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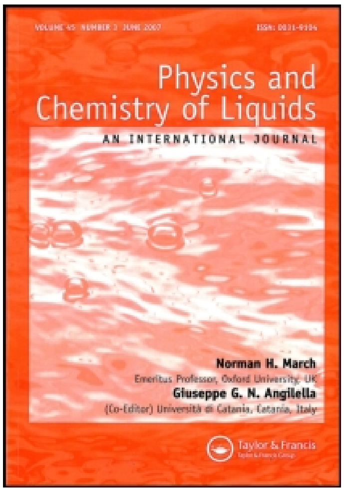

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SOME PROPERTIES OF A MODEL LIQUID OF C_{60} BUCKYBALLS

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Utilizing the results of published simulations for the liquid C_{60} phase using a model of rigid C_{60} molecules, it is pointed out that the liquid phase has a critical compressibility ratio $Z_c = p_c/(\rho_c k_B T_c)$ in terms of the usual critical thermodynamic variables (critical pressure p_c, critical density ρ_c and critical temperature T_c), of 0.32. This is to be compared with the value 0.29 for the heavy condensed rare gases Ar, Kr and Xe, in spite of their much lower T_c, and with the prediction of 0.27 from Dieterici's phenomenological equation of state. The global shape of the coexistence curve, as embodied in the behaviour of the normalized difference density $(\rho_l - \rho_g)/\rho_c$ *versus* the average density $(\rho_l + \rho_g)/2\rho_c$, where ρ_l and ρ_g are the liquid and the gas densities, respectively, is also consistent with the shape of the coexistence curve of insulating fluids. Going beyond the assumption of rigid C_{60} molecules has interesting consequences on the stability and observability of the liquid phase, and those effects are discussed.

Keywords: Buckyballs; Critical point; Compressibility ratio; Liquid C_{60}

1. INTRODUCTION

There have been numerous computer simulations devoted to clarifying the existence, or otherwise, of a liquid phase of C_{60}. For a rather complete list of references the reader can consult the recent paper by Hasegawa and Ohno [1]. The study of these authors and of earlier works was of a liquid of rigid buckyballs, and the well known

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Girifalco potential [2] giving the interaction between rigid C_{60} molecules, was used. Our main focus in this study is on the discussion of the properties of such a liquid phase near the critical point, and this is presented in Section 2. Then in Section 3 we discuss the main assumption of that simple model, namely the assumed rigidity of the buckyball, and the analysis clarifies the range of validity of the results presented in Section 2.

2. PROPERTIES OF THE MODEL LIQUID OF RIGID C_{60} MOLECULES NEAR THE CRITICAL POINT

Girifalco derived his intermolecular C_{60}–C_{60} potential by assuming a Lennard–Jones pair interaction between carbon atoms on the two different C_{60} molecules and averaging the carbon atom distribution so as to have a uniform density of carbon atoms over the buckyball surface [2]. It is now well established that the intermolecular potential proposed by Girifalco produces a stable liquid phase in a narrow range of temperatures [1]. The critical thermodynamic constants T_c (critical temperature), p_c (critical pressure), and the molecular number density ρ_c were found in the Monte Carlo simulations of Hasegawa and Ohno [1] to have the values $T_c = 1980\,\mathrm{K}$, $p_c = 38\,\mathrm{bar}$ and $\rho_c = 0.44\,\mathrm{molecules/nm^3}$. As emphasized elsewhere, there are considerable regularities among experimental T_c, p_c and ρ_c data for the heavier condensed rare gases Ar, Kr and Xe, and in particular we stress here (i) the observation of Chapman and March [3] that

$$T_c \rho_c^2 \approx \text{constant}, \tag{1}$$

and (ii) the well-known fact [4] that the critical compressibility ratio Z_c defined by

$$Z_c = \frac{p_c}{\rho_c k_B T_c}, \tag{2}$$

with k_B denoting Boltzmann's constant, has a value near 0.29 for Ar, Kr and Xe. This value can be compared with that obtained by inserting in Eq. (2) the critical point data of Hasegawa and Ohno [1] for their model of liquid C_{60}, namely Z_c (C_{60}) $= 0.32$. It is not surprising that the values of Z_c for the C_{60} liquid and for the heavier condensed rare gases are rather close, for it is well known that a Lennard–Jones potential describes realistically the weak interaction between rare gas atoms. On the other hand, Z_c varies significantly through the five alkali metals [3], and for all of them the compressibility ratio is substantially lower then the above value of 0.29.

As March and Tosi [5] noted elsewhere, the equation of state of Dieterici, namely

$$p(V - b)\exp(a/k_B TV) = k_B T, \tag{3}$$

where $V = 1/\rho$ is the *atomic* volume, a is a constant proportional to the difference in the potential energies for an atom in the interior of the fluid and near the container walls, and the constant b accounts for excluded volume effects, leads to the prediction $Z_c = 2/e^2$, with $e = 2.718$, or $Z_c = 0.27$. This value, independent of the particular system, is much nearer to the above experimental value of 0.29 for the atomic condensed rare gases than the result of the Van der Waals equation of state, which yields $Z_c = 3/8 = 0.375$. In this context, it is to be noted that if it is valid to expand the exponential factor on Eq. (3) to first order only, then the Van der Waals equation of state can be recovered after only inessential approximations. The foundations of Eq. (3), at a phenomenological level, are discussed, for instance, in the text book by Blinder [6]. The value Z_c (C_{60}) $= 0.32$ for the model liquid C_{60}, obtained from Hasegawa's simulations, is midway between the Dieterici and Van der Waals compressibility ratios.

An independent confirmation of the critical constants and compressibility ratio of liquid C_{60} can be obtained from the data provided by in the work by Tau *et al.* [7], who used the Hierarchical Reference Theory (HRT) to obtain the coexistence curve. For the critical temperature and critical density they find $T_c = 2138\,\mathrm{K}$ and $\rho_c = 0.5$ molecules/nm^3. We have then calculated the critical pressure in the following way. From the Virial equation of state for a density-independent pair potential $\Phi(r)$ with a corresponding pair distribution function $g(r)$ we have the perfect gas value of the pressure, corrected (reduced) by a structural integral term to yield [8]

$$p = \rho k_B T - \frac{\rho^2}{6} \int g(r) r \frac{\partial \Phi(r)}{\partial r} d^3 r, \tag{4}$$

and hence, evaluating the structural integral in Eq. (4) at the critical point,

$$p_c = \rho_c k_B T_c - \frac{\rho_c^2}{6} \int_0^\infty g(r) r \frac{\partial \Phi(r)}{\partial r} 4\pi r^2 dr. \tag{5}$$

The study of Tau *et al.* has resulted in a plot of $g(r)$ at the critical point that is given in Fig. 12 of their paper [7]. Numerical calculation of the integral of Eq. (5), using the Girifalco pair potential $\Phi(r)$ and the pair function of Tau *et al.* gives $p_c = 46.5$ bar, and a value of the compressibility ratio Z_c (C_{60}) $= 0.32$; precisely the same as that obtained from Hasegawa's data.

A further property of the liquid C_{60} phase simulated by Hasegawa and Ohno is the shape of the coexistence curve. In the light of the recent discussion of Leys *et al.* [9] on the shape of this liquid–vapour coexistence curve in a variety of monatomic liquids, we have examined from the data of Ref. [1] both the difference density $\rho_l - \rho_g$, scaled with the critical density ρ_c, along the coexistence curve, that is the variable

$$\eta = \frac{\rho_l - \rho_g}{\rho_c}, \tag{6}$$

where the subscripts l and g denote liquid and gas respectively, and also the average

$$\xi = \frac{\rho_l + \rho_g}{2\rho_c}. \tag{7}$$

In Fig. 1, following Ref. [9], we have plotted the three functions η, η^2 and η^3 *versus* ξ from the coexistence curve data in Fig. 7 of Hasegawa and Ohno [1]. It is clear that only the η^3 function provides a good fit

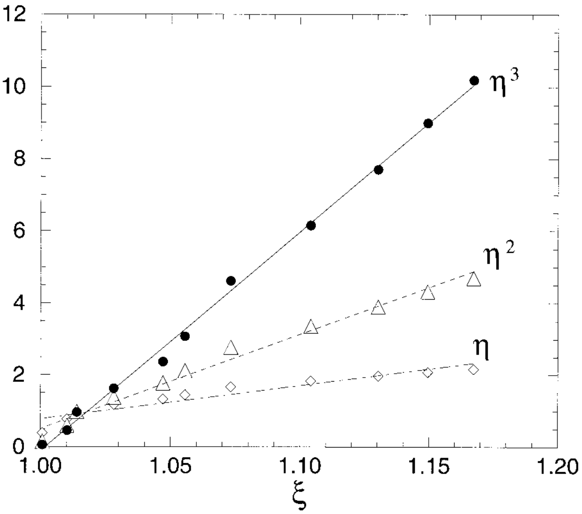

FIGURE 1 Different powers η, η^2, η^3 of the density difference η, defined in Eq. (6), *versus* average density ξ, defined in Eq. (7), along the liquid–vapour coexistence curve of the model liquid C_{60} calculated by Hasegawa and Ohno [1].

to the Monte Carlo simulation data in the whole range of densities plotted, in particular near $\xi = 1$. The best fit is given by the relation

$$\xi = 1 + 0.0164\,\eta^3, \tag{8}$$

and one can notice a nearly perfect agreement with the empirical relation valid for insulating fluids like neon and ethylene [10,11]

$$\xi = 1 + 0.017\,\eta^3. \tag{9}$$

Instead, Leys *et al.* [9] have found that the corresponding relation between ξ and η for the heavy alkali metals Rb and Cs is a linear function of η^2. This result again shows that the behaviour of the model liquid C_{60} near the critical point is in line with that of the above insulating fluids.

In Fig. 2 we have plotted ξ as a function of $(1 - T/T_c)$ again from data along the coexistence curve [1]. The simulation results are well represented by the function

$$\xi = 1 + 0.92(1 - T/T_c). \tag{10}$$

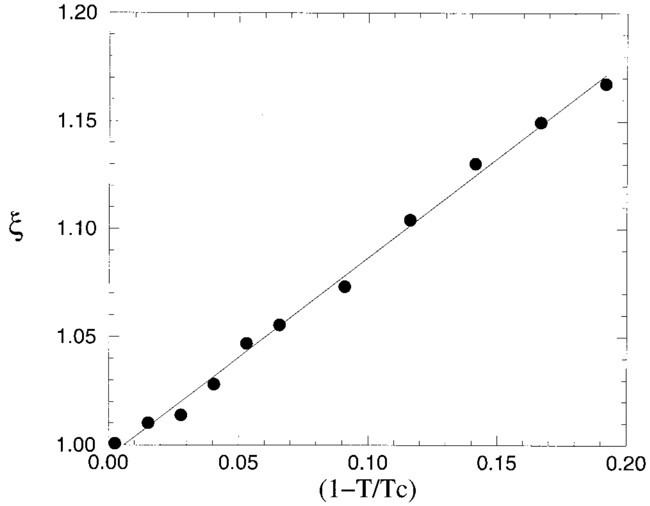

FIGURE 2 Average density ξ, defined in Eq. (7), plotted *versus* $(1 - T/T_c)$, along the liquid–vapour coexistence curve using the data of Hasegawa and Ohno [1].

This relation means that the law of rectilinear diameters, valid for the insulating fluids Ne and ethylene [10], is also valid for liquid C_{60}. Deviations from this law have been discussed for other systems [12–14], and in particular for the alkali metal fluids [15].

3. BEYOND THE MODEL OF RIGID BUCKYBALLS

Having completed the discussion of the properties and the liquid-vapour coexistence curve of the model liquid C_{60} near the critical point, we want to turn to a number of related topics. The first one is concerned with the assumption of rigid spherical buckyballs. Of course, C_{60} molecules have internal degrees of freedom, and a modest acknowledgment of this latter point is made in the study of Broughton *et al.* [16]. They used a model of non-rigid C_{60} spheres in which a low frequency breathing mode was introduced; that is, the radius of each molecule was allowed to be a dynamical variable. Then the total potential energy of the system was written as the sum of C_{60}–C_{60} interactions, described by a potential similar to

Girifalco's potential (but with C_{60} spheres of variable radii), plus a term representing the breathing of non-rigid C_{60} molecules. The properties of the phase diagram of such a model of C_{60} were then obtained by isothermal–isobaric molecular dynamics simulations. While no stable liquid phase was found in this model of non-rigid spheres, it proved possible to make predictions of some properties of a metastable liquid phase. As summarized in the conclusions of Ref. [16], the critical thermodynamic constants were found to have the values $T_c = 1850\,\mathrm{K}$, $p_c = 30\,\mathrm{bars}$ and $\rho_c = 0.51\,\mathrm{molecules/nm^3}$. Compared with the corresponding critical thermodynamic constants calculated by Hasegawa and Ohno [1] or by Tau *et al.* [7], all of them reported for convenience on Table I, the additional degree of freedom introduced by the non-rigidity of the buckyball leads to a lower critical temperature, a lower critical pressure and a higher critical density. The changes in p_c and ρ_c dominate the change of the compressibility ratio, which becomes $Z_c\,(C_{60}) = 0.23$, lower compared to the rigid buckyball model and the condensed rare gases. No doubt the non-rigidity of the molecule has an effect on the characteristics of the liquid phase, but one should be cautious with this model because, as Broughton *et al.* acknowledge in their paper [16], the value of the isolated breathing mode frequency used in the model is much lower that any of the experimentally observed intramolecular vibrational frequencies of C_{60}. Our attempts to fit the data for ξ *versus* η taken from the liquid–vapour coexistence curve reported in [16], using linear functions of η, η^2 and η^3, gave unsatisfactory results.

The second point deals with the vacancy formation energy E_v of crystalline fcc fullerite and its use via an established empirical relation with the thermal energy of melting, $k_B T_m$. Here we must address the question of whether widely known empirical relations between the vacancy formation energy E_v and the melting temperature T_m of

TABLE I Temperature T_c, density ρ_c, pressure p_c and compressibility ratio Z_c at the critical point obtained in different computer simulations for the liquid C_{60}

	Tau et al. [7]	*Hasegawa and Ohno* [1]	*Broughton et al.* [16]
T_c (K)	2138	1980	1850
ρ_c (nm^{-3})	0.50	0.44	0.51
p_c (bar)	46.5	38	30
Z_c	0.32	0.32	0.23

monatomic close-packed crystals such as Argon can be utilized to estimate T_m for fcc fullerite. Specifically, we note that experimental values of E_v are quoted [17] to be in the range 0.050–0.069 eV for Argon and 0.077–0.086 eV for Krypton. For the later case, with $T_m = 117$ K, one finds the dimensionless ratio $E_v/(k_B T_m)$ in the range 8.0–8.9 (see also the theoretical study of this ratio by Bhatia and March [18]). We next note that Girifalco, in his original work on the C_{60}–C_{60} pair potential [2], estimated a vacancy formation energy for the fcc structure of C_{60} of $E_v = 20$ kcal/mol, that is just less than 1 eV. This, as Girifalco noted, is comparable to E_v in fcc metals and much larger than the values quoted above for the condensed rare gas crystals of Ar and Kr, the reason being the large size of the buckyball. Using Girifalco's estimation for E_v and the known ratio $E_v/(k_B T_m)$ from the condensed rare gases, $k_B T_m$ for fcc fullerite is approximately 0.12–0.13 eV, corresponding to a value of T_m near 1500 K. This is to be compared with the range of the stable liquid state predicted by the simulations of the rigid buckyball model or the range of the metastable liquid state in the non-rigid sphere Molecular Dynamics simulation of Broughton *et al.* [16], and although somewhat lower than the triple point temperature of those simulations, the general accord is quite satisfactory.

We turn next to compare and contrast this situation of the *melting* of crystalline fcc fullerite with the experimental facts established only recently by Togaya [19] on the melting curve of graphite under pressure. His results show a relatively small variation of T_m for pressures from 0 to about 10 Gpa, with values in the range between 4600 and 4790 K and a maximum value $T_m = 4790$ K at a pressure $p = 5.6$ GPa. From that data one can estimate a melting temperature of approximately 4600 K at zero pressure. The large difference between the melting temperature of graphite and fullerite has a simple explanation: melting in graphite implies massive breaking of the strong carbon–carbon bonds in the graphite layers and a change in the type of hybridization, while the melting of fullerite modeled in the computer simulations [1] accounts for the disruption of the fcc lattice while maintaining the internal integrity of the buckyballs.

The very question of the thermal stability of the C_{60} molecules has a crucial influence on the practical observability of a stable or metastable C_{60} liquid. Experiments [20] indicate that in the gas phase under equilibrium conditions, C_{60} stability is limited to 1100–1200 K. The characteristic time scales for decomposition at temperatures $T=$ 1720–1970 K are in the milliseconds range [21]. The heating of solid fullerite [22,23] also leads to the decomposition of the material into amorphous carbon and graphite at temperatures $T=1000$–1300 K. In these solid state experiments the reaction took minutes to complete. Two physical processes are responsible for the decomposition of C_{60}. The first one is the reaction between neighbour C_{60} molecules in solid fullerite (or between colliding molecules in the gas phase), that becomes facilitated at high temperatures by the formation of local structural defects, like open windows, in the carbon cage [24]. Those defects generate dangling bonds that give rise to highly reactive sites. In this context, we mention two phenomena related to such a thermally induced reactivity. One is the photoinduced polymerization of solid C_{60} films observed by Rao *et al.* [25] under exposure of the material to visible and ultraviolet light for several hours. The second, for a closely related material, is the thermal coalescence of bundles of single wall carbon nanotubes to produce multiwall nanotubes [26]. In this case the coalescence is driven by the formation of structural defects, that migrate through the nanotube and become anchored in the regions of contact between neighbour nanotubes.

Finally, the second physical process responsible for the thermal instability of fullerene materials in the gas or condensed phases concerns, this time, the isolated C_{60} molecules. The recent analysis of Matt *et al.* [27] has been able to reconcile the results of experiment and theory for the energy required to fragment the C_{60} molecules (into C_{58} and C_2). This fragmentation energy is about 10 eV. For a gas of C_{60} molecules in equilibrium with a vibrational temperature of 2000 K, the energy stored in the molecule is about 29 eV (or 14.5 eV for a vibrational temperature of 1000 K). Those excitation energies are high enough to allow, in principle, for the statistical fragmentation of the molecule in sufficiently large time scales. The two physical processes just discussed, the metastability of C_{60} above about 1000 K, and the high reactivity at those temperatures, point towards the practical difficulties of heating solid fullerite to temperatures in the range where the hypothetical liquid C_{60} phase could be stable (roughly between 1900 and 2000 K). If fullerite could be fastly heated to those temperatures, the liquid phase will only be stable for a short time before the molecules begin to decompose. Those characteristics make that liquid certainly peculiar.

A final comment on the practical observability of liquid C_{60} concerns low dimensional C_{60} systems. The melting temperature of low dimensional systems, i.e., surfaces and clusters, is, in general, lower than that of the corresponding bulk material [28]. The open surfaces of the fcc fullerite, e.g., the (1,1,0) surface, and small clusters of C_{60} molecules are, then, good candidates for exhibiting melting temperatures lower than that of the bulk fullerite, and, eventually, lower than the decomposition temperature of C_{60} molecules. Therefore, liquid C_{60} could be observed in those low-dimensional systems. Indeed, it has been shown [29], through Molecular Dynamics simulations using the Girifalco potential, that $(C_{60})_7$ clusters (where all the molecules are at the cluster surface) exibit a solidlike-to-liquidlike phase transition with a melting temperature of about 600 K, well below the decomposition temperature of C_{60} molecules.

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