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UNDERSTANDING THE PHASE DIAGRAMS OF QUADRUPOLAR MOLECULES

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Recent research on the effect of a quadrupole moment on the phase diagram of linear molecules is reviewed. In particular the effect of the quadrupole on the vapour-liquid and solid-liquid equilibria will be discussed. It is found that the quadrupole moment increases the critical temperature, pressure and density of the fluid over the model without a quadrupole and leads to deviations from the principle of corresponding states. The effect of the quadrupole on a molecular model with a spherical repulsive core is larger than on one with a nonspherical core. The presence of the quadrupole stabilizes solid structures which are not close packed. This leads to a shrinkage of the liquid range as measured by the ratio of the triple to critical point temperature and exhibited by systems like carbon dioxide and acetylene.

1 INTRODUCTION

The distribution of electronic charge in a molecule is generally not symmetric, leading to the presence of multipoles. The interaction between these multipoles on different molecules can have a significant impact on the thermodynamics and phase equilibrium. In this paper we will discuss such effects for molecules of linear geometry with a quadrupole moment but with no dipole moment. A good example of the molecules we have in mind is carbon dioxide. For such molecules a measure of the anisotropy of the charge distribution is given

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by the quadrupole moment. The quadrupole moment is a second rank symmetric and traceless tensor [1]. However, for linear molecules this tensor has only one independent component which is usually denoted as the quadrupole moment. For instance, for a discrete distribution of charge on a linear axis the quadrupole moment Q is given by $Q = \sum q_i z_i^2$ where q_i is the value of the charge located at a distance z_i from the origin. When one takes the limit of increasing charge magnitude and decreasing charge separation (i.e z_i tends to zero) while keeping Q constant, the resulting quadrupole is denoted as an ideal or point quadrupole. In this work we shall consider linear molecules with an ideal quadrupole and the role of this quadrupole in determining the phase diagram. In the first instance we will consider the effect of the quadrupole moment on the vapour-liquid equilibrium. By using Gibbs ensemble simulations [2] the critical properties with and without quadrupole have been determined for linear molecules of various elongations [3]. The quadrupole moment also strongly affects the solid-liquid equilibrium. Using computer simulation it has been shown [4] how the quadrupole moments stabilizes the $\alpha - N_2$ structure for molecules like carbon dioxide. The stability of this expanded solid structure strongly affects the location of the triple point. By using a simple theoretical scheme based on the generalized van der Waals theory of Longuet-Higgins and Widom [5] it has been shown that the quadrupole increases substantially the triple point temperature [6,7]. The outline of the paper is as follows. In Section II, the vapour-liquid equilibria of linear quadrupolar fluids will be discussed. In Section III we shall consider the fluid-solid equilibrium and in Section IV, the conclusions of this work will be presented.

2 EFFECT OF THE QUADRUPOLE IN THE FLUID PHASE

In this section we shall discuss the effect of the quadrupole on several properties of the fluid phases based on the recent computer simulation studies [3,8,9]. In this work the Kihara potential [10,11] was used, choosing the molecular core as a rod. The core is shown in fig.1 , and the pair potential between two molecules is given by :

$$u_{Kihara}(s) = 4\epsilon((\frac{\sigma}{s})^{12} - (\frac{\sigma}{s})^{6}) \tag{1}$$

where s is the shortest distance between the molecular cores, σ is the diameter of the molecule and ϵ is the well depth. The *molecular shape* represented by the Kihara potential with the core of fig.1 is that of an spherocylinder [12]. The geometry of the molecule is described by the dimensionless parameter $L^* = L/\sigma$ where L is the length of the rod. For $L^* = 0$ the molecule presents spherical shape whereas high values of L^* correspond to very elongated molecules. According to Eq.(1) the well depth of the potential does not depend on the relative orientation.

The pair potential between a pair of point quadrupoles is given by [1]:

$$u_{QQ}(r,\omega_1,\omega_2) = \frac{3Q^2}{4r^5}(1 - 5(c_1^2 + c_2^2 + 3c_1^2c_2^2) + 2(s_1s_2c_{12} - 4c_1c_2)^2) \tag{2}$$

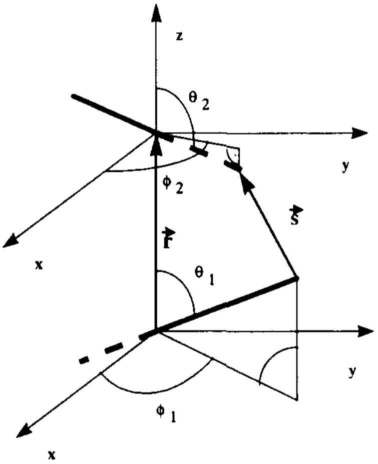

Fig. 1. Shortest distance, s, between a pair of rods of length L. The meaning of r, and the angles entering into the expression of the quadrupole potential are shown.

where Q is the quadrupole moment of the molecule, r is the distance between the center of mass of the molecules, ω_1 and ω_2 denote the orientational coordinates of the two molecules, $c_i = cos(\theta_i)$, $s_i = sin(\theta_i)$, and $c_{12} = cos(\phi_2 - \phi_1)$ (see fig.1).

Usually a reduced (dimensionless) quadrupole moment, Q^* , is defined. In this section the reduced quadrupole moment is defined as:

$$Q^{*2} = Q^2/(\epsilon\sigma^5) \tag{3}$$

The most favorable orientation for two molecules interacting through the quadrupolar potential (Eq.(2)) is the so-called "T" orientation in which the two molecules are in a plane, with the molecular axes in a perpendicular configuration and the center of mass vector coincident with one of the molecular axes [1].

The full pair potential between two molecules is given by:

$$u = u_{Kihara} + u_{QQ} \tag{4}$$

All results presented in this Section correspond to the pair potential given by Eq.(4).

2.1 EFFECT OF THE QUADRUPOLE MOMENT ON THE STRUCTURE

When dealing with linear molecules it is customary to expand the pair correlation function $g(r, \omega_1, \omega_2)$ using spherical harmonics as basis functions [13]. The coefficients of the

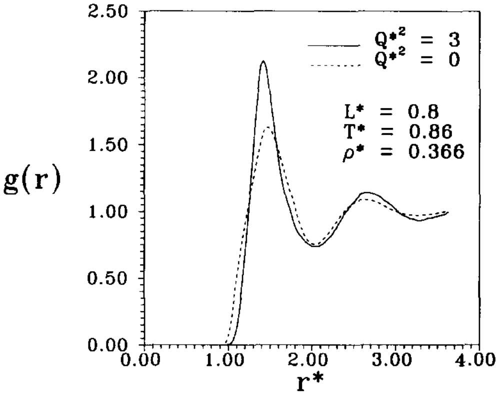

Fig. 2. Orientation averaged radial distribution function for a linear molecule interacting through the Kihara potential as a function of $r^* = r/\sigma$. Results are presented for two values of the quadrupole moment. Reduced temperature and density are defined as $T^* = T/(\epsilon/k)$ and $\rho^* = \rho\sigma^3$ where ρ is the number density.

expansion are denoted as $g_{ll'm}(r)$. In fig.2 results are presented for orientation averaged distribution function ($g_{000}(r)$) for a model of elongation $L^* = 0.8$ (appropriate for carbon dioxide) with a quadrupole moment ($Q^{*2} = 3$) and for the same elongation with zero quadrupole moment. Clearly the quadrupole affects the structure of the fluid as was noted some time ago for a similar model [13]. Results for other coefficients also show the important role played by the quadrupole in determining the structure of the fluid [8].

The reason why the quadrupolar interaction changes the structure of the fluid is because of its strong orientation dependence. For instance, when the a pair of molecules are in the "T" orientation the quadrupolar interaction energy has a large negative value. However, for the parallel orientation with both molecules perpendicular to the intermolecular axis the quadrupole interaction is positive and strongly repulsive. For other studies concerning the structure of oblate quadrupolar molecules and mixtures the reader is referred to reference [9].

2.2 *EFFECT OF THE QUADRUPOLE ON THE CRITICAL PROPERTIES*

Garzón et al. [3] have performed Gibbs ensemble simulations for a number of models interacting through the pair potential given by Eq.(4). In the case of spherical quadrupolar models critical properties are also known [14,15]. For a given elongation, the critical properties were computed for several values of the quadrupole moment. Comparison with results for the case of zero quadrupole moment which are also available [16] reveals the effect of the quadrupole moment on the critical properties. In Table I the critical properties as obtained from the Gibbs ensemble simulations are presented for several elongations and/or values of the quadrupole moment.

Table 1
Critical properties of quadrupolar linear Kihara fluids as obtained from Gibbs ensemble simulations

L^*	Q^{*2}	$T_c/(\epsilon/k)$	$\rho_c\sigma^3$	$p_c/(\epsilon/\sigma^3)$	Z_c
0.3	0	1.114	0.219	0.073	0.30
0.3	1.2	1.163	0.220	0.078	0.31
0.3	2.4	1.296	0.231	0.089	0.30
0.6	0	1.000	0.161	0.051	0.32
0.6	1.2	1.061	0.164	0.050	0.29
0.6	2.4	1.192	0.179	0.058	0.27
0.8	0	0.952	0.140	0.038	0.29
0.8	1.2	1.014	0.147	0.044	0.30
0.8	2.4	1.157	0.152	0.049	0.28

For a given elongation the quadrupole moment raises the critical temperature, pressure and density of the model. It also decreases slightly the value of the compressibility factor at the critical point (Z_c), although the uncertainties do not permit a firm conclusion on this point. Using the information obtained from the simulations we can estimate the effect of the quadrupole moment on the critical properties for a real substance. For instance, Garzón et al. [3] have estimated that for carbon dioxide the quadrupole moment raises the critical temperature and pressure by about 50K and 16 bar respectively.

Another question we might want to answer is the following: Do quadrupolar interactions affect more strongly the critical properties for molecules with spherical repulsive cores than those with nonspherical cores ? In fig.3a the increase in the critical temperature on adding a quadrupole to a model is plotted as a function of the reduced quadrupole moment.

It is clear that for a given quadrupole moment the critical properties of the spherical core model are more strongly affected than those of nonspherical core models. However, the comparison presented in fig.3a is slightly misleading. The way we define the reduced quadrupole does not take into account for the difference in molecular volume as we change the shape of the repulsive core so that it is not convenient for *comparing molecules with different elongations.* For instance for $Q^{*2} = 1$ the increase in the critical temperature of the spherical model is 8 times larger than for the model with $L^* = 0.8$. This large difference has its origin partly in the way we reduce the quadrupole moment. To compare molecules with different elongations Garzón et al. [3] introduce the equivalent reduced quadrupole moment defined as:

$$Q^{*\,2}_{eq} = Q^2/(\epsilon V_m^{5/3}) \tag{5}$$

where V_m is the molecular volume. In fig.3b the increase in the critical temperature is

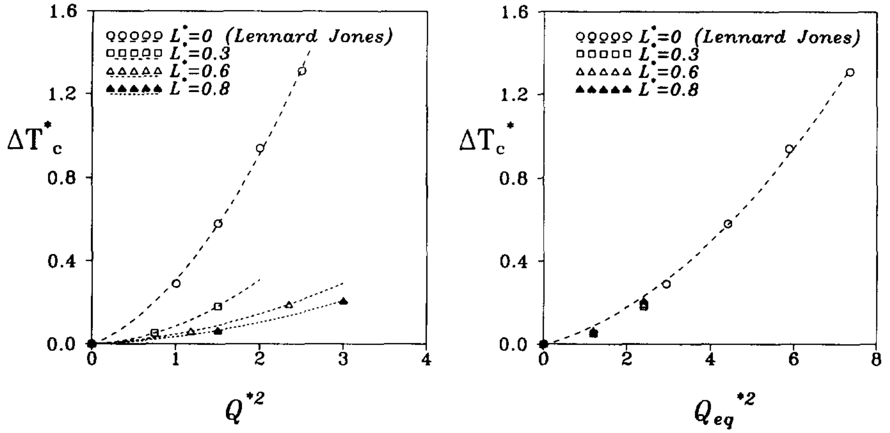

Fig. 3. Increases in the critical temperature on adding a quadrupole as a function of the quadrupole moment for several elongations. a) Reduced quadrupole defined by Eq.(3). b) Equivalent quadrupole moment as defined in Eq.(5).

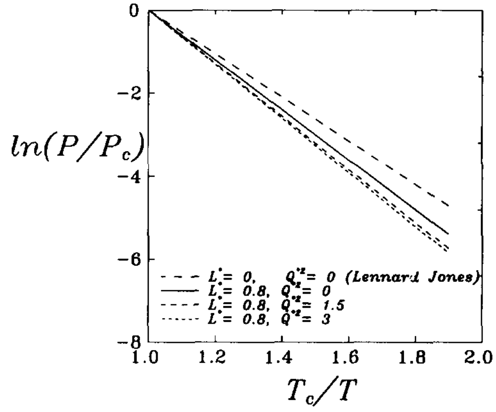

Fig. 4. Logarithm of the vapour pressure plotted as a function of the inverse of the temperature. Vapor pressure and temperature are reduced by their critical values. Results correspond to a spherical non polar molecule, a linear non polar molecule and two linear quadrupolar molecules.

plotted as a function of the equivalent quadrupole. It is clear that when plotted in this way the increase in the critical temperature does not depend much on the molecular elongation for a fixed value of the equivalent quadrupole.

The quadrupole moment and nonspherical molecular shape lead to deviations from the principle of corresponding states [17]. This is illustrated in fig.4 where the vapour pressure curve is plotted versus temperature using reduced units defined in terms of the critical properties.

It can be seen that : i) the non-sphericity of the molecule provokes deviations from the principle of corresponding states even when no quadrupole moment is present (compare the results for $Q^{*2} = 0$ when $L^* = 0$ and when $L^* = 0.8$) as has been seen in work on the diatomic 12-6 potential [18]. The non spherical shape increases the slope of the vapour pressure curve; ii) the presence of a quadrupole further increases the slope of the vapour pressure curve; iii) the slope of the curve, which is related to the so-called acentric factor [19,20] depends on the shape of the molecule and on the presence of polar forces. The non-spherical forces (shape and quadrupole moment) not only change the vapour pressure curve but also the coexistence densities leading to a broadening of the vapour-liquid coexistence envelope.

3 EFFECT OF THE QUADRUPOLE ON SOLID PHASES

We now consider the effect of the quadrupole moment on the solid phases and on the solid-fluid equilibrium. One could in principle consider each value of L^* and quadrupole moment, determine the stability of the different solid structures and to compute the solid-fluid equilibrium. In this way a complete view of the phase diagram of quadrupolar fluids could be obtained. At this point this is still a challenge that remains to be done. A somewhat less ambitious approach, but one which is sufficient for a qualitative understanding is to use the following strategy [4,7]. We consider first hard quadrupolar fluids. It is expected that solid structures are mainly determined by molecular shape and polar forces, so that dispersion forces play a minor role in determining the type of stable solid. In this way some features on the effect of the quadrupole moment on the solid structure can emerge. Since hard quadrupolar fluids do not exhibit vapour-liquid equilibrium one can follow the classical work of Longuet-Higgins and Widom [5] and incorporate dispersion forces in a mean field way for the fluid and solid phases. In this way vapour-liquid and liquid-solid equilibrium is obtained and some discussion on the effect of the quadrupole moment on the location of the triple point is possible.

The model chosen to perform this study is a hard quadrupolar dumbbell. The quadrupolar interaction is that described by Eq.(2). The dumbbell is formed by two hard spheres of diameter σ, being the bond length given by L. The reduced bond length is usually denoted as L^*. Since we are using hard quadrupolar models the reduced quadrupole will be defined as $Q^{*2} = Q^2/(kTd_{HS}^5)$ where d_{HS} is the diameter of a hard sphere with the same volume than the dumbbell.

3.1 SOLID STRUCTURES FOR QUADRUPOLAR HARD DUMBBELLS

Recently Vega,Paras and Monson [21,22] have performed computer simulation studies of hard dumbbells and quadrupolar hard dumbbells [4] in the fluid and solid phase. Equation of state and free energies were determined for the fluid and solid phases. In this way the

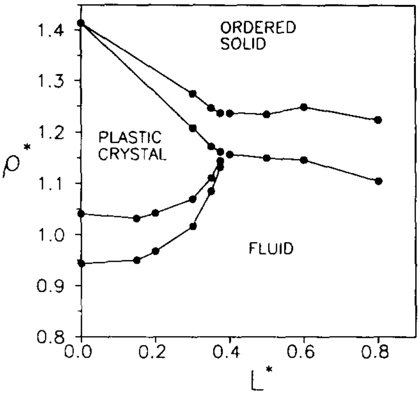

Fig. 5. Phase diagram of hard dumbbells as obtained from computer simulation [21,22,30]. The solid phases are the plastic crystal, and an orientationally ordered solid which yields close packing for the dumbbells. Coexistence densities are plotted as a function of the reduced bond length.

phase diagram for these models was obtained. In fig.5 the phase diagram of hard dumbbells (without quadrupole) is presented [21,22].

For slightly anisotropic molecules freezing occurs into a plastic crystal solid. In the plastic crystal solid the centers of mass of the molecules are located on the lattice positions but there is no long range orientational order. At high pressures the plastic crystal transforms into a close packed solid. For anisotropies larger than $L^* = 0.38$ freezing occurs into a close packed monoclinic structure. In this structure both the center of mass and orientations of the molecules are clearly defined. When a quadrupole moment is added to the molecule the situation changes dramatically [4]. In fig.6 the stable solid phases found at freezing for quadrupolar hard dumbbells are plotted as a function of the elongation L^* and the reduced quadrupole moment.

An interesting feature is now the appearance of two new types of solid structure, the $\alpha - N_2$ structure and an orthorhombic structure. The appearance of the $\alpha - N_2$ structure can be easily understood, since for this solid, pairs of nearest neighbours molecules are in a relative orientation close to the T one. This is the reason why at very high quadrupole moments the stable solid structure at low pressure is the $\alpha - N_2$ structure regardless of the molecular elongation. Another interesting feature of fig.6 is that a high quadrupole moment prevents the appearance of a plastic crystal phase. Quadrupolar interactions limit the orientational freedom of the mildly anisotropic molecules. The results of fig.6 resemble those of English and Venables [23], although these authors used internal energy rather than free energy for defining the stability of a solid phase.

Can we understand some features of the phase diagram of linear or linear-like molecules by using fig.6 ? Nitrogen and oxygen are molecules with small anisotropy and quadrupole moment. According to fig.6 they should freeze into an plastic crystal phase. This is in-

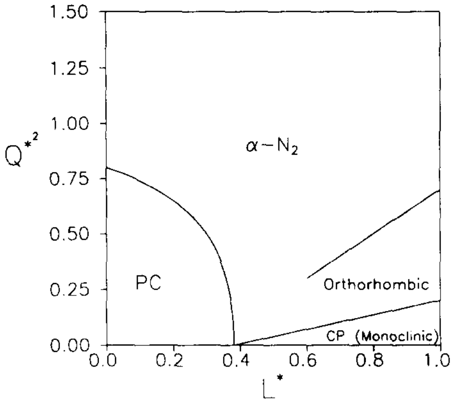

Fig. 6. Stable solids at freezing for quadrupolar hard dumbbells for several values of the reduced bond length L^* and quadrupole moment Q^{*2}.PC,CP,orthorrombic and $\alpha - N_2$ denotes the plastic crystal, close packed, orthorrombic and $\alpha - N_2$ structures respectively.

deed found in experiments. Acetylene and carbon dioxide are molecules with a very large value of the quadrupole moment. According to fig.6 they should freeze into an $\alpha - N_2$ structure. Experimentally it is found that this is the case. For the halogens, Cl_2, Br_2, I_2 according to fig.6 an orthorrombic structure should be stable and this also in agreement with experiment. Evidently the quadrupolar hard dumbbell is a simple but useful model to understand the freezing behavior of linear quadrupolar molecules.

3.2 EFFECT OF THE QUADRUPOLE MOMENT ON THE LOCATION OF THE TRIPLE POINT

The ratio of the triple to critical temperature gives an idea of the liquid range of a given substance viewed from a corresponding states perspective. For simple fluids such as Ar or Kr, the ratio of the triple to critical point temperature is about 0.55. Low values of this ratio indicate a wide liquid range, whereas high values of this ratio indicate a narrow liquid range. Just to give a few examples of the big variations found in nature for this ratio, let us mention that for n-propane it takes the value 0.23 whereas for carbon dioxide it amounts to 0.71. In 1964 Longuet-Higgins and Widom [5] found a simple way of explaining the value of the triple-to-critical point temperature found for the noble gases. They used computer simulation values for the equation of state and free energies of hard spheres in the the fluid and solid branches and added the contribution of the attractive forces via a mean field approximation. We have

$$A = A_H - a\rho \tag{6}$$

$$p = p_H - a\rho^2 \tag{7}$$

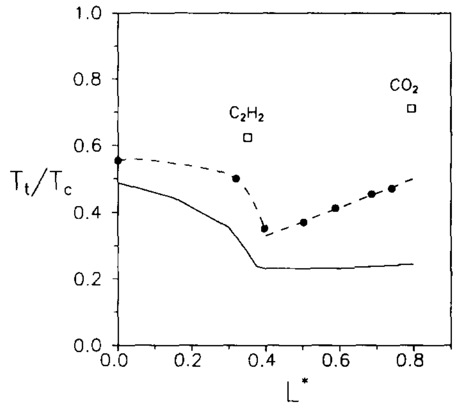

Fig. 7. The ratio of the triple to critical point temperatures for linear non polar diatomic fluids as obtained from Eqs.(6-7) (solid line). Non labeled points are experimental values for (from left to right) Ar, N_2,O_2,F_2,Cl_2,Br_2,I_2. Squares are experimental values for acetylene and carbon dioxide.

where A_H and p_H are the free energy and pressure of the hard system, ρ is the number density and a is the mean field constant. Paras et al. [6] have extended the treatment of Longuet-Higgins and Widom to a hard dumbbell reference system by using the simulation values of the free energy and pressure for this system in Eqs.(6-7). In fig.7 we present results for the ratio of the triple to critical point temperature of linear nonpolar molecules. Some experimental results are also included.

The agreement with experiment suffers partly from the effect of the mean field approximation but some common trends between theory and experiment are clearly visible. The ratio T_t/T_c decreases substantially when going from noble gases to molecules of moderate anisotropy such as N_2 or O_2. For elongations larger than $L^* = 0.38$ this ratio increases. Both features are captured by this simple treatment. The presence of two lines which meet at $L^* = 0.38$ follow directly from the freezing of hard dumbbells presented in fig.5. One line corresponds to the freezing into the plastic crystal solid whereas the other one corresponds to the freezing into the close packed orientationally ordered solid.

Nevertheless in fig.7 some discrepancies are evident. For instance the experimental values of T_t/T_c found for acetylene (C_2H_2) and carbon dioxide (CO_2) can not be explained by Eqs.(6-7) using a hard dumbbell reference system. However the Longuet-Higgins and Widom treatment can be extended by including the quadrupolar forces into the reference term so that [7]:

$$A = A_{H,Q} - a\rho \tag{8}$$

$$p = p_{H,Q} - a\rho^2 \tag{9}$$

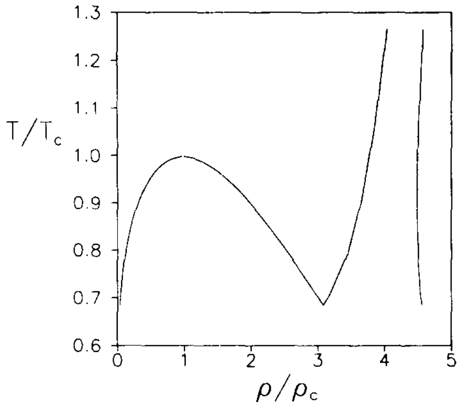

Fig. 8. **The phase diagram of quadrupolar linear molecule with $L^* = 0.8$ as obtained from Eqs.(8-9). The quadrupole moment was chosen to mimic that of carbon dioxide. Vapour-liquid and solid-fluid equilibrium for this model are shown. Temperature and density are reduced by their critical values.**

Free energies and EOS for quadrupolar hard dumbbells have been obtained from simulation by Vega and Monson [4] so that Eqs.(8-9) can be easily implemented. When this is done for a quadrupolar hard dumbbell with $L^* = 0.8$ and a quadrupole moment adequate for CO_2 the obtained phase diagram is presented in fig.8.

The T_t/T_c ratio found from this treatment for this model is about 0.69, in good agreement with the experimental value found for carbon dioxide which is of 0.71. The conclusion is clear: the quadrupole increases the ratio of the triple to critical point temperature and decreases the liquid range of a substance. The explanation is rather simple. In fig.8 the solid phase in equilibrium with the fluid presents the $\alpha - N_2$ structure. In this structure the molecules are not packed very efficiently so that the solid has a rather low density. The whole solid-fluid coexistence curve is then shifted to lower densities so that it intersects the vapour-liquid equilibrium curve at higher temperatures.

4 CONCLUSIONS

In this paper we have reviewed recent theoretical work on the effect of a quadrupole moment on the phase diagram of a linear molecules. From the results of this work we can make the following conclusions:

i) The quadrupole significantly affects the structure of a fluid. Unlike dispersive forces the quadrupole changes the structure of the fluid even at high densities.

ii) The quadrupole moment raises the critical temperature, pressure and density of a fluid.

iii) The increase in the critical temperature due to the quadrupole moment depends very weakly on the molecular elongation, when plotted as a function of the equivalent quadrupole defined by Eq.(5).

iv) Shape and polarity effects lead to deviations from the principle of corresponding states. The presence of nonspherical shape and/or a quadrupole results in the broadening of the coexistence curve and an increase of the slope of the vapour pressure curve.

v) The quadrupole moment introduces new solid structures in the phase diagram of linear molecules. In particular the $\alpha - N_2$ and the orthorhombic structure are stabilized by the quadrupolar interactions.

vi) At very high values of the quadrupole moment freezing is expected to occur into an $\alpha - N_2$ structure. Large values of the quadrupole moment also suppress the presence of a plastic crystal phase.

vii) Molecules with a very large quadrupole moment exhibit a narrow liquid range (i.e a high value of the T_t/T_c ratio).

Although in this paper we have focused primarily on simulation results, similar conclusions can also be obtained by using theoretical treatments for the model systems studies. For instance using perturbation theory, it is possible to understand in a qualitative way the main features of the vapour-liquid equilibrium of quadrupolar fluids presented in this work [24,25]. Solid phases of quadrupolar linear molecules can also be handled with theory. In fact recent work has shown that it is possible to implement successfully the cell theory of Lennard-Jones and Devonshire [26] for these kind of solids [7,27].

There remain several areas for further investigation. One such area is the study of quadrupolar oblate molecules as benzene. For oblate molecules not much in known either about the effect of the quadrupole on the vapour-liquid equilibrium or on the solid-fluid equilibrium. Another area concerns mixtures of quadrupolar molecules. We can also anticipate that improved knowledge of the phase diagram will impact the development of our understanding of transport phenomena in these systems [28,29].

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