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## LETTER TO THE EDITOR

## A double Yukawa potential for the van der Waals interaction of $C_{60}$ molecules: application to a determination of the critical temperature

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**Abstract.** A double Yukawa (DY) potential, fitted on the carbon–carbon (CC) van der Waals (vdW) Lennard-Jones 12,6 (LJ) potential and integrated on two facing spheres, yields another DY function, whose parameters are simply related to those of the original CC LJ. We exploit this fact to obtain a new analytic expression of the DY type that describes the high-temperature physical interactions between  $C_{60}$  molecules in good agreement with the well-known Girifalco potential, which was obtained from the direct spherical integration of the LJ potential. The main advantage of having a DY pair potential comes from the fact that analytic expressions of thermodynamic functions can be obtained within the Percus–Yevick approximation of the Ornstein–Zernike equation. As an example, an analytic expression of the Helmholtz free energy is derived, and the double tangent construction on its vdW loop allows the determination of the liquid–vapour coexistence line and an estimation of the  $C_{60}$  critical parameters ( $T_c = 1940$  K,  $\rho_c = 0.50$  nm $^{-3}$ ). This is in good agreement with the results predicted from various other theories with the Girifalco potential.

At high temperatures, the van der Waals (vdW) intermolecular interactions between two  $C_{60}$  molecules have so far been well described by the Girifalco potential (Girifalco 1992), which was constructed by spherical integrations of the carbon–carbon (CC) vdW Lennard-Jones 12,6 (LJ) potential function. It has since been extensively used to study the physical properties of  $C_{60}$  solid (Girifalco 1992), the structure of  $C_{60}$  clusters,  $(C_{60})_N$  (Rey *et al* 1994, Doye and Wales 1996), as well as the  $C_{60}$  high-temperature phase diagram (Shchelkatcheva 1996, Caccamo 1996 and references therein). Recently, other analytic representations of the  $C_{60}$  vdW interactions with more than two parameters were also proposed based on the spherical integrations of the three-parameter vdW Buckingham (or exp(6)) CC potential (Guérin 1998). Although analytic, all these potential functions have rather complex structures that preclude the derivation of thermodynamic functions of the dense fluid in analytic form.

The aim of this letter is to propose a new high-temperature potential interaction function for  $C_{60}$  molecules of the double Yukawa DY type. This is of particular interest when calculating thermodynamic functions, since the analytic solution of the Yukawa closure of the Ornstein–Zernike (OZ) equation has been intensively studied (Herrera *et al* 1996, Caccamo 1996 and references therein). In order to build up such a potential, we shall use the fact that the CC vdW LJ potential can be closely approximated by a DY function (Foiles and Ashcroft 1981, Konior and Jedrzejek 1988, Rudisill and Cummings 1989, Kalyuzhnyi and Cummings 1996, Tang *et al* 1997), which after two spherical integrations yields, as

we shall show below, another DY function, the parameters of which are simply related to those of the CC LJ potential. Starting from the values used by Girifalco (1992) for the CC interaction parameters, it is possible to obtain a  $C_{60}$  DY potential that fits closely the  $C_{60}$  Girifalco potential.

As a simple application of this new DY function, we obtain the Helmholtz free energy of the  $C_{60}$  dense fluid in analytical form following a method recently proposed for colloidal fluids (Tejero *et al* 1994, 1995). Below the critical temperature  $T_c$ , this expression develops a vdW loop, which allows the construction of the liquid–vapour part of the phase diagram.

Let us consider two exohedral spherical uniform distributions of carbon atoms with radii  $R_1$  and  $R_2$  ( $R_1 < R_2$ ), the centres of which are separated by  $r$  ( $r > R_1 + R_2$ ), containing respectively  $N_1$  and  $N_2$  carbon atoms. An atom  $i$  on one shell interacts with an atom  $j$  on the other shell at a distance  $d_{ij}$  through an LJ potential written as

$$V_{ij}^{LJ} = A_{12}/d_{ij}^{12} - A_6/d_{ij}^6 = 4\varepsilon \left[ (\sigma/d_{ij})^{12} - (\sigma/d_{ij})^6 \right] \quad (1)$$

where the parameters  $A_{12}$ ,  $A_6$ ,  $\varepsilon$  and  $\sigma$ , as determined by Girifalco (1992), are given in table 1. Due to its mathematical simplicity in solving the OZ equation, the DY potential

$$\begin{aligned} V_{ij}^{DY} &= \frac{E}{d_{ij}} \left\{ \exp[-z_2(d_{ij} - \sigma)] - \exp[-z_1(d_{ij} - \sigma)] \right\} \\ &= \frac{E}{d_{ij}} \sum_{k=1,2} (-1)^k \exp[-z_k(d_{ij} - \sigma)] \end{aligned} \quad (2)$$

has been proposed to represent the LJ potential with various relations between the DY and LJ parameters. For our purpose, which is to reproduce the Girifalco potential as closely as possible, we found that the fit chosen by Foiles and Ashcroft (1981) is the most effective. The DY parameters are then given by

$$E = 2.0199\varepsilon\sigma \quad z_1 = 2.6793/\sigma \quad z_2 = 14.735/\sigma. \quad (3)$$

**Table 1.** Values of the CC vdW LJ potential parameters used by Girifalco (1992).

$A_{12}$ (erg cm <sup>12</sup> )	$A_6$ (erg cm <sup>6</sup> )	$\varepsilon$ (erg)	$\sigma$ (Å)
$55.77 \times 10^{-105}$	$32.00 \times 10^{-60}$	$4.5903 \times 10^{-15}$	3.4690

Now, the total interaction potential between the two shells is obtained as a sum of pairwise interactions:  $V_{N_1 N_2} = \sum_{i,j}^{N_1, N_2} V_{ij}^{DY}(d_{ij})$ . In the surface continuum approximation, the discrete summations over  $i$  and  $j$  are replaced by the integrations over the two spherical surfaces of the Yukawa functions:  $(1/d_{ij}) \exp[-z_k(d_{ij} - \sigma)]$ . Replacing first the summation over  $j$  by the integration over the sphere of radius  $R_2$ , we obtain the interaction energy of a spherical fullerene of radius  $R_2$  with an atom  $i$  (here a C atom) at a distance  $l_{i2}$  from its centre as another combination of Yukawa functions written as:

$$V_{i, N_2}(l_{i2}) = \frac{N_2 E}{l_{i2}} \sum_{k=1,2} (-1)^k \left( \frac{\sinh(z_k R_2)}{z_k R_2} \right) \exp[-z_k(l_{i2} - \sigma)]. \quad (4)$$

Carrying out next the second integration over the sphere of radius  $R_1$ , which replaces the discrete sum over  $i$ , we obtain the total interaction energy between two spherical fullerenes in exohedral position as yet another DY function written as:

$$V_{N_1, N_2}(r) = \frac{N_1 N_2 E}{r} \sum_{k=1,2} (-1)^k \left( \frac{\sinh(z_k R_1)}{z_k R_1} \right) \left( \frac{\sinh(z_k R_2)}{z_k R_2} \right) \exp[-z_k(r - \sigma)]. \quad (5)$$

For the special case  $N_1 = N_2 = N = 60$  and  $R_1 = R_2 = R = 3.55 \text{ \AA}$ , we obtain a DY representation of the Girifalco potential. In equation (5), the exponential coefficients are different and  $\sigma$  represents the zero of the CC LJ potential. In order to transform the DY function (5) into the more usual form in which the coefficients of the two exponentials are equal, we introduce the parameters  $\Sigma$  and  $\Delta$  such that  $V_{N,N}(\Sigma) = 0$  and  $\Delta = \Sigma - \sigma$ , and equation (5) becomes:

$$V_{N,N}(r) = \frac{N^2 E}{r} \sum_{k=1,2} (-1)^k \left( \frac{\sinh(z_k R)}{z_k R} \right)^2 \exp(-z_k \Delta) \exp[-z_k(r - \Sigma)]. \quad (6)$$

The introduction of the dimensionless quantities  $x = r/\Sigma$ ,  $a = z_2 \Sigma = 14.735 \Sigma/\sigma$ ,  $b = z_1 \Sigma = 2.6793 \Sigma/\sigma$  and

$$c = \frac{N^2 E}{\Sigma D} \left( \frac{\sinh(z_k R)}{z_k R} \right)^2 \exp(-z_k \Delta) \quad k = 1 \text{ or } 2 \quad (7)$$

where  $D$  represents the minimum of  $V_{N,N}(r)$ , allows the DY potential (6) to be set into the form used by Tejero *et al* (1995) for colloidal fluids, which reads:  $V_{N,N}(r) = D\phi(x)$  with

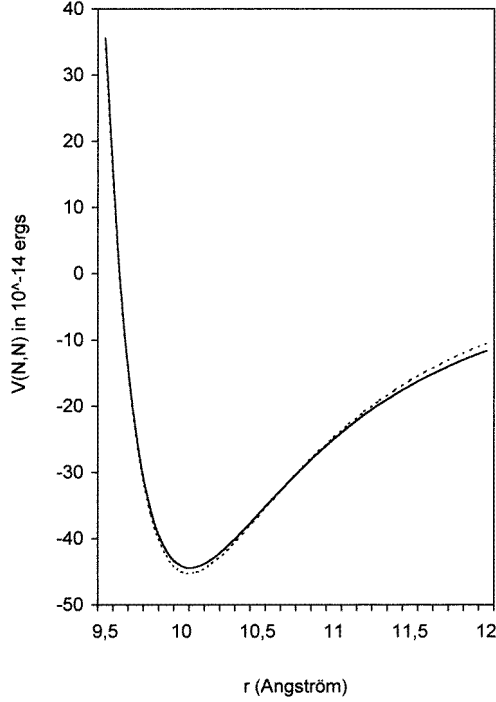
$$\phi(x) = \frac{c}{x} [e^{-a(x-1)} - e^{-b(x-1)}]. \quad (8)$$

The numerical values of  $D$ ,  $\Sigma$ ,  $a$ ,  $b$  and  $c$  obtained from the CC LJ potential used by Girifalco (1992) are shown in table 2, and a comparison of the Girifalco and DY potentials is made in figure 1. Tejero *et al* (1994, 1995) have also characterized the shape of the DY potentials (8) by three parameters:  $x_0$ ,  $x_1$  and  $\delta = (x_1 - x_0)/x_0$ , where  $x_0$  is such that  $\phi(x)$  is minimum, and  $x_1$  is the value of  $x$  for which  $\phi(x)$  has dropped to 1% of its value, i.e.  $\phi(x_1) = -0.01$ . The numerical values of these parameters characterizing the  $C_{60}$  DY potential are also given in table 2. The value  $x_1 = 1.6397$  is of particular interest, since it is slightly above the threshold ( $x_1 = 1.6$ ) for the disappearance of the liquid phase found by Tejero *et al* (1994, 1995) in their study of phase diagrams of colloidal fluids. This is in complete agreement with previous works on the  $C_{60}$  phase diagram (Hasegawa and Ohno 1996, 1997, Caccamo 1996 and references therein), where it has been shown that liquid  $C_{60}$  can either exist in a very narrow range of temperature or not at all. The DY potential presented here clearly shows then that the  $C_{60}$  system represents a borderline transition case between two types of phase diagram in which the liquid phase is about to disappear or has just disappeared.

**Table 2.** Values of the DY and Girifalco (G)  $C_{60}$  potential parameters.

	$D$ (erg)	$\Sigma$ ( $\text{\AA}$ )	$r_{min}$ ( $\text{\AA}$ )			
G	$44.430 \times 10^{-14}$	9.5929	10.056			
DY	$45.250 \times 10^{-14}$	9.5904	10.053			
	$a$	$b$	$c$	$x_0$	$x_1$	$\delta$
DY	40.7360	7.4071	1.8738	1.0482	1.6397	0.5643

As an example of the utility of the above  $C_{60}$  DY potential, we derive in this section an analytic expression for the free energy,  $f$ , per molecule. Following the method of Tejero *et al* (1994, 1995) for colloidal fluids, the free energy is obtained from a variational procedure based on the Gibbs–Bogoliubov inequality (Hansen and McDonald 1986) in which the reference system consists of hard spheres (HS), the diameter ( $\Sigma_{HS}$ ) of which is



**Figure 1.** Comparison of the DY (dashed line) and Girifalco (full line)  $C_{60}$  potentials.

taken as the variational parameter. In this context, the particular utility of the DY form of the potential follows from the fact that

$$\int g_{HS}(r) \frac{\exp(-zkr)}{r} dr = 4\pi \int r g_{HS}(r) \exp(-zkr) dr \quad (9)$$

where  $g_{HS}(r)$  is the HS pair-correlation function. Equation (9) implies that the computation of  $f$  involves the Laplace transform of  $rg_{HS}(r)$  which, along with the HS free energy, can be obtained in analytic form within the Percus–Yevick approximation of the OZ equation (Wertheim 1963). This approach yields the following expression for the variational free energy  $f_V$  of  $C_{60}$  (Tejero *et al* 1995)

$$\beta f_V(\eta, t, \lambda) = \ln \eta - \frac{3}{2} \ln t + C - 1 + f_{ex}^*(\eta\lambda^3) + 12c\eta\lambda^3 t^{-1} [ae^a H(a\lambda, \eta\lambda^3) - be^b H(b\lambda, \eta\lambda^3)] \quad (10)$$

with

$$f_{ex}^*(x) = \frac{3x(2-x)}{2(1-x)^2} - \ln(1-x) \quad (11)$$

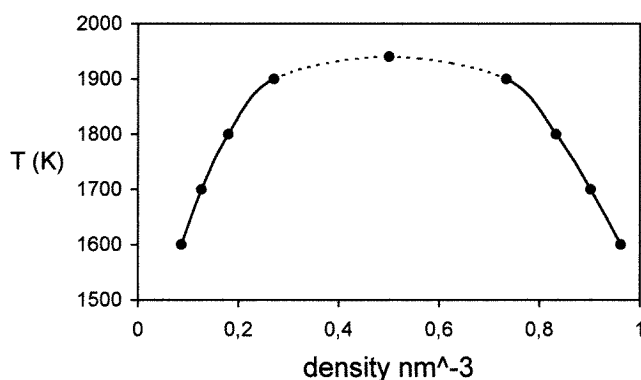
$$H(z, x) = \frac{L(z, x)}{12xL(z, x) + S(z, x)e^z} \quad (12)$$

$$L(z, x) = (1+x/2)z + 1 + 2x \quad (13)$$

$$S(z, x) = (1-x)^2 z^3 + 6x(1-x)z^2 + 18x^2 z - 12x(1+2x) \quad (14)$$

$$C = \ln \left( 6\Lambda_0^3 / \pi \Sigma^3 \right) \quad \Lambda_0 = h / \sqrt{2\pi m D} \quad (15)$$

where the symbols have the following meanings:  $\beta = 1/k_B T$ ;  $\eta = \pi\rho\Sigma^3/6$  is the packing fraction,  $\rho = N/V$  is the number density;  $t = k_B T/D$ ;  $\lambda$  is the variational parameter such that  $\lambda = \Sigma_{HS}/\Sigma$  and  $\eta_{HS} = \eta\lambda^3$ ;  $f_{ex}^*$  is the HS excess free energy;  $m$  is the mass of the  $C_{60}$  molecule;  $x$  and  $z$  here are dummy variables; and the numerical values  $a$ ,  $b$ ,  $c$ ,  $\Sigma$  and  $D$  which define the  $C_{60}$  DY potential are given in table 2. The free energy is given by  $f(\eta, t) = f_V(\eta, t, \lambda_{min})$ , where  $\lambda_{min}$  is the value of  $\lambda$  for which  $f_V$  is minimum. The expressions (10)–(15) can now be used to construct the liquid–vapour coexistence line (figure 2) in the following way: at constant temperature and below the critical temperature  $T_c$ , the variations of  $f$  with respect to  $1/\eta$  present a vdW loop, which separates the low- and high-density branches. Each branch can then be determined by performing a double tangent construction in which the points of tangency correspond to phases of equal pressure and equal chemical potential. The results obtained in figure 2 and the estimated values of the critical parameters ( $T_c = 1940$  K,  $\rho_c = 0.50$  nm $^{-3}$ ), shown in table 3, are in reasonable agreement with the results of various other methods (Caccamo 1996, Hasegawa and Ohno 1996, 1997) which all use the Girifalco potential as a starting point. The discrepancies between the results of the various methods presented in table 3, and the related question of the existence of liquid  $C_{60}$  have already been thoroughly discussed elsewhere (Caccamo 1996, Hasegawa and Ohno 1996, 1997, Ashcroft 1993). Our purpose here was simply to point how the  $C_{60}$  DY potential presented above may be used for the analytic evaluation of the  $C_{60}$  thermodynamic functions.



**Figure 2.**  $C_{60}$  liquid–vapour coexistence line obtained from the DY potential.

**Table 3.** Critical parameters  $T_c$  (K) and  $\rho_c$  (nm $^{-3}$ ) obtained from the  $C_{60}$  DY potential and comparison with the values obtained from various theories with the Girifalco potential. HRT (hierarchical reference theory, Tau *et al* 1995); HMSA (Zerah–Hansen mean spherical approximation, Cheng *et al* 1993); MHNC (modified-hypernetted-chain, Caccamo 1995); MD (molecular dynamics, Cheng *et al* 1993); MC (Monte Carlo, Hagen *et al* 1993); DF (density functional, Hasegawa and Ohno 1996, 1997).

	DY	HRT	HMSA	MHNC	MD	MC	DF
$T_c$ (K)	1940	2138	2050	1920	1900	1798	1960
$\rho_c$ (nm $^{-3}$ )	0.50	0.50	0.56		0.56	0.42	0.40

**References**

- Ashcroft N W 1993 *Nature* **365** 387  
Caccamo C 1995 *Phys. Rev. B* **51** 3387  
Caccamo C 1996 *Phys. Rep.* **274** 1  
Cheng A, Klein M L and Caccamo C 1993 *Phys. Rev. Lett.* **71** 1200  
Doye J P K and Wales D J 1996 *Chem. Phys. Lett.* **262** 167  
Foiles S M and Ashcroft N W 1981 *J. Chem. Phys.* **75** 3594  
Guérin H 1998 *J. Chim. Phys.* **95** 561  
Girifalco L A 1992 *J. Phys. Chem.* **96** 858  
Hagen M J H, Meijer E J, Moij G C A M, Frenkel D and Lekkerkerker H N W 1993 *Nature* **365** 425  
Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)  
Hasegawa M and Ohno K 1996 *Phys. Rev. E* **54** 3928  
Hasegawa M and Ohno K 1997 *J. Phys.: Condens. Matter* **9** 3361  
Herrera J N, Blum L and Garcia-Llanos E 1996 *J. Chem. Phys.* **105** 9288  
Kalyuzhny Y V and Cummings P T 1996 *Mol. Phys.* **87** 1459  
Konior J and Jedrzejek C 1988 *Mol. Phys.* **63** 655  
Rey C, Callego L J and Alonso J A 1994 *Phys. Rev. B* **49** 8491  
Rudisill E N and Cummings P T 1989 *Mol. Phys.* **68** 629  
Shchelkacheva T I 1996 *Phys. Lett. A* **214** 95  
Tang Y, Tong Z and Lu B C Y 1997 *Fluid Phase Equilib.* **134** 21  
Tau M, Parola A, Pini D and Reatto L 1995 *Phys. Rev. E* **52** 2644  
Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1994 *Phys. Rev. Lett.* **73** 752  
Tejero C F, Daanoun A, Lekkerkerker H N W and Baus M 1995 *Phys. Rev. E* **51** 558  
Wertheim M S 1963 *Phys. Rev. Lett.* **10** 321