A generalized van der Waals theory of solid-fluid equilibria for non-spherical molecules

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A generalized van der Waals theory of solid–fluid equilibria for non-spherical molecules

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By making use of recently obtained theoretical and Monte Carlo simulation results for solid state thermodynamics and solid–fluid equilibria for systems of hard dumbbells a generalized van der Waals theory of solid–fluid equilibria has been formulated. The theory predicts how the temperature dependence of the solid–liquid (and vapour–liquid) equilibrium is influenced by non-spherical molecular shape for diatomic molecules. Two regimes of behaviour are identified, depending on whether the underlying hard dumbbell reference system freezes into a plastic crystal or an orientationally ordered crystal. The theory correctly predicts a decrease in the triple point temperature and density change on freezing between spherical molecules, such as argon, and slightly non-spherical molecules which freeze into plastic crystal phases such as nitrogen. An extension of the theory which includes a simplified treatment of the influence of quadrupolar interactions provides a plausible explanation for the relatively high reduced triple point temperature of carbon dioxide.

1.   Introduction

Some time ago Longuet-Higgins and Widom [1] suggested that an equation of state of the van der Waals form could be applied to the freezing of argon. The key feature of their approach was to replace the equation of state for hard spheres implied by the original van der Waals equation with a more accurate one based on results from molecular simulations. Since the simulation results for hard spheres exhibit a solid–fluid phase transition at high pressure, any generalized van der Waals equation of state that incorporates these results for the hard-sphere equation of state will likewise exhibit such a transition. In this way Longuet-Higgins and Widom were able to obtain quite accurate results for the freezing properties of argon near its triple point [1].

In this paper we explore the possibility of extending the Longuet-Higgins and Widom approach to the solid–fluid equilibria of diatomic molecules. Extensive results for the properties of solid phases formed by hard-sphere models of diatomic molecules (hard dumbbells) for several bond lengths L^* ($= L/\sigma$ where L is the bond length and σ is the atom diameter) using both Monte Carlo simulation results [2, 3] and cell theory [4] are now available. This work together with an accurate equation of state for hard-dumbbell fluids provides a reference system for a generalized van der Waals treatment of solid–fluid equilibria for diatomic molecules. We have

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assumed that the stable crystal structure to be used in the generalized van der Waals theory is that of the hard-dumbbell reference system. Monte Carlo simulation work has shown that two types of solid phase are important in the freezing of hard dumbbells. For mildly anisotropic molecules [2, 3] ($L^* < 0.38$) the stable phase on freezing seems to be a cubic (fcc or hcp) plastic crystal, resembling to some extent the β-phase of nitrogen. The freezing properties show a strong dependence upon L^* in this regime [2, 3]. The coexistence densities and pressure increase sharply between $L^* = 0.2$ and $L^* = 0.38$. Also the density change on freezing into the plastic crystal decreases sharply with L^* in this range and vanishes at the limit of stability of the plastic crystal phase. Freezing into the plastic crystal phase of hard dumbbells seems to provide a good structural model of the freezing of liquid nitrogen into β-nitrogen, which is also accompanied by a small density change. For more anisotropic molecules [2] ($L^* > 0.38$) the stable solid phases on freezing are orientationally ordered base-centred monoclinic structures which allow the dumbbells to achieve their maximum packing densities and which are closely related to the structures formed by the solid halogens [5]. In this range the freezing properties show a much less strong dependence upon L^*. Both the coexistence densities and pressure show a slight maximum in the range $L^* \sim 0.6$. The density change on freezing is comparable to that for hard spheres.

One of the principal results of this work is a prediction of a variation of the reduced triple point temperature (defined as the triple point temperature as a fraction of the critical temperature) with molecular anisotropy. When the stable solid phase is a plastic crystal the reduced triple point temperature decreases with increasing molecular anisotropy. This is consistent with the observed behaviour for nitrogen and oxygen, both of which freeze into plastic crystals. When the stable solid phase is orientationally ordered, the triple point temperatures show a slight increase with increasing molecular anisotropy. This is to some extent consistent with the observed behaviour for the halogens. An adaptation of the approach to systems with quadrupolar interactions offers a plausible explanation for the especially high reduced triple point temperature of carbon dioxide.

2.   Generalized van der Waals theory

The basic equation of the generalized van der Waals theory is

$$A = A_0 - a\rho, \tag{2.1}$$

where A is the Helmholtz free energy per molecule, A_0 is the Helmholtz free energy per molecule of the reference system, ρ is the molecular density and a is a parameter which measures the strength of the attractive intermolecular forces in the system. Differentiation gives the equation of state

$$P = P_0(\rho, T) - a\rho^2. \tag{2.2}$$

In our work A_0 and P_0 are calculated for fluids from the equation of state developed by Tildesley and Streett [6] for hard-dumbbell fluids (which for hard spheres reduces to the Carnahan–Starling [7] equation of state), and for solids from Monte Carlo simulation results [2] and the cell theory [4] obtained recently for hard dumbbells. We should point out that although to our knowledge this is the first application of

Table 1. Triple point properties for argon as determined from application of the Longuet-Higgins and Widom (LHW) theory based on Monte Carlo (MC) and cell theory (CT) data as compared with experiment [26]. λ is defined as $a\rho_{cp}/kT$. ρ_{cp} stands for the close packing density of hard spheres. The reduced densities are defined as $\rho^* = \rho d^3$ where d is the diameter of the hard sphere. α and β are the thermal expansion coefficient and isothermal compressibility respectively. The subscript f denotes properties of the fluid phase. The original results of (LHW) [1] are also included.

	λ	ρ_f^*	ρ_s^*	ρ_f/ρ_s	$\ln(pV_f/NkT)$	$\Delta S/Nk$	$U_f NkT$	$T\alpha_f$	$NkT\beta_f/V_f$
MC	16·8	0·897	1·093	1·218	−6·85	2·20	−9·99	0·52	0·0505
CT	16·2	0·883	1·102	1·248	−6·96	2·51	−10·11	0·51	0·0518
LHW	14·7	0·83	0·99	1·19	−5·9	1·64	−8·6	0·50	0·058
Exp.	–	0·841	0·937	1·114	−5·88	1·69	−8·53	0·366	0·0495

equation (2.2) to solid–fluid phase equilibria for non-spherical molecules it has previously been applied to vapour–liquid equilibria by Rigby [8] and also to the study of nematic–isotropic equilibria in liquid crystals by Barboy and Gelbart [9].

As a starting point we have repeated the calculations of Longuet-Higgins and Widom [1] for the case of spheres. Our calculations differ in some respects from those of Longuet-Higgins and Widom and this does affect the results obtained. The principal difference is that the estimates of the solid–fluid coexistence pressure and densities used by Longuet-Higgins and Widom are too low, since they were based on the early estimates by Ree and Hoover [10] which have since been superseded by more accurate results by the same authors [11]. For the hard-sphere solid we used the equation of state of Hall [12] which gives a good fit of the molecular dynamics data [13] and also the cell theory [4]. Table 1 gives a comparison with experiment for some properties of argon at the triple point as calculated by us and by Longuet-Higgins and Widom [1]. Our results differ from those of Longuet-Higgins and Widom because of the different estimates of the hard sphere freezing properties used. Evidently our results, which represent a more correct implementation of the theory, are in most cases in somewhat poorer agreement with experiment than those of Longuet-Higgins and Widom. Nevertheless, the agreement is still good given the simplicity of the theory, and are sufficiently good to warrant investigation of the influence of the molecular shape within the context of the theory. Also the results are not significantly changed when the cell theory is used to determine the properties of the hard-sphere solid.

3. Influence of molecular shape on solid–fluid equilibria

We begin with a general discussion of the phase diagrams produced from equation (2.1) for various values of L^*. Figure 1 shows reduced temperature versus reduced density for values of $L^* = 0·0$, 0·3, 0·6, 1·0, showing both vapour–liquid and solid–liquid equilibria. In these calculations the cell theory was used to determine the properties of the hard-dumbbell solids. Notice the broadening of the vapour–liquid coexistence region with increasing anisotropy. Plots of the logarithm of the reduced vapour pressure versus the reciprocal of the reduced temperature for different values of L^* show that the reduced vapour pressure decreases with increasing L^* at a given value of the reduced temperature, and
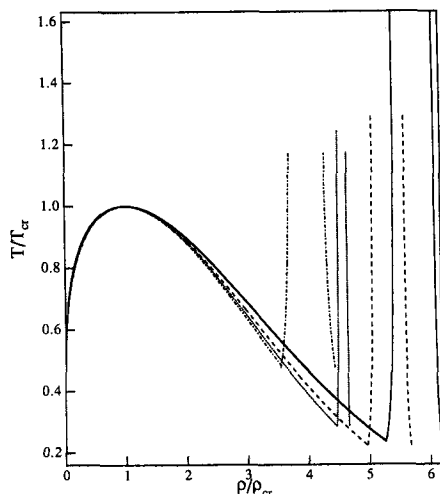
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Figure 1. Coexistence curves for diatomic systems. The lines correspond to: solid, $L^* = 1.0$; dashed, $L^* = 0.6$; dotted, $L^* = 0.3$; dot-dashed, $L^* = 0.0$.

provide a theoretical basis in terms of molecular shape effects for the acentric factor correlation of Pitzer [14]. These effects were first studied in the context of a generalized van der Waals theory by Rigby [8] and are qualitatively similar to those observed in a more sophisticated theoretical study of the two-centre Lennard-Jones model [15] and in experiments [16].

The variation of the solid–fluid coexistence densities with L^* at any temperature is related to that in the underlying hard-dumbbell system [2] and for the systems shown here the densities increase with L^* when reduced by the critical density. The coexistence densities increase sharply with L^* when the dumbbells freeze into a plastic crystal and more slightly when the dumbbells freeze into an orientationally ordered structure. There is a slight difference in the observed behaviour when the freezing densities are plotted as volume fractions rather than as densities reduced by the critical density as we have done here. In the former case a slight maximum is exhibited in the coexistences densities for freezing into an orientationally ordered structure [2], as we described earlier. This is because in our model the critical volume fraction is a decreasing function of L^*. Notice that the solid–fluid coexistence region is especially narrow for $L^* = 0.3$. This is due to the sharp decrease in the density change on freezing for a hard-dumbbell system for values of L^* close to that where the plastic crystal solid phase becomes unstable with respect to an orientationally ordered structure [3, 17]. The fractional density change observed is similar to that seen in the freezing of nitrogen.

The variation of the reduced temperature at the triple point with L^* can be interpreted in terms of a balance between two effects: the broadening of the vapour–liquid coexistence region with increasing L^* and an increase in the solid–fluid coexistence densities with increasing L^*. For small values of L^* where the hard-dumbbell reference system freezes into a plastic crystal the latter effect is more significant and the reduced triple point temperature decreases sharply with increasing L^*. For larger values of L^* where the hard-dumbbell reference system freezes into an orientationally ordered crystal the former effect is more significant and the reduced triple point temperature shows a slight increase with increasing L^*.
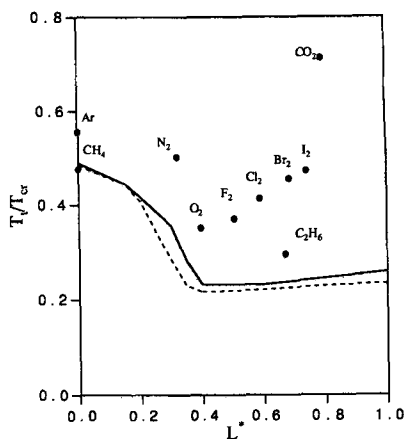
Figure 2. The reduced triple point temperature versus L^* for diatomic systems. The solid and dashed lines refer to the GVDW theory as applied on MC simulation and cell theory results, respectively. The points are experimental data for several systems [18].

Figure 2 shows the variation with L^* of the reduced triple point temperature calculated from the theory using both the cell theory and the simulation results for the properties of the hard-dumbbell solids. Experimental results [18] for various molecules are also shown using values of L^* based upon treating the molecule as a two-centre Lennard-Jones system [5, 19, 20]. For $L^* = 0.0$ we see that the value of T_t/T_c from the theory is somewhat lower than that for argon. This may be principally a consequence of the effect of the mean field approximation. Thus for $L^* < 0.4$ variation of T_t/T_c with L^* from the theory seems to be roughly consistent with the experimental results for nitrogen and oxygen which both freeze into plastic crystals. It is interesting to point out that if one assumes that the error introduced by the use of the mean field approximation does not depend on L^* then the theory would predict quite nicely the reduced triple point temperatures of Ar, N_2 and O_2. For $L^* > 0.4$, T_t/T_c shows a slight increase with L^*. The data for the halogens are to some extent consistent with this although the increase of T_t/T_c with molecular anisotropy is somewhat steeper in this case. Again we note that the use of the cell theory for the hard-dumbbell solid properties does not affect significantly the observed results.

We have also shown results for methane and ethane. The good agreement between the value of T_t/T_c for methane and the theory for $L^* = 0.0$ is surely fortuitous since a united atom model for methane may be too drastic a simplification in the solid phase. In any case the theory is roughly consistent with the decrease in T_t/T_c seen in passing from methane to ethane.

Figure 3 shows solid–fluid equilibria on a pressure versus temperature plot at higher temperatures and the influence of molecular shape upon the slope of the equilibrium line is clearly exhibited. Some experimental results [21, 22] are shown in figure 4 and the qualitative similarities with the theoretical results in figure 3 are striking. The slight nonlinearity in the experimental solid–fluid equilibrium lines are presumably due to effects such as pressure dependence in the heat capacity which are neglected in the van der Waals treatment. The influence of molecular shape on the slope of the solid–fluid equilibrium line as it arises in the theory can be understood in
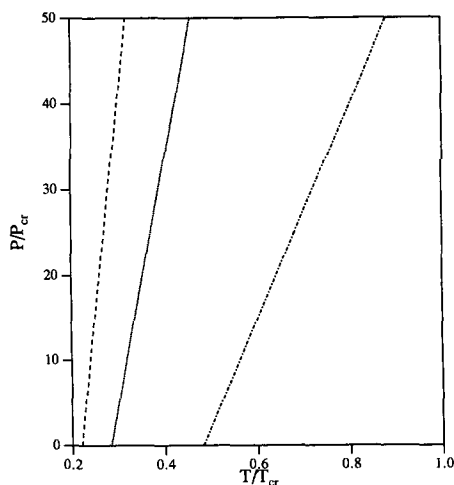
Figure 3.   High pressure solid–fluid equilibria for diatomic systems. The lines correspond to: dashed, $L^* = 0.6$; dotted, $L^* = 0.3$; dot-dashed, $L^* = 0.0$.

terms of the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} = \frac{\Delta U + P \Delta V}{T \Delta V}$$

$$= \frac{1}{T}\left(\frac{-a \Delta \rho}{\Delta V} + P\right) = \frac{1}{T}(P + a\rho_l \rho_s)$$

$$= \frac{1}{2T}[P_0^l + P_0^s - a(\Delta \rho)^2], \tag{3.1}$$

where P_0^l and P_0^s are the contributions to the pressure of the coexisting liquid and solid phases from the hard-dumbbell reference system, and the last equality shows that these quantities dominate the slope of the melting line. Generally we should expect that P_0^l and P_0^s should show roughly the same dependence upon L^* as the
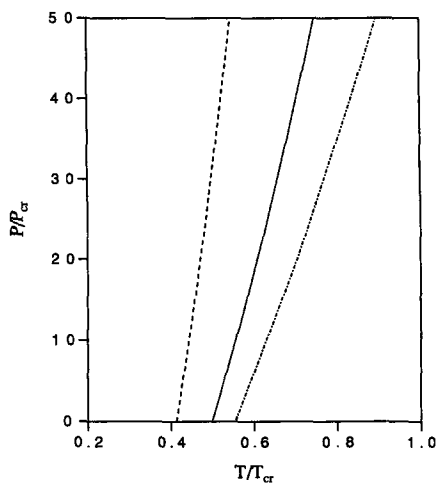

Figure 4.   Experimental [21, 22] data for the solid–fluid equilibria of diatomic systems. The lines correspond to: dashed, Cl_2; dotted, N_2; dot-dashed, Ar.

solid–fluid coexistence pressure for hard dumbbells. Indeed they both approach this value in the limit of high temperature. The coexistence pressure for hard dumbbells increases with L^* but exhibits a slight maximum at around $L^* = 0.6$. Thus we expect the slope of the solid–liquid equilibrium line to increase as L^* increases from zero and this is what is seen in figure 6.

4. A simplified treatment of the influence of quadrupolar interactions

In order to investigate the influence of quadrupolar interactions we have formulated a simple extension of the theory described above. Such interactions cannot be treated in a simple mean field approximation since the orientation average of the quadrupole–quadrupole interaction vanishes. For the solid phase the simplest approximation to the contribution from these interactions to the free energy is just the static lattice (zero temperature) sum of the quadrupole–quadrupole interaction. Thus we write

$$A = A_0 - a\rho + U_{QQ}(T = 0), \qquad (4.1)$$

where $U_{QQ}(T = 0)$ is the static lattice sum per molecule of the point quadrupole–quadrupole interaction for the crystal structure of interest. This expression neglects the influence of thermal fluctuations upon the quadrupolar free energy, as well as the coupling between the molecular shape, dispersion force and quadrupole–quadrupole effects. Nevertheless it is consistent with the overall level of approximation used in this work. The value U_{QQ} may be evaluated by performing lattice summation at the close-packing density of the considered solid structure for a unit value of the reduced quadrupole. Then it can be readily computed at any arbitrary density and quadrupole moment by noting that U_{QQ} scales as $Q^2(\rho/\rho_{cp})^{5/3}$ where Q is the value of the quadrupole and ρ_{cp} is the closest-packing density of the considered solid structure. We used of the order of 10^3 molecules to estimate U_{QQ} and this exhibited good agreement with the values obtained by using 10^4 molecules. In implementing equation (4.1) we used only the cell theory for the hard-dumbbell solid properties. For the liquid we used an expression of the form

$$A = A_0 - a\rho + A_{QQ}, \qquad (4.2)$$

where A_{QQ} is the quadrupolar contribution to the free energy per molecule of a system of quadrupolar hard dumbbells which can be approximated quite well using expressions developed recently by Vega [23]. This equation reduces to equation (2.1) for zero quadrupole moment. In order to apply the theory we need to choose a ratio for the relative strength of the dispersion and quadrupole–quadrupole interactions. We define a dimensionless parameter R as:

$$R = (Q^2/d^5)/(a/d^3), \qquad (4.3)$$

where

$$d^3 = \sigma^3(1 + \tfrac{3}{2}L^* - \tfrac{1}{2}L^{*3}), \qquad (4.4)$$

and d is the diameter of a sphere with the same volume as the dumbbell. R provides a measure of the ratio of quadrupolar to dispersion forces. To estimate an adequate value of R for CO_2 we proceeded as follows. By using the experimental critical temperature and quadrupole moment [24], as well as the collision diameters from the Lennard-Jones 12-6 model of CO_2 suggested by Singer *et al.* [19] and a choice of
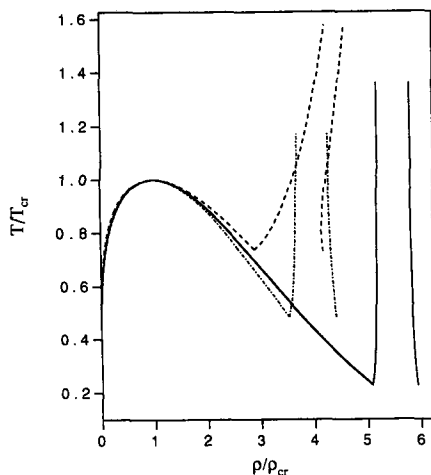
Figure 5.   Coexistence curve for diatomic systems with quadrupolar interactions. The lines correspond to: solid, $L^* = 0.8$, $R = 0.0$; dashed, $L^* = 0.8$, $R = 0.109$; dot-dashed, $L^* = 0.0$, $R = 0.0$.

L^* which was taken in this work as $L^* = 0.80$ (which is close to value of $L^* = 0.79$ from [19]), one can compute $Q^{*2}_{c,exp} = Q^2/(kT_c d^5)$ where the subscript c stands for critical values. Then a trial value of R was chosen and the vapour–liquid equilibrium was computed from (4.2) so that the reduced critical temperature $\tau_c = kT_c d^3/a$ is obtained. We then computed $Q^{*2}_{c,theo} = R/\tau_c$. We proceeded in this way until the theoretical value matched the experimental one.

In figure 5 we show results in the form of a reduced temperature versus reduced density plot. Also shown are results without the quadrupolar interaction for both $L^* = 0.8$ and $L^* = 0$. In the solid the presence of the quadrupolar interaction stabilizes the α-nitrogen structure (freezing into which occurs at much lower densities) relative to the base-centred monoclinic structure. The quadrupole–quadrupole interaction also leads to a significant broadening of the vapour–liquid coexistence curve. These two effects in combination give rise to the considerable increase in the value of T_t/T_c relative to the non-quadrupolar case. We find that $T_t/T_c = 0.74$ which compares quite favourably with the experimental value of $T_t/T_c = 0.71$. Although we can only expect this calculation to be qualitatively accurate, we believe that to a large degree this explains the high value of T_t/T_c seen experimentally for CO_2. Notice also the large density change on freezing, which is comparable with the roughly 30% increase in density seen experimentally for CO_2 at its triple point [25].

5.   Summary and conclusions

We have presented a generalized van der Waals theory for the influence of molecular shape upon solid–fluid equilibria in diatomic molecules. Although the approach is a very simple one, and in some respects oversimplified, it does offer an interesting picture of the influence of molecular anisotropy on phase equilibria. The theory predicts variations of both vapour–liquid and solid–liquid equilibria with molecular shape. Two regimes of behaviour are apparent, depending upon the bond length. For short bond lengths, where the hard-dumbbell reference system

freezes into a plastic crystal, the theory predicts a decrease in the reduced triple point temperature and density change on freezing with increasing bond length. It provides a plausible explanation for the change in these properties in passing from argon to nitrogen. For longer bond lengths, where the hard-dumbbell reference system freezes into an orientationally ordered crystal, the theory predicts a slight increase in the reduced triple point temperature, and a density change on freezing which is comparable with that for spherical molecules. This behaviour is somewhat similar to that of the halogens but the predicted change in the triple point temperature with bond length is less than that seen experimentally.

We have implemented the theory using both results from cell theory and from Monte Carlo simulation for the properties of hard-dumbbell solids. Our results indicate that the use of cell theory does not significantly alter the results obtained and offers a useful approach to extending these results to more complex systems.

We have extended the theory to the case of quadrupole–quadrupole interactions by assuming that the quadrupolar energy of the solid is simply that of the static lattice. This leads to results which provide a plausible explanation for the high triple point temperature and large density change on freezing for CO_2 [25].

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