Optmizied random phase approximation for the phase diagram of C_{60} material

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Abstract

This paper determines the phase diagram of C_{60} fluid by an efficient and robust optimized random phase approximation (ORPA) method of Pastore *et. al* (1995), imposes physical requirements as in the original ORPA scheme with a view to achieving consistency within the liquid structure factor. Our perturbation/variational approach for the Helmholtz free energy of the C_{60} molecules is based on the Lennard-Jones intermolecular interaction. We observe that higher accuracy is obtainable by treating all the grid points within the exclusion hole of the pair distribution function as independent variables. Our numerical results show appreciable improvement in both the thermodynamic functions and the structure factor.

1.0 Introduction

The fundamental properties of C_{60} molecules are still of particular interest. Among the Interesting peculiarities of this material are the thermodynamic properties of its liquid phase compared to its solid phase. Calculations describing phases in C_{60} material has been placed in two categories; some authors employed simulation technique via molecular dynamics (MD) while others used thermodynamic integral equation for the liquid structure to ascertain the existence of a liquid phase for C_{60} molecules within a narrow range of temperatures and densities. Some other groups claimed to have used the Gibbs' ensenble (GE) simulation method on one hand and the integration procedure of the Clausius-Clapeyron equation on the other hand to obtain the phase diagram of the same C_{60} liquid model. This latter group concluded that C_{60} molecules did not (and should not) exist in a stable liquid phase. They claimed that their results indicated that the sublimation line pass above the metal-stable line by a few degrees (cf. Caccamo (1995) and references therein).

There have been interesting speculations regarding the apparently contradicting results. The most accurate modern integral equations of the theory of liquids such as the hard-mean-spherical approximation (HMSA) and modified hyper-netted-chain (MHNC) approximation have already been used to determine the phase diagram of C_{60} molecules. One major disadvantage of the integral equations which has limited their scope of applicability is the problem of multiple solutions like those encountered in Ref. 4.

Yet another successful theory of liquid that has hitherto not been applied to the C_{60} material is the optimized random phase approximation (ORPA) technique which is essentially a perturbation theory.

Fundamental to the theory of ORPA is a notion that the volume-excluded effects are the most important interactions that determine the structural properties of the liquid and that these effects are well represented by hard spheres. The original theory of ORPA, based on the pioneering work of van der Waal, has undergone so many modifications by different groups of researchers. Of particular interest is the Andersen, Chandler and Weeks (ACW) (1972) version of ORPA which has also been modified and used extensively (Hafner (1987), Pastore et. al (1995, 1998)). In all, a judicious choice of reference system (liquid) has been made crucial to the success of ORPA.

It is the aim of the present paper to produce further calculations leading to a more accurate phase diagram of C_{60} liquid which should help in resolving the phase diagram controversy. We shall apply the well-known ORPA algorithm of Pastore et. al (1995) to determine the boundaries of the Lennard-Jones fluid phase.

The outline of the remaining part of the work is as follows: section 2 presents the theoretical developments while section 3 discusses the relationship between the liquid structure and the ORPA version of Pastore et. al (1995) and the prescription of thermodynamic consistency. In the meantime, we shall outline the calculation procedure in section 4 and discuss our numerical results for C_{60} molecules using Lenard-Jones' fluid as reference system in section 5 before the work is brought to conclusion.

2.0   Theory

The system under consideration is a Lennard-Jones' liquid of N molecules, in a volume V, whose average number density $\rho=N/V$. We shall write the total potential energy Φ as a sum of the pair potential $\phi(r_{ij})$ i.e.

$$\phi = \sum_{i<j=1}^{N} \varphi(r_{ij}) \tag{2.1}$$

r_{ij} = distance between molecules i and j and

$$\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{2.2}$$

The classical liquid consists of an interaction coming from a pair-wise potential made up of two parts: a reference system (repulsive) potential and a perturbation (attractive) potential i.e.

$$\varphi(r)= \varphi_0(r) + \varphi_1(r) \tag{2.3}$$

The attractive potential term is recast in the excluded-volume region (where particles do not penetrate) in a manner that makes $g(r)$ to continually varnish there. Then, the implementation of ORPA reduces to choosing a suitable reference system and obtaining the free energy via variational calculation using perturbation. Thus the excess free energy (total free energy minus the reference system free energy) is expressed as an infinite series of terms involving functions of the reference system. The first term of the series neglects correlation among density Fourier components with different wave vectors and this is the well-known Random Phase Approximation (RPA). Higher order terms constitute systematic corrections to RPA.

3.0   Structure of liquid and ORPA

The relationship between the Fourier transform of the static response function $\chi(r, r')$ and the structure factor $S(k)$ is given by $\chi_0(k) = -\beta\rho S(k)$ where $S(k)$ is the Fourier transform of the density-density correlation function; it measures the response of the liquid to a wave-like distortion of the fluid density. The fluid average number density ρ is related to the pair distribution function $g(r)$ via equation

$$\rho\, g(r) = 1/(2\pi)^3 \int exp(i\, \boldsymbol{k} \cdot \boldsymbol{r})\, [S(k) -1]\, d^3k \tag{3.1}$$

The split in Eq.(4) naturally leads to a similar decomposition of the total correlation function $h(r)$ $[= g(r) -1]$ and the direct correlation function $c(r)$ as in

$$h(r) = h_0(r) + \Delta h(r) \tag{3.2}$$
$$c(r) = c_0(r) + \Delta c(r) \tag{3.3}$$

Here, $h_0(r)$ and $c_0(r)$ are the total correlation function and the direct correlation function of the reference system respectively and they are linked by the Ornstein-Zernike (OZ) equation

$$h(r) = c(r) + \rho\int d^3r'\ c(|r-r'|)\, h(r') \tag{3.4}$$

for the two particles at r and r'. A relationship also exists between the Fourier transform of $\Delta h(r)$ and $\Delta c(r)$ written as (Hansen and McDonald (1986))

$$\Delta \hat{h}(q) = \frac{\Delta \hat{c}(k)[S_{0}(k)]}{1 - \rho \Delta \hat{c}(k)S_{0}(k)} \qquad (3.5)$$

where $S_0(k)$ is the structure factor of the reference system. A hat (^) on Δh and Δc shows that they are the three dimensional Fourier transforms of $\Delta h(r)$ and $\Delta c(r)$.

The static structure factor $S_0(k)$ used in this work is based on the modified ORPA technique which some of our publications (Pastore et. al (1995), (1998), Matthew-Ojelabi (2005)) have shown to be the best in terms of self-consistency between the pressure equation and compressibility equation of state. This brand of ORPA demands that the real liquid (C_{60} material) potential be described by the Lennard-Jones potential while treating the residue of the inter-atomic potential by perturbation method. We therefore define the radius σ of this region as the value of r below which the pair distribution function $g(r)$ becomes too small in computer simulation. The ORPA closure then becomes $\Delta c(r) = -\beta\varphi_1(r)$ for $r > \sigma$ such that

$$\Delta h(r) = 0, \text{ for } r > \sigma \qquad (3.6)$$

We seek a variational procedure where a free energy functional is defined as

$$F_{ring}[\Delta c(r)] = -1/[\rho(2\pi)^3] \int d^3k \, [\rho \, S_0(k) \, \Delta \hat{c}(k) + \log\{1 - \rho \, S_0(k) \, \Delta \hat{c}(k)\}] \qquad (3.7)$$

The derivative of F_{ring} with respect to $\Delta \hat{c}(k)$ is

$$\frac{\partial F_{ring}}{\partial \Delta \hat{c}(k)} = \frac{-\rho \Delta \hat{h}(k)}{(2\pi)^3} \qquad (3.8)$$

whose Fourier transform gives

$$\frac{\partial F_{ring}}{\partial \Delta c(r)} = -\rho \Delta h(r) \qquad (3.9)$$

The extremum condition on F_{ring} is equivalent to the physical requirement that the size of the exclusion hole of the reference system be preserved by the perturbation. Equation.(3.9) is now a variational condition; the requirement that $g(r) = 0$ for $r < \sigma$ implies the variations of $\Delta c(r)$ inside σ. The ORPA approximation for the free energy then becomes

$$A = A_0(\sigma) + \tfrac{1}{2}\rho^2 \int dr \, g_0(r;\sigma) \, \beta \, \phi_1(r) - 1/(2\rho) \, F_{ring}[\chi(r)] \qquad (3.10)$$

We shall optimize F_{ring} by introducing an auxiliary (unknown) function $\Lambda(r)$ via equation

$$\Delta c(r) = -\beta\varphi_1 + \Lambda(r), \text{ for } r < \sigma \qquad (3.11)$$

All the grid points within $\Delta c(r)$ (i.e. inside σ) could be treated as unknowns instead of expressing $\Lambda(r)$ in Taylor series or Legendre polynomials which is not very efficient for problems posed by C_{60} liquid. The minimization algorithm (Pastore et. al (1995)) allows the N_g grid values of the unknown i.e. we set $\Lambda(r_i)$, $[r_i = (i-1)\delta r, i = 1, \ldots, N_g]$ as independent variables. This technique increases the number of the variational parameters (degrees of freedom) and enhances accuracy as well as maintains thermodynamic consistence.

4.0   Calculation procedure

The C_{60} molecule is a truncated icosahedron. The combination of the pentagonal and hexagonal faces found in a C_{60} molecule is identical to that of a soccer ball, suggesting that the cluster is close to a spherical shape with a diameter of 10.34Å. The C_{60} molecules, separated from each other by 10Å are held together by van der Waals forces. For a fuller account of the C_{60} cluster see Hebbard (1991), Kaxiras (2003) and Matthew-Ojelabi (2004).

We implement the ORPA computational scheme described above for the C_{60} molecules interacting via L-J pair potentials using the neutral hard spheres (NHS) as a reference system. We set $N_g = 2049$ points with a spacing of $r = 0.025$ to represent the pair correlation function.

The cutoff of $\Delta c(r)$ is taken at $r = 5\sigma$ where σ is the diameter of the hard sphere (C_{60} molecule). Then, we seek the minimum of the ring term closest to $\Delta g(r)$ along a straight line in the direction of the maximum decrease of the ring term. The simplest implementation uses the steepest descent (SD) method which facilitates the calculation of the displacement along the gradient direction by choosing a suitable value that guarantees a monotonic approach of the extremum. The iterative procedure is such that the gradient is continually evaluated at the new point followed by the

same set of operations. The cycle continues until a satisfying minimum is reached for the ring term. We perform the operation of SD method efficiently using the fast Fourier transform (FFT) algorithm (cf. Brigham (1974)).

5.0   Results and discussion

The numerical values of present work for the thermodynamic properties agree reasonably well with simulation results as shown in the tables below. We sum up in table I the calculated results of the excess free energy (using L-J liquid as a reference system) compared to the experimental values (molecular dynamics results) taken from Ref.1.

Table I: Excess free energy of C_{60} liquid compared with simulation data (a) ORPA results of present work, (b) MHNC results of Ref.4. (c) MD results as in Ref.1.

	Density ρ (nm^{-3})			*Excess free energy ($\beta U^{exc}/N$)*		
T(K)	(a)	(b)	(c)	(a)	(b)	(c)
1785	0.889		0.944	5.705		-5.630
1900	0.614		0.964	5.418		-5.499
2172	1.05	0.837		-4.020	-3.986	

Table II: Calculated values of the thermodynamic properties of liquid molecules compared with simulation data.

	(a)	(b)	(c)
T_c(K)	1922	1920	> 1920
ρ_c(nm^{-3})	0.991	1.00	1.033
T_{tr}(K)	1679.5	1620	1780 ± 50

The temperature-density (T - ρ) quantities computed in this work are plotted in the Figure below. ORPA predicts a triple point (T_{tr} =1679.5K) which is closer to the MD value of Ref.1 than the MHNC calculation of Caccamo (1995) whose result is T_{tr} =1620K. Also, our estimates for the critical temperature and the freezing point are T_c = 1922K and ρ_c=0.991nm^{-3} respectively: they compare satisfactorily with the MD results displayed on table II.

Our results indicate the existence of a liquid phase of the rigid C_{60} molecules in the range 0.6 nm^{-3} < ρ < 1 nm^{-3} and 1600K < T <1930K. The temperature range is considerably larger than those reported previously in Ref. 4.

6.0   Conclusion

We have demonstrated that the modified ORPA technique (a self-consistent theory of liquid with respect to energy, compressibility and pressure equations of state (Pastore et. al (1995 & 1998)) has been able to predict the phase diagram of the C_{60} molecules. The actual intermolecular interaction is interaction is
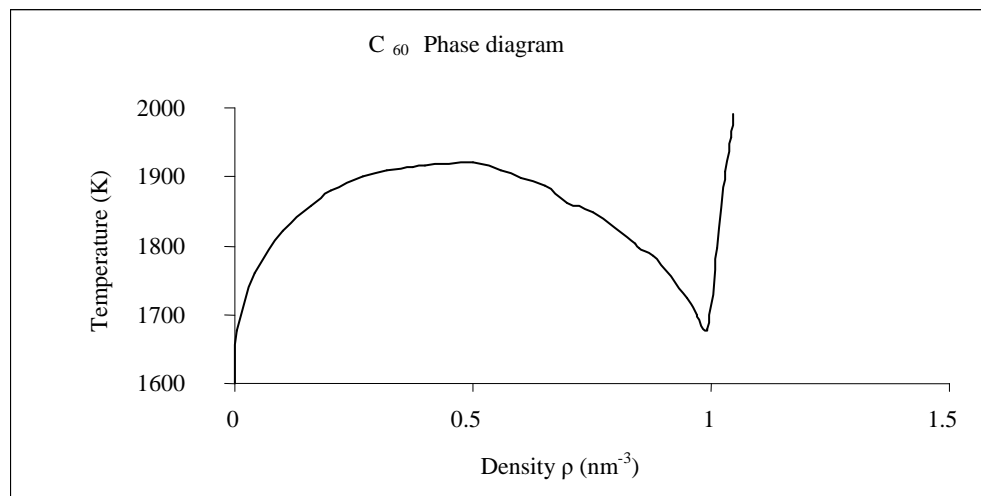
Figure: *T - ρ phase diagram of present work using the L - J liquid as reference system in ORPA.**

modelled with a Lennard-Jones fluid as reference system in an accurate manner which compares favourably with simulation data and other theoretical predictions. Also, it has been possible to check that the full grid minimization allows $\Delta g(r) = 0$ within machine precision inside the exclusion hole with less effort. Other calculations based on the integral equation methods will always yield spurious results because of their tendency towards multiple results.

The present work on the basis of our results has been able to confirm the existence of a stable liquid phase for the rigid molecule model of C_{60}.

Acknowledgement

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