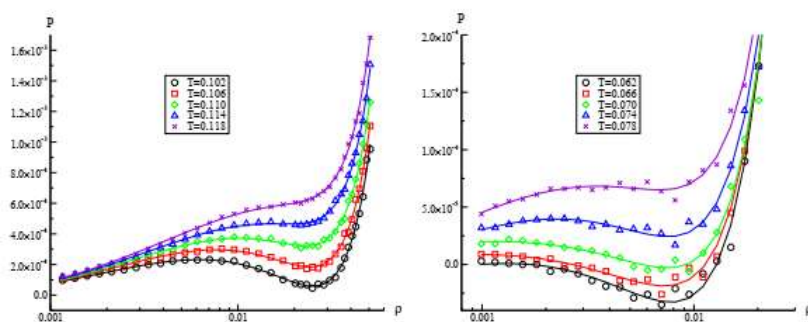


Figure 4.: Isotherm of the DSS liquid with $\mu = 1.0$ in different $E^{(\infty)}$ fields. Left: $E^{(\infty)} = 0.5$; right: $E^{(\infty)} = 0.05$. The symbols are the results from the simulations. The lines are the fitted lines using the modified vdW equation of state.

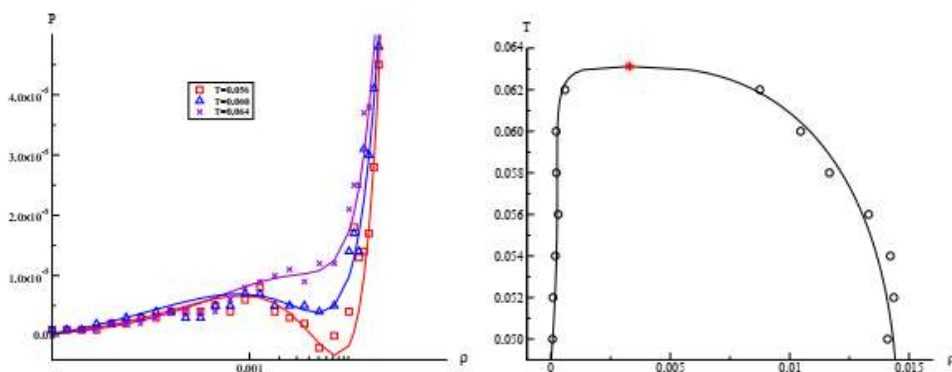


Figure 5. Isotherm and phase diagram of the DSS liquid with $\mu = 1.0$ at Absence of the outer field. Left: isotherm. The symbols are the simulation results. The lines are the fitted lines using

the modified vdW equation of state. Right: phase diagram. The circles have been determined by Maxwell's construction on the isotherms. The red star shows the position of the critical point of the DSS liquid in the absence of the outer field. The lines are the fitted lines using Eqs. Of state.

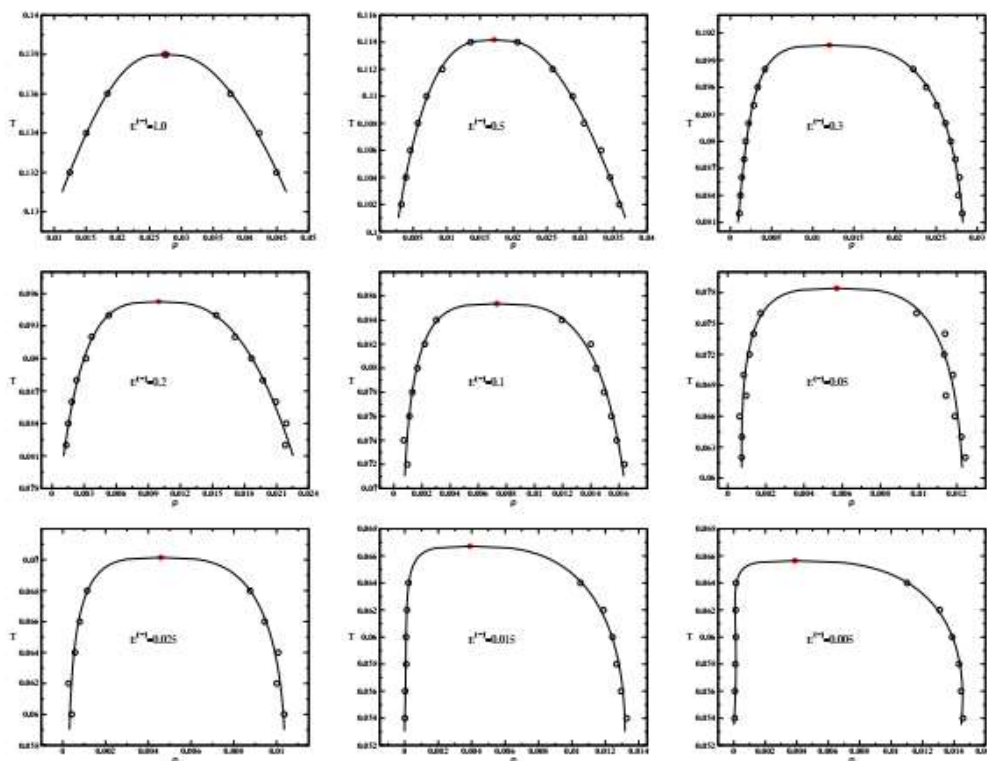


Figure 6.: Phase diagrams of the DSS liquid with $\mu = 1.0$ in the presence of $E^{(ext)}$ with different field strengths as marked in the pictures. All circles have been specified by the Maxwell construction with the vdW equation of state. The asterisks denote the critical points for the respective field strength. The lines are the adjustments made using the equation of state.

$E^{(ext)}$	T_c	$\rho c E^{(ext)}$	T_c
0	0.0631	0.0033	0.01
0.005	0.0642	0.0034	0.025
0.015	0.0667	0.0039	0.05
0.025	0.0701	0.0046	
0.05	0.0784	0.0057	
0.1	0.0854	0.0073	
0.2	0.0953	0.0100	
0.3	0.1007	0.0120	
0.5	0.1142	0.0171	

Table 1.: The critical parameters of the DSS liquid for $\mu = 1.0$ in the absence and presence of the external electric fields from the MD simulations.

The factor for the critical compressibility of the ST system is around 0.35. This value indicates the behavior of a simple liquid. Compared to the ST system the compressibility factor of the DSS system is much smaller (≈ 0.04). This can be explained through the Flory state formula for the reversible dipole chains [19]. Theoretically, one obtains the dependence of the compressibility factor on the chain length for the reversible long chains. However, the Onsager theory does not take any chain formation of the dipoles into account. Therefore, the mean field theory here is not consistent with the LL theory for the DSS liquid.

Figure 7 also contains the critical temperatures for all cases with the E^{ext} field fixed. For the ST liquid, The non-zero E^{ext} leads to a lower critical temperature. This phenomenon can in principle be explained by the constriction of the critical temperature of the DSS liquid. It is however numerically impossible to construct the vdW loops with a constant E^{ext} field, so that both the critical temperature and the critical density cannot be determined. However, it is still possible to observe a pressure drop in the isotherms near the critical temperature. Estimates of the critical temperatures of the DSS liquid in a constant E^{ext} field are shown as crosses in the figure 7

3.2. Isochoric heat capacity of the DSS liquid

The form of the specific isochoric heat capacity can also contain information about the g-l phase transformation. We represent the heat capacities of a DSS liquid with the dipole moment $\mu = 1.0$ in the fields $E^{(\infty)} = 0.1$ and $E^{(\infty)} = 0.5$ as a function of the system density ρ in Figure 8. The shapes are similar to those of the other dipolar liquids, but the absolute values of C_V/N are much larger than the previously discussed results because of the very low temperatures and the long chains (or large aggregates) in the DSS system. Since the investigations were carried out in the area with very low densities and temperatures, the results from our method of determination are very sensitive to the mix parameters. The maxima of the curves show only roughly the positions of theoretical densities in the same electric fields. The order of the curves according to the temperatures still remain the same as those for ST and pST fluids

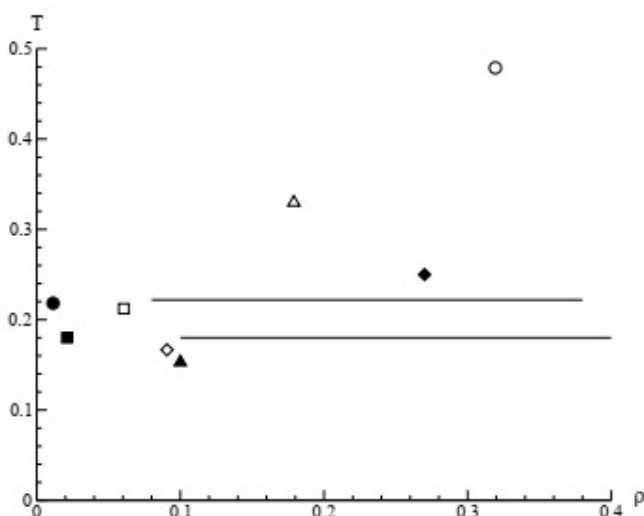


Figure 7. Graphic overview of the critical points of the dipolar sphere systems from different references. horizontal lines[19]; open circle [20];open square [21]; open triangle [22]; open diamond [14]stuffed diamond [23]; filled square [24]; filled triangle [25]; filled circle: this work.

With a big difference from the previous results, the specific isochoric heat capacities of the DSS liquid in the absence of the external electric field shown in Figure 9. The order of the curves at relatively low temperatures is quite the opposite. There is also no significant curvature at low temperatures. Until $T \geq 0.086$, which is far higher than that determined by us, which is the critical temperature, the desired curvatures reappear in the curves. At high densities, the curves collapse again at these temperatures. For the DSS system with long reversible chains, it is very difficult in the simulations, to reach the appropriate balance. At relatively higher temperatures, the

Aggregates also relatively smaller, therefore, the simulation for the DSS liquid reaches quickly and easily the equilibrium. We find that the results at $T = 0.086$ and 0.090 in Figure 9 can still be trusted. The curvatures on the two curves convey the information of g-l phase coexistence at low temperatures. And the maxima are also close to those determined by us critical density.

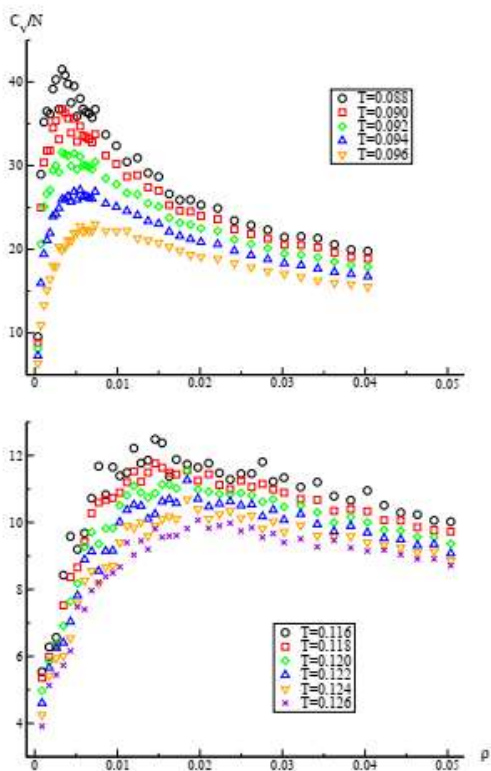


Figure 8.: The specific isochoric heat capacity C_v/N of the DSS liquid with the dipole moment $\mu = 1.0$ in the external electric fields as Function of the system density ρ from our computer simulations. Upper Image: $E^{(\infty)} = 0.1$; bottom picture: $E^{(\infty)} = 0.5$.

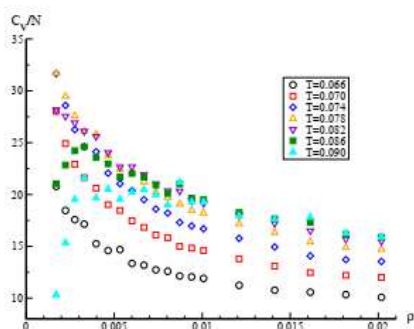


Figure 9.: The specific isochoric heat capacity C_V/N of the DSS liquid with the dipole moment $\mu = 1.0$ in the absence of the external electric field as a function of the system density ρ from our computer simulations.

Summary

The ST potential is one of several early model potentials for small polar onesmolecule. The numerous computer simulations that followed were unexpectedcomplex phase behavior of the ST model revealed. The ST model can handle real liquids with small polar molecules, e.g. there seems to be forno similar liquid in the real world during the transition to the ferroelectric order with low molecular mass. However, it is still useful because of its simplicity provides insight into the dipolar interactions in liquids and so manystructural, dynamic and thermodynamic properties of the liquids are examined. In this work we focused on the effect of external electric fields on polar liquids. Based on the new pressure term, we determined with the help of the so-called Maxwell. A detailed study of the g-l phase coexistence in the DSS fluid withelectric fieldwas also carried out in this work. We first observed the aggregate structures in the DSS system at different temperatures and densities. In the $E^{(\infty)}$ fields we have found clear phase coexistence and determined the critical parameters.

In the limiting case with no external electric field, we actually found the vdW loops in the isotherm curves. Thus we have determined the critical point of the DSS in the absence of the external field. The critical temperature and Densities are 0.0631 and 0.0033, respectively, which are much smaller than in the ST system.

The specic heat capacities discussed in this work were determined in the micro-canonical ensemble. One can still use this quantity in the canonical ensemble determined by the Nos e-Hoover method.

So far we have only studied systems with dipole moments. One can extend this work with multipole moments. Besides, one can study the shifts of the triple points of dipolar liquids in external fields. The scientists discovered a crystal structure in the dipolar system. It is also a very interesting question how the external field affects the crystal structure.