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RESEARCH NOTE

Solid–liquid equilibrium for quadrupolar molecules

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Theoretical calculations are presented of solid–liquid equilibrium for linear quadrupolar molecules, focusing especially on the ratio of the triple point temperature to the critical temperature. The proposed treatment uses the hard quadrupolar dumbbell model as the reference system, and incorporates the effect of dispersion forces through a mean-field term. The reference system of quadrupolar hard dumbbells is described using perturbation theory for the liquid and cell theory for the solid. Good agreement with simulation results of quadrupolar hard dumbbells is obtained through the theoretical description. After incorporating attractive dispersion forces, the temperature dependence of solid–liquid and vapour–liquid equilibrium was studied and the triple point determined for two linear quadrupolar model systems. The two models were representative of carbon dioxide and acetylene, respectively. The ratio of the triple to critical point temperatures determined from the theory was about 0·7, in good agreement with experiment.

1. Introduction

During recent years our knowledge of the vapour–liquid equilibria of linear fluids has increased considerably. Perturbation theories of linear molecules [1–4] and computer simulations of vapour–liquid equilibrium using such methods as the Gibbs ensemble [5] have contributed significantly to advances in this area [4, 6, 7]. The effect of polar forces (i.e. a dipole or quadrupole moment) on the vapour–liquid equilibrium of spherical [8–10] and linear fluids has also received considerable attention. It can be said that our understanding of the vapour–liquid equilibria of linear polar molecules is now quite good [6, 7, 11, 12].

On the other hand, much less is understood about the solid–liquid equilibrium in such systems, and how this is related to the anisotropy of the intermolecular forces. The relationship between the vapour–liquid and solid–liquid regions of the phase diagram is quite sensitive to details of the molecular anisotropy, and this relationship determines the relative size of the liquid range on the phase diagram. One way of quantifying this is the ratio of the triple point temperature to the critical temperature T_t/T_c. For instance, for argon, ethane, and carbon dioxide this ratio takes the values 0·55, 0·30, and 0·71, respectively [13]. Evidently this ratio is sensitive to quite modest changes in molecular structure.

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We have recently considered the problem of determining T_t/T_c for linear molecules. This problem was approached in several steps. First, the fluid–solid equilibrium of hard dumbbells was obtained from computer simulations [14–16]. The main conclusion of these studies is that hard dumbbells freeze into a plastic crystal phase for $L^* < 0.38$, and into a close-packed structure for $L^* > 0.38$. The reduced length L^* is defined as $L^* = L/\sigma$, where L is the bond length and σ the diameter of the interaction site. In a second step, the cell theory of Lennard-Jones and Devonshire [17] was applied to the description of the solid phase of hard dumbbells, and good agreement with simulation was found [18]. This theory is less demanding computationally than simulations, by two orders of magnitude, and is more accurate quantitatively than the extensions of density functional theory which have been applied to these systems [19, 20]. The cell theory has also been applied to studying spherical particles with attractive forces [21]. Finally, the properties of hard dumbbells were used in a generalized van der Waals theory of solid–fluid equilibria [22], very similar to that used in the seminal work of Longuet-Higgins and Widom [23]. The variation of T_t/T_c with L^* obtained from this treatment was described in [22], and comparison with experimental data was made. Although the agreement between theory and experiment was not quantitative, trends in the variation of T_t/T_c with L^* predicted by the theory were similar to those seen experimentally. However, CO_2 exhibits a rather high value of T_t/T_c which cannot be explained by considering the molecular shape only. In [22] it was conjectured that incorporation of the quadrupole moment of the molecule is necessary to explain the value of T_t/T_c found in CO_2. A prelininary calculation using a simple treatment of the effect of quadrupolar forces on the phase yielded a value of T_t/T_c in good agreement with experiment. It was assumed that quadrupole forces stabilize the α-N_2 structure instead of the close-packed structure of hard dumbbells. Recently, we have performed a computer simulation study of the phase diagram of quadrupolar hard dumbbells [24]. One of the conclusions of this work was that, for sufficiently high quadrupole moments, the solid phase in equilibrium with the fluid is the α-N_2 structure. In this paper the problem of the determination of T_t/T_c for linear molecules with large quadrupole moments is considered on a more rigorous footing than that used in our earlier work [22]. Our goal is twofold. First, the ability of the cell theory to describe a quadrupolar hard dumbbell system is tested. Secondly, the van der Waals-like treatment proposed in [22] is applied to quadrupolar molecules, but with a more accurate treatment of the solid phase. Theoretical predictions of T_t/T_c for carbon dioxide and acetylene are compared with experimental results.

2. Theoretical treatment of the properties of quadrupolar hard dumbbells

To determine the fluid–solid equilibrium of quadrupolar hard dumbbells (HDQ) a description of the fluid and solid phases is needed. In this work a point quadrupole will be considered [8]. For the fluid phase we have used a perturbation theory of HDQ described in [25]. The theory is an extension due to Boublik [26] to molecular fluids of the theory proposed for spherical polar molecules by Pople–Gubbins [8]. In this perturbation theory, the equation of state (EOS) of hard dumbbells is needed, and the one proposed by Tildesley and Streett has been used [27] (see [25] for further details). This theory provides the free energy and EOS of the HDQ fluid phase. In [25] the theory was tested by comparing theoretical predictions with simulations results of quadrupolar dumbbells with $L^* = 0.6$. Since new simulation data have been

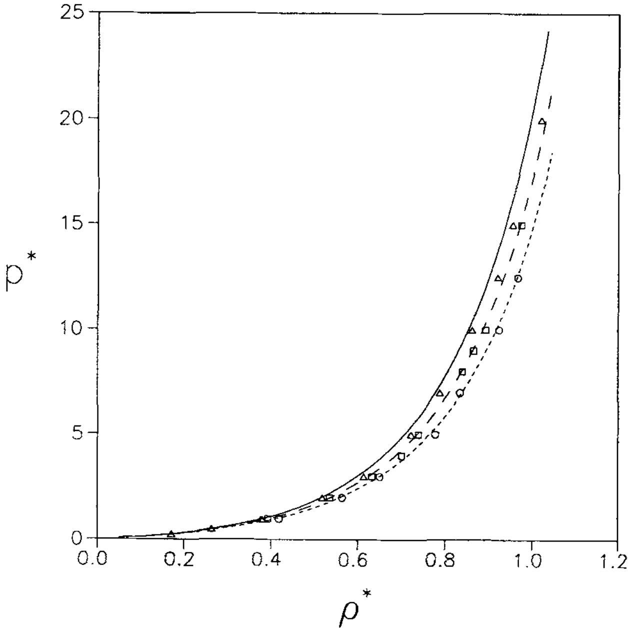

Figure 1. Equation of state of the fluid phase of quadrupolar hard dumbbells with $Q^{*2} = 0{\cdot}5$ as obtained from Monte Carlo simulations (symbols) [24], and from perturbation theory [25] (curves): triangles, $L^* = 0{\cdot}8$; squares, $L^* = 0{\cdot}6$; circles, $L^* = 0{\cdot}3$; solid curve, $L^* = 0{\cdot}8$; dashed curve, $L^* = 0{\cdot}6$; short dashed curve, $L^* = 0{\cdot}3$. Pressures and densities are reduced as in [24].

obtained recently for quadrupolar hard dumbbells [24], a more complete test of the theory can be performed. In figure 1 a comparison between the EOS obtained from the theory of [25] and computer simulations of the fluid phase of quadrupolar hard dumbbells is shown. The agreement is good, suggesting that we have a reasonable theoretical description of the fluid phase properties. Let us now focus on the solid phase. In [18] it was shown that the cell theory of Lennard-Jones and Devonshire [17] can be implemented to describe the behaviour of the solid phase of hard dumbbells. Here, we discuss the implementation of the cell theory for quadrupolar hard dumbbells. Gibbons and Klein [28] have previously applied the cell theory to the properties of solid CO_2 but solid–fluid equilibrium was not considered. Let us define $U(\boldsymbol{r}_1, \omega_1)$ as the potential energy experienced by a central molecule in a cell, labelled as 1 with a position given by $\boldsymbol{r}_1$ and an orientation by ω_1, owing to interactions with the rest of the molecules of the solid. Then $U(\boldsymbol{r}_1, \omega_1)$ is given by

$$U(\boldsymbol{r}_1, \omega_1) = \sum_{j=2}^{j=N} u_{\mathrm{HD}}(\boldsymbol{r}_1, \omega_1, \boldsymbol{r}_j, \omega_j) + u_{\mathrm{QQ}}(\boldsymbol{r}_1, \omega_1, \boldsymbol{r}_j, \omega_j), \tag{1}$$

where u_{HD} is the pair potential between hard dumbbells and u_{QQ} is the interaction between ideal quadrupoles [8]. In evaluating $U(\boldsymbol{r}_1, \omega_1)$ of equation (1) all the molecules of the solid remain at their equilibrium positions and orientations. The energy U will be divided into two terms [29]:

$$U(\boldsymbol{r}_1, \omega_1) = U^0 + \Delta U(\boldsymbol{r}_1, \omega_1), \tag{2}$$

where U_0 is the lattice energy of molecule 1 when fixed on the lattice position with the equilibrium orientation. For quadrupolar hard dumbbells U_0 is just the quadrupolar energy of a central molecule due to interaction with the other molecules of the crystal. The free energy of the solid phase A^{HDQ} is approximated within the cell theory by [18, 29, 30]

$$A^{\mathrm{HDQ}} = -NkT \ln ((q/V)Z'_1) + NU_0/2, \tag{3}$$

where q is the molecular partition function which includes all the contributions from the internal degrees of freedom, and V is the volume of the system. The cell partition function Z'_1 is given by

$$Z'_1 = 1/(4\pi) \int \exp(-\beta \Delta U(\mathbf{r}_1, \omega_1))\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\omega_1, \tag{4}$$

where $\beta = 1/kT$. The lattice energy U_0 can be evaluated readily by lattice summation and in [24] it has been given for any value of Q^* for several L^* and solid structures. In order to evaluate Z'_1 a Monte Carlo numerical integration procedure was performed. Details of the procedure may be found in [18]. The numerical evaluation of Z'_1 at a given density of the solid takes only a few seconds on a typical workstation. Values of Z'_1 obtained in this way at several densities were fitted to the expression [18, 31]

$$Z'_1 = C\alpha^5 \exp(a_1\alpha + a_2\alpha^2 + a_3\alpha^3), \tag{5}$$

where α is defined as

$$\alpha = (\rho_{\mathrm{cp}} - \rho)/\rho_{\mathrm{cp}}, \tag{6}$$

here ρ is the number density and ρ_{cp} is the maximum packing density of the structure under consideration. Values of ρ_{cp} for different solid structures of hard dumbbells have been reported in [15]. In this work, we have performed cell theory calculations for quadrupolar hard dumbbells in the α-N_2 structure. It has been shown recently that this is likely to be the stable solid structure of quadrupolar hard dumbbells when the quadrupole moment is sufficiently high [24]. The reduced quadrupole moment is defined via

$$Q^{*2} = Q^2/(kTd_{\mathrm{HS}}^5), \tag{7}$$

where Q is the quadrupole moment, and d_{HS} is the diameter of a hard sphere with the same volume as the hard dumbbell, given by

$$d_{\mathrm{HS}}^3 = \sigma^3(1 + 1{\cdot}5L^* - 0{\cdot}5L^{*3}). \tag{8}$$

In figure 2 we present the EOS for the quadrupolar hard dumbbell system with $L^* = 0{\cdot}8$ and $Q^{*2} = 1$ as obtained from simulation, and by using the cell theory for the solid phase and the perturbation theory for the fluid phase. Tie lines corresponding to the fluid–solid equilibrium are given for both theory and simulation. The cell theory provides a good description of the properties of the solid. In addition the fluid–solid transition predicted by the theory is in good agreement with simulation. In these calculations the quadrupole–quadrupole potential was truncated in the manner described in [24]. It is worth noting that we have found that the cell theory can be implemented without significant loss of accuracy by including only the nearest neighbour contribution to ΔU. This reduces the computer time by about a factor of four. The full cell theory has a computational requirement which is about two orders of magnitude smaller than an NVT Monte Carlo simulation of the solid.

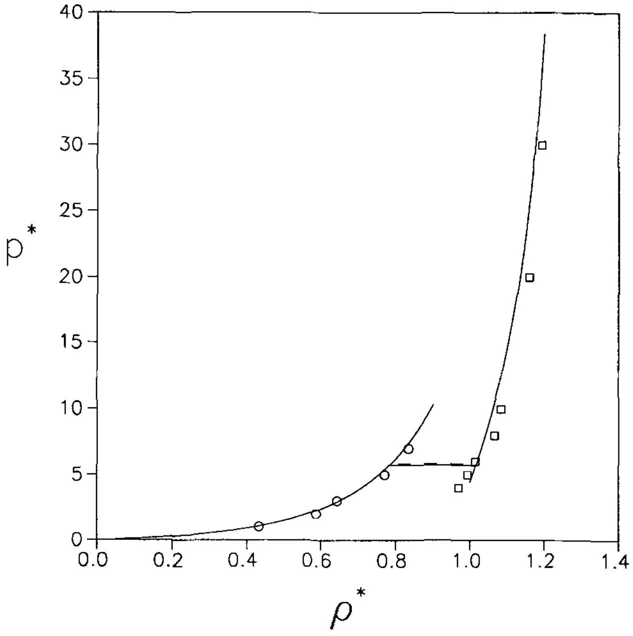

Figure 2. Equation of state of quadrupolar hard dumbbell with $L^* = 0{\cdot}8$ and $Q^{*2} = 1$. The symbols correspond to Monte Carlo simulation results for the fluid phase (circles) and α-N_2 solid structure (squares) [24]. The solid curves represent theoretical results from perturbation theory [25] for the fluid phase and from the cell theory for the solid phase. Tie lines for the fluid–solid transitions as obtained from Monte Carlo simulations (dashed line) and from theory (solid line) are also shown.

3. Generalized van der Waals theory

Following our previous work [22], attractive forces have been incorporated through a mean-field term in the manner first proposed by Longuet-Higgins and Widom [23]. It was also applied by Rigby [32] to determine the vapour–liquid equilibrium of molecular fluids. The basic equations of this theory are [22]

$$A/N = A^{\mathrm{HDQ}}(Q^2, \rho, T, L^*)/N - a\rho, \tag{9}$$

and

$$p = p^{\mathrm{HDQ}}(Q^2, \rho, T, L^*) - a\rho^2, \tag{10}$$

where A^{HDQ} and p^{HDQ} are the free energy and pressure, respectively, of a hard quadrupolar dumbbell reference system. The parameter a measures the strength of the dispersion forces. Equation (9) can be regarded as the simplest way of incorporating the effect of attractive dispersion forces into the free energy of the fluid and solid phases. Eventually, for the solid phase the term $-a\rho$ could be replaced by the lattice energy due to the attractive dispersion forces [33].

Free energies and pressures of the HDQ system are obtained in the manner just described. A useful parameter in these calculations is the ratio of the quadrupole moment energy to the dispersion energy. This can be expressed via the dimensionless parameter R as [22]

$$R = (Q^2/d_{\mathrm{HS}}^5)/(a/d_{\mathrm{HS}}^3) \tag{11}$$

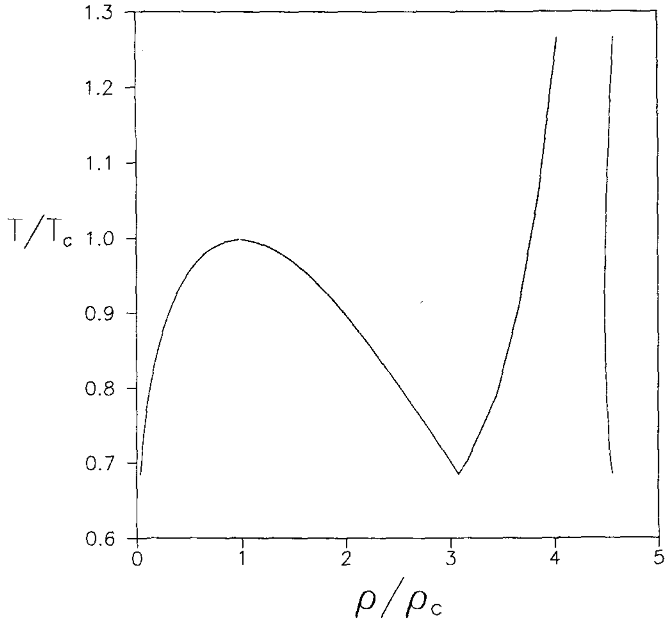

Figure 3. Corresponding states plot of the phase diagram of carbon dioxide as obtained from the present theory.

In order to apply equations (9) and (10) to a comparison of theory with experiment, a knowledge of L^* and R is necessary. In this work two linear quadrupolar molecules were considered: acetylene and carbon dioxide (CO_2). The elongations were fixed as $L^* = 0{\cdot}35$ for acetylene and $L^* = 0{\cdot}8$ for CO_2, which approximately reproduce the anisotropy of the molecules and are close to previous estimates of L^* for diatomic models of these molecules [2, 34, 35]. The procedure for obtaining R is that adopted in [22] for carbon dioxide, now described briefly. By using the experimental critical temperature [13] and quadrupole moment [8] of these molecules, and an estimate for σ [2, 34, 35], the value of $Q^{*2}_{c,\mathrm{exp}} = Q^2/(kT_c d^5_{\mathrm{HS}})$ was obtained. Here, the subscript c stands for the critical values. Then a trial value of R was chosen and the vapour–liquid equilibrium was computed from equations (9) and (10). The reduced quadrupole moment at the critical point obtained from theory is given by $Q^{*2}_{c,\mathrm{theory}} = Ra/(kT_c d^3_{\mathrm{HS}})$. We proceeded in this way until $Q^{*2}_{c,\mathrm{theory}}$ matched $Q^{*2}_{c,\mathrm{exp}}$. The experimental quadrupole moment of carbon dioxide is known precisely [8]. However, for acetylene the uncertainty of the quadrupole moment is very large (up to 40%). The experimental value of the quadrupole moment of acetylene was taken as $Q = 19{\cdot}34$ cm^2. This value corresponds to the average of the quadrupole moments of acetylene reported in [8]. The values of R obtained as described earlier were $R = 0{\cdot}17$ for acetylene and $R = 0{\cdot}11$ for CO_2. In figure 3 the phase diagram for carbon dioxide obtained from equations (9) and (10) is presented in a reduced temperature versus reduced density plot. From our calculations $T_t/T_c = 0{\cdot}69$, which compares favourably with the experimental value $T_t/T_c = 0{\cdot}71$ [13]. The theory predicts a large change in density at freezing, which is in agreement with experimental results of CO_2 at the triple point [36]. Results of this work agree with those presented in [22], although now the treatment of the solid phase of HDQ is performed in a more rigorous manner.

Figure 4 shows the phase diagram of acetylene based on equations (9) and (10).

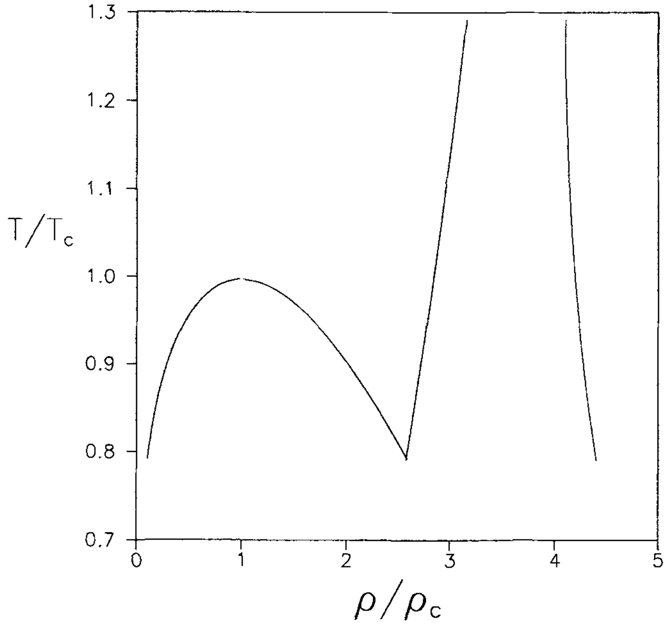

Figure 4. Corresponding states plot of the phase diagram of acetylene as obtained from the present theory.

The value of T_t/T_c found from our theoretical treatment is 0·79 and the experimental result is 0·62 [37]. The agreement may be considered as satisfactory given the large uncertainty in the experimental value of the quadrupole moment of acetylene. For acetylene the ratio T_t/T_c is quite sensitive to the assumed value of the quadrupole moment. For instance, if the $Q = 14{\cdot}67\ \mathrm{cm}^2$ is assumed then we obtain $T_t/T_c = 0{\cdot}68$ and the density change at freezing is reduced considerably, in better agreement with experiment. In addition to the issue of the large uncertainty of the quadrupole moment of acetylene, it should be mentioned that the dumbbell model may not be the best description of the molecular shape for this molecule. In any case, the significant result of our treatment is that acetylene should present a large value of T_t/T_c, and this is in agreement with experiment. The anisotropy of acetylene is similar to that of oxygen, and the experimental value of T_t/T_c for oxygen is 0·35. The present theory predicts that the quadrupole moment of acetylene is responsible for the large difference in T_t/T_c between oxygen and acetylene. Note that in our theoretical treatment the α-N_2 structure (the stable structure on freezing for acetylene and CO_2) is not imposed arbitrarily for the solid, since it is indeed the stable phase of the HDQ when the quadrupole moments of acetylene and carbon dioxide are used [24]. On the basis of lattice energy calculations, English and Venables [38] also concluded that the α-N_2 structure is the stable one for linear quadrupolar systems when the quadrupole moment is sufficiently high.

4. Conclusions

A simple theory for the solid–fluid equilibrium of quadrupolar linear molecules has been considered. Our theoretical treatment is based on considering the quadrupolar hard dumbbell model as the reference system and incorporating attractive forces through a mean-field term. Our calculations have focused on the ratio T_t/T_c, which measures the relative size of the liquid region of the phase diagram, for two molecules: acetylene and carbon dioxide. These two molecules solidify into the α-N_2 structure at the triple point. By using reasonable estimates of the molecular elongation and of the ratio of quadrupolar to dispersion attractive forces, we found values of T_t/T_c in good agreement with the experimental results.

The rare gases have a value of T_t/T_c of about 0·55 [13]. In previous work [22], we showed how T_t/T_c changes with molecular elongation when no multipolar forces are present. In this work it is shown that when a large quadrupole moment is present then T_t/T_c is much larger than for spherical molecules. Consequently, linear molecules with a large quadrupole moment should present a rather small liquid range. The correlation between T_t/T_c and the quadrupole moment has been noted before [37, 39]. The present work provides the first theoretical description of the molecular phenomena underlying this behaviour.

Our results lead us to speculate that whenever multipolar forces stabilize a solid structure with a much lower density than would be obtained by the optimal packing of the repulsive cores of the molecules, then a rather large value of T_t/T_c and, consequently, a small liquid range are expected. In our case the quadrupolar forces stabilize the α-N_2 structure, which is not especially efficient in packing hard dumbbells. The density of the solid will be lower than for a more closely packed structure, and hence the triple point will occur at a higher temperature. Of course the treatment presented in this work is rather qualitative, and it cannot be expected to describe all the features of the phase diagram exhibited by linear quadrupolar molecules. However, it suggests that molecular shape and quadrupolar forces are principal factors in determining the phase diagram.

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