

## Modified-hypernetted-chain determination of the phase diagram of rigid C<sub>60</sub> molecules

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The modified-hypernetted-chain theory is applied to the determination of the phase diagram of the Lennard-Jones (LJ) fluid, and of a model of C<sub>60</sub> previously investigated [Phys. Rev. Lett. 71, 1200 (1993)] through molecular-dynamics (MD) simulation and a different theoretical approach. In the LJ case the agreement with available MD data is quantitative and superior to other theories. For C<sub>60</sub>, the phase diagram obtained is in quite good agreement with previous MD results: in particular, the theory confirms the existence of a liquid phase between 1600 and 1920 K, the estimated triple point and critical temperature, respectively.

In a previous work<sup>1</sup> a rigid molecule model of C<sub>60</sub> (Ref. 2) has been investigated both through molecular-dynamics (MD) simulation, and a thermodynamically consistent liquid structure theory. This study indicated a narrow range of temperatures and densities in which C<sub>60</sub> could exist in the liquid phase.

In a successive study, other authors<sup>3</sup> have obtained the phase diagram of the same C<sub>60</sub> model by using the Gibbs ensemble (GE) simulation technique<sup>4</sup> and an integration procedure of the Clausius-Clapeyron equation;<sup>5</sup> the sublimation line was found to pass a few degrees above the (metastable) critical point of the binodal line, thus justifying the opposite conclusion that C<sub>60</sub> should not exist in a stable liquid phase.

While interesting speculations about these two apparently contradictory sets of results have been proposed,<sup>6</sup> it seems worthwhile to produce further and accurate phase diagrams of C<sub>60</sub> that can help to solve the controversy. This article reports the results of such an effort. We apply the well-known modified-hypernetted-chain<sup>7</sup> (MHNC) theory to the determination of the boundaries of the fluid phase (that is the binodal and the freezing line) of the Lennard-Jones (LJ) fluid and of C<sub>60</sub> modeled as in Refs. 1 and 3. We observe that the MHNC was developed by Rosenfeld and Ashcroft<sup>7</sup> in 1979, and is known to be a highly accurate structural theory of fluids; however, to the best of our knowledge, no calculation of the liquid-vapor coexistence or freezing line based on it has yet been published.

The LJ phase diagram is here preliminarily investigated, since it is accurately known from previous studies and this allows us to test the MHNC predictions. We then apply the same theoretical scheme to the determination of a C<sub>60</sub> fullerene's phase diagram. Such calculations are complemented by a molecular-dynamics investigation of the self-diffusion coefficient of the C<sub>60</sub> molecule to ascertain the dynamical properties of the model in the predicted liquid phase region.

In the MHNC the well-known Ornstein-Zernike equation for the pair- and direct-correlation function,  $h(r)$  and  $c(r)$ , respectively, is associated to the exact cluster expression for the radial distribution function<sup>8</sup>

$$g(r) = h(r) + 1 = \exp[-\beta v(r) + h(r) - c(r) + E(r)]$$

$$\left[ \beta = \frac{1}{k_B T} \right]$$

to form a couple of equations in three unknown functions, namely,  $h(r)$ ,  $c(r)$ , and the bridge function  $E(r)$ . A closure is then obtained by assuming  $E(r) = E_{\text{HS}}(r; \sigma_{\text{HS}})$ , the otherwise-known<sup>7</sup> hard-sphere bridge function calculated at a hard-sphere diameter  $\sigma_{\text{HS}}$  such that thermodynamic consistency between the virial and the compressibility equation of state<sup>8</sup> (EOS) is achieved. Specifically, one requests that the derivative of the virial pressure

$$(\beta \partial P^v / \partial \rho)_T = (\rho k_B T K_T)^{-1}, \quad (1)$$

where  $K_T$  is the isothermal compressibility obtained from fluctuations and  $\rho$  is the number density of particles.<sup>9</sup>

In order to determine the binodal or the freezing line, the Helmholtz free energy  $F^{\text{ex}}$  is then calculated according to the following equation:<sup>8</sup>

$$\beta F^{\text{ex}}(\rho, T) = \int_0^\rho \left[ \frac{\beta P^v(\rho', T)}{\rho'} - 1 \right] \frac{d\rho'}{\rho'}, \quad (2)$$

where  $F^{\text{ex}}$  is the excess free energy with respect to the ideal gas value,  $\beta P^v(\rho, T)/\rho$  is the virial EOS, and the integration is taken along an isothermal path at temperature  $T$ .

Now, if  $\beta F^{\text{ex}}$  is to be calculated at a *subcritical* temperature  $T_0$  and at a density  $\rho_0$ , which rests on the liquid side of the binodal, the isothermal integration path (1) would cross the phase coexistence line, inside which line (except for a narrow metastable region immediately close to the binodal) no solution to the MHNC will exist.

This difficulty can be circumvented by adopting a composite integration path by which after having calculated  $\beta F^{\text{ex}}$  along a supercritical isotherm  $T$  up to density  $\rho_0$ , one adds the contribution

$$\Delta \beta F^{\text{ex}}(\rho_0, T_0) = \int_T^{T_0} \frac{U_{\text{ex}}(\rho_0, T')}{k_B T'} \frac{dT'}{T'}, \quad (3)$$

TABLE I. Thermodynamic consistency of the MHNC (see text). Top: Lennard-Jones fluid at  $\rho^*=0.5$  and  $T^*=1.4$ . Path 1 is the isothermal integration at  $T^*=2.74$  followed by isochore integration at  $\rho^*=0.5$  down to  $T^*=1.4$ . Path 2 is the isothermal integration at  $T^*=1.4$  up to  $\rho^*=0.5$ . Bottom:  $C_{60}$  at 2172 K and  $\rho=0.837 \text{ nm}^{-3}$ . Path 1 is the isothermal integration at  $T=2585 \text{ K}$  followed by isochore integration at  $\rho=0.837 \text{ nm}^{-3}$  down to  $T=2172 \text{ K}$ , Path 2 is the isothermal integration at  $T=2172 \text{ K}$  up to  $\rho=0.837 \text{ nm}^{-3}$ .

	$\frac{\beta P}{\rho}$	$\frac{\beta U^{\text{ex}}}{N}$	$\beta F^{\text{ex}}$	$s^{\text{ex}}$
Path 1	3.894	-3.358	-1.053	-1.345
Path 2	3.894	-3.358	-1.061	-1.336
Path 1	0.968	-3.986	-0.966	-3.020
Path 2	0.966	-3.986	-0.960	-3.026

obtained by integrating the excess internal energy  $U_{\text{ex}}$  along an isochore path at fixed density  $\rho_0$ , down to the desired temperature  $T_0$ . [Equation (3) expresses the well-known “energy route” to thermodynamics.<sup>8</sup>]

We observe that thermodynamics constructed through Eq. (3) will not generally be consistent with the virial and compressibility routes; such a “residual” [with respect to the fulfillment of condition (1)] inconsistency between the three paths to the EOS’s has already been evaluated in a previous work<sup>10</sup> on the LJ fluid, where it was found to be close to 1%. In Ref. 10 the phase diagram was obtained through the joint use of the so-called HMSA approximation,<sup>11</sup> and of a “one-phase” freezing criterion<sup>12</sup> based on the behavior of multiparticle contributions to the excess entropy of the liquid (see below). Here, we perform a similar calculation in the context of the MHNC.

We employ the well-known Verlet-Weis parametrization of the hard-sphere bridge function with a cutoff at  $r=5\sigma$ , where  $\sigma$  is the repulsive parameter of the 12-6 LJ

TABLE II. Comparison of MHNC thermodynamic quantities with computer simulation data. Top: LJ fluid; bottom:  $C_{60}$ .  $N$  is the total number of particles. Other quantities are defined in the text.

$T^*$	$\rho^*$	$\frac{\beta P}{\rho}$	$\frac{U_{\text{ex}}}{N\epsilon}$	$s_{\text{ex}}$
1.35	0.7	1.166 <sup>a</sup> (1.169)	-4.684 <sup>a</sup> (-4.675)	
0.75	0.87	1.253 <sup>b</sup> (1.327)	-6.206 <sup>b</sup> (-6.208)	-3.720 <sup>b</sup> (-3.734)
$T \text{ (K)}$	$\rho \text{ (nm}^{-3}\text{)}$	$P \text{ (bar)}$	$\frac{U_{\text{ex}}}{Nk_B T}$	
1785	0.944	153 <sup>c</sup> (93)	-5.63 <sup>c</sup> (-5.81)	
1900	0.964	275 <sup>c</sup> (235)	-5.499 <sup>c</sup> (-5.69)	

<sup>a</sup>Reference 14.

<sup>b</sup>Reference 12.

<sup>c</sup>Reference 19.

potential. The Newton-Raphson solution method of Gillan<sup>13</sup> is adopted, with a grid of 2048 points and a grid spacing  $\Delta r=0.02$ , all distances being measured in  $\sigma$  units. An accuracy of better than  $10^{-12}$  in the solution of the MHNC equations, and better than 0.1% in satisfying (1), respectively, was usually requested. Reduced units are used for the number density of particles  $\rho^*=\rho\sigma^3$ , and temperature  $T^*=k_B T/\epsilon$ ,  $\epsilon$  being the depth of the LJ potential.

The overall consistency of the MHNC for the LJ fluid is appreciable from Table I. It appears that the differences between thermodynamic quantities obtained along different paths are practically negligible. On the other hand, as is visible in Table II, the theoretical predictions often reproduce within 1% the simulation re-

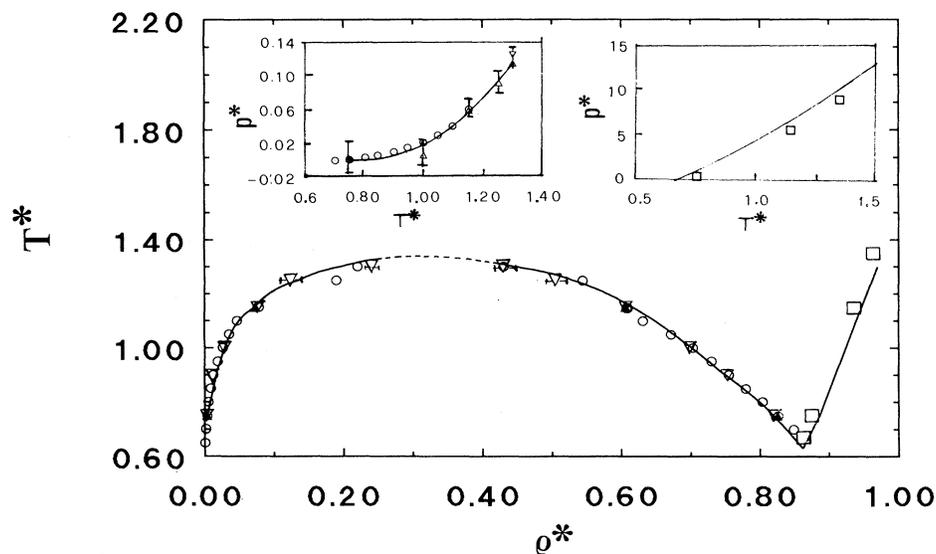


FIG. 1. Binodal and freezing line of the Lennard-Jones fluid. Circles: Monte Carlo (Ref. 15); filled triangles and squares: gas-liquid coexistence and freezing data, respectively (Ref. 14); triangles: GE simulation (Ref. 4); full line: MHNC results. Inset: temperature-pressure equilibrium lines along the binodal (left), and the freezing line (right). In the left inset, downward and upward triangles refer to the gas and liquid phase data (Ref. 4), respectively, and are displayed with their error bars. Pressures are in units of  $\epsilon/\sigma^3$ .

sults, at both supercritical and subcritical temperatures (see below).

The phase diagram of the LJ fluid is reported in Fig. 1: the binodal line is determined by equating the pressure and the chemical potential  $\mu$  (obtained from the free energy and the pressure through Euler's equation  $\mu = F + P/\rho$ ) of the liquid and vapor phase.

It appears that the MHNC reproduces within the error bars the computer simulation binodal line. In the region very close to the critical point no theoretical results are displayed (dashed curve in Fig. 1). The reason is that as the LJ fluid critical temperature is approached, it becomes increasingly difficult to impose an accurate thermodynamic consistency *and* to keep convergent the iterative solution procedure. Possible sources of problems in this concern could be the use of a limited spatial grid in a density-temperature regime, where correlations tend to become long ranged,<sup>16</sup> or the chosen functional form of the bridge function.

The MHNC critical-point parameters can, however, be determined from an interpolation of the data available at lower temperatures. We estimate  $T_{cr}^* = 1.34$  and  $\rho_{cr}^* = 0.31$ , while simulation yields  $T_{cr}^* = 1.32 - 1.33$  (Refs. 4, 8, and 14) and  $\rho_{cr}^* = 0.31 \pm 0.02$  (Ref. 4).

As far as freezing is concerned, this takes place when (Ref. 12)

$$\Delta s = s_{ex} - s_2 = 0, \quad (4)$$

where

$$s_{ex} = \sum_{n=2}^{\infty} s_n, \quad s_2 = -\frac{1}{2}\rho \int \{g(r)\ln[g(r)] - g(r) + 1\} dr;$$

in Eqs. (4),  $s_{ex}$  is the excess entropy expressed as a sum of  $n$ th particle contributions  $s_n$ , and  $s_2$  is the first term of the series (see Ref. 12 for more details).

We first calculate  $\Delta s$  in the MHNC for the hard-sphere fluid; we find  $\rho_{freez}^* = 0.947$ , a result that practically reproduces the computer simulation estimate  $\rho_{freez}^* = 0.943$  and whose accuracy is comparable to previously reported results.<sup>12</sup>

The LJ freezing line is then obtained. It appears from Fig. 1 that the agreement with the computer simulation data is satisfactory also in this case and comparable to that achieved in Ref. 10 through the use of the HMSA.

From the knowledge of the binodal and freezing line we can estimate through a spline interpolation the triple-point temperature and density,  $T_{tr}^* = 0.63$  and  $\rho^* = 0.862$ , respectively; both of these two quantities compare satisfactorily with the computer simulation results  $T_{tr}^* = 0.67 \pm 0.02$  and  $\rho^* = 0.86 \pm 0.01$ .<sup>4,8,14</sup> We have also obtained preliminary results<sup>17</sup> for the binodal line of the hard-core Yukawa fluid; the comparison with the computer-simulation data<sup>18</sup> is quantitative also in this case.

Turning now to the  $C_{60}$  case, we recall that the molecule is assumed to be spherical with a diameter of 7.1 Å.<sup>1,2</sup> Other details about the model and the simulation procedure can be found in Ref. 1.

One can see in Table I that, similarly to the LJ case, one has almost exact consistency between thermodynam-

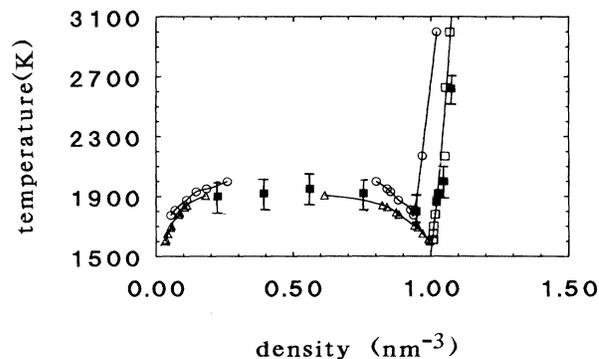


FIG. 2. The  $T$ - $\rho$  phase diagram of model  $C_{60}$ . Filled squares: MD (Ref. 1); circles: HMSA results (Ref. 1); triangles and squares: MHNC results. Solid lines across the calculated points are drawn as a guide for the eye.

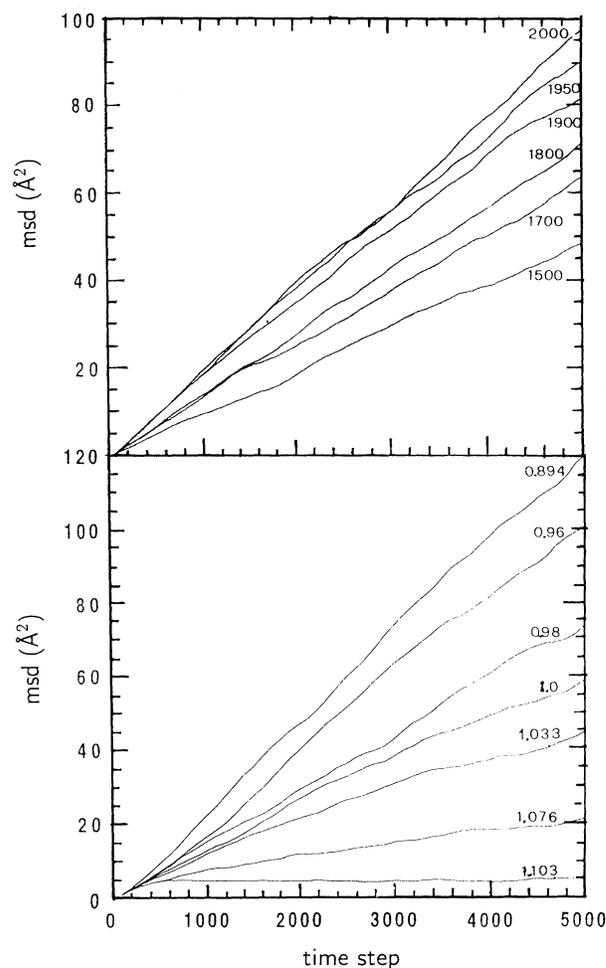


FIG. 3. Top: MD mean-square displacement (Ref. 19) (MSD) of the  $C_{60}$  molecule at fixed density  $\rho = 0.944 \text{ nm}^{-3}$ ; labels on the curves are temperatures (in K). Bottom: MD MSD (Ref. 20) at average temperature  $1780 \pm 50 \text{ K}$ ; labels on the curves are densities (in  $\text{nm}^{-3}$ ).

ic quantities estimated via different paths. The comparison with computer simulation data is reported in Table II and is also satisfactory.

The phase diagram is reported in Fig. 2. The agreement with the computer simulation results previously generated<sup>1</sup> is better than that obtained with the HMSA.<sup>1</sup> In the temperature region close to the critical point difficulties similar to those experienced in the LJ case arise; for the rest, the MHNC binodal fits quite well with the MD calculated points; note in this concern the relatively large error bars. The MD freezing line also now appears well reproduced, especially in the high-temperature region.

The MHNC predicts  $T_{tr} \approx 1620$  K, a triple-point temperature substantially lower than the previous HMSA estimate<sup>1</sup>  $T_{tr} = 1780$  K, the latter being a circumstance that could be more favorable to the formation of a liquid phase. The critical temperature, estimated by interpolation, is  $\sim 1920$  K and is also lower than its HMSA counterpart. The freezing density  $\rho = 1 \text{ nm}^{-3}$  is slightly higher than  $0.944 \text{ nm}^{-3}$ , the previously obtained result.<sup>1</sup> The triple-point pressure is  $\sim 5$  atm.

Constant volume molecular-dynamics simulations with 864 (Ref. 19) and 560 (Ref. 20)  $C_{60}$  molecules have also been performed, according to a procedure quite similar to that detailed in Ref. 1 and within the same modelization. The simulations covered a 25-ps time range after 10 ps of equilibration with a time step  $\tau = 0.5 \times 10^{-15}$  sec.

The mean-square displacements (MSD's) obtained<sup>19</sup> at  $\rho = 0.944 \text{ nm}^{-3}$ , which is well inside the liquid-state region of  $C_{60}$  (see Fig. 2), and different temperatures are reported in Fig. 3. At  $T = 1800$  K one can estimate  $D = 4.6 \times 10^{-5} \text{ cm}^2/\text{sec}$ , a typical liquid-state value at this temperature. Note that the MSD's remain

moderately diffusive down to 1500 K.

The MSD's have also been calculated<sup>20</sup> through several MD runs at "fixed" temperature as a function of the increasing density; the average final temperature of these simulations was  $1780 \pm 50$  K. The results are shown in Fig. 3.

It appears that at  $\rho = 1.033 \text{ (nm}^{-3}\text{)}$ , corresponding to freezing at the chosen temperature (see Fig. 2), the MSD is already substantially reduced with respect to  $\rho = 0.95$ , and that at  $\rho = 1.103$  it completely flattens by attaining a solid-state-like behavior. The results reported indicate the existence of a liquid phase of rigid  $C_{60}$  molecules in the range  $0.6 < \rho < 1 \text{ nm}^{-3}$ ,  $1600 \text{ K} < T < 1920 \text{ K}$ ; this temperature range is considerably larger than those previously found.<sup>1</sup>

In conclusion, we have shown that the modified-hypernetted-chain theory<sup>7</sup> is, in practice, self-consistent with respect to all three routes to thermodynamics and that it is able to predict the phase diagram of the Lennard-Jones fluid in a quantitative accurate manner with respect to simulation. The overall calculation time necessary in order to map the phase equilibrium lines is of the order of 10–20 h on a powerful RISC machine. On the basis of this successful result, the phase diagram of a rigid molecule model of  $C_{60}$ , recently investigated with contradictory results<sup>1,3</sup> as far as the existence of a stable liquid phase is concerned, has been similarly determined. The present results agree with previous<sup>1</sup> simulation and theoretical predictions of the existence of such a liquid phase.

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