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Molecular interactions in fullerenes and equilibrium of higher fullerites C_{76} and C_{84} with their vapors

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Abstract. From simple topological considerations on the molecular shapes, a new method for calculating the coefficients of the Girifalco intermolecular potential for various fullerenes is proposed. This eliminates the necessity for fitting the coefficients to data of measurements for each specific fullerene. We calculate them for C_{76} and C_{84} and apply this potential to perform research on the equilibrium of these fullerites with their vapors. The temperature dependence of the lattice parameters, the saturated vapor pressures and the enthalpies of sublimation is studied. Results are in good agreement with available experimental data.

PACS. 34.20.Gj Intermolecular and atom-molecule potentials and forces – 61.48.+c Fullerenes and fullerene-related materials – 64.70.Hz Solid-vapor transitions

It is known (see, *e.g.* [1]) that intermolecular potentials are at the heart of statistical mechanical calculations of thermophysical properties of materials, either analytical and numerical. The best plan to be followed is to obtain such potentials from first principles. However, *ab initio* deductions of good interaction potentials present great difficulties. In practice, a form of a potential function can be derived on the basis of the knowledge of the nature of chemical bonds in materials under investigation while their parameters may be fitted to some reference experimental data (lattice parameter, cohesive energy or heat of sublimation, compressibility, etc.). More frequently it is taken in the pair-wise form, sometimes many-body, usually three-body, forces are included.

One of the first well appropriated pair-wise potentials, the Lennard-Jones potential

$$\Phi_{\rm LJ}(r) = -A/r^6 + B/r^{12} \qquad (1)$$

contains the attractive part that can be deduced *ab initio* (dipole-dipole dispersive forces) and the phenomenological repulsive term. The two coefficients A and B or the minimum point r_0 and the depth of the potential well ε are commonly determined from the experimental lattice parameter and the cohesive energy near the absolute zero of temperature. More accurate and complex potential functions have also been proposed for materials with van der Waals bonds such as condensed noble gases (*e.g.*, Barker *et al.* [2]).

Interactions in ionic crystals are well described by potentials involving a Coulombic part and terms representing repulsion due to overlapping of ionic electron shells. Finally, interactions in materials with metallic and covalent bonds are generally not pair-wise. The scarle pair potentials which nevertheless ensure reasonable results for metals usually have oscillatory form related to the Friedel oscillations of conduction electron density. Such oscillations have been deduced from first principles but parameters of interionic potentials are fitted to experimental data, *e.g.* [3].

In the case of molecular crystals, very profitable is the atom-atom potentials approach in which intermolecular potentials are expressed in terms of interaction potentials between atoms included into the neighboring molecules. Among the molecular solids, of special interest are the fullerites, *i.e.* crystals formed by molecules of fullerenes – new modifications of carbon discovered in the middle of the eighties [4]. Even not mentioning possible practical applications of these materials in the future, today they are of fundamental scientific importance. The point is that the fullerites acquire the significance of reference substances in molecular crystals physics in the same manner as the condensed noble gases in statistical thermodynamics. By now the crystals of the most stable and therefore the most widespread fullerene C_{60} have been much studied. The properties of the next in abundance C_{70} are under intensive investigation now.

At low temperatures, the molecules in these fullerites are orientationally ordered and at high ones they rotate rather freely in the FCC lattice. Both structures of C_{60} possess cubic symmetry and at 261.4 K the only phase transition (orientational melting) is clearly observed

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between them [5,6]. The low-temperature modification of C_{70} is monoclinic and between it and the disordered phase there exist several intermediate partially oriented states [7,8]. At $T > 340$ K, the FCC lattice also occurs in this fullerite, possibly with a little admixture of the HCP phase [7] that is energetically very close to the former. A similar behavior should be expected for other fullerites.

The atoms of carbon are retained in the fullerene molecule by covalent bonds and interact with atoms of other molecules through van der Waals forces. Generally the interaction of two fullerene molecules is expressed by a sum of atom-atom potentials (1) and Coulombic potentials between charges located in the atomic nuclei and in the covalent bonds [9,10]. For orientationally disordered (gaseous, high-temperature crystalline and hypothetical liquid) phases, the Coulombic parts disappear by virtue of the electro-neutrality of molecules. Taking into consideration the near-spherical shape of C_{60} molecules with the radius $a = 3.55 \times 10^{-8}$ cm, and averaging the atom-atom interactions (1) over the orientations of molecules, Girifalco [11] obtained the following pair-wise intermolecular potential for such phases:

$$\Phi_G(r) = -\alpha\left(\frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4}\right) + \beta\left(\frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{1}{s^{10}}\right), \quad (2)$$

where $s = r/2a$, r is the distance between the centers of molecules,

$$\alpha = \frac{n^2 A}{12(2a)^6}, \qquad \beta = \frac{n^2 B}{90(2a)^{12}}, \quad (3)$$

n is the number of atoms in the molecule (in this case, $n = 60$). The parameters of the potential have been fitted to the experimental data for the lattice constant and the heat of sublimation. The obtained values are:

$$A = 3.200 \times 10^{-59}\,\mathrm{erg\,cm^6},\ B = 5.577 \times 10^{-104}\,\mathrm{erg\,cm^{12}}. \quad (4)$$

The shape of the C_{70} molecule is close to an oblong uniaxial ellipsoid with semi-axes $a^{(1)} = a^{(2)} = 3.61 \times 10^{-8}$ cm and $a^{(3)} = 4.26 \times 10^{-8}$ cm. Nevertheless, it can be separated in five groups of $n_l = 10$ or 20 atoms, which lie on spherical shells of certain radii $R_i(a^{(1)} \le R_i \le a^{(3)})$. Generalizing the procedure of Girifalco, Verheijen *et al.* [8] have derived the intermolecular potential for orientationally disordered phases of C_{70}. It consists of a sum of 25 terms. Each of them expresses the interaction between two spheres with radii R_i and R_j possessed by different molecules. In order to calculate its parameters it is necessary a more detailed information about the shape of the molecule. Values of A and B obtained for the potential Verheijen *et al.* are somewhat different from (4). Kniaz *et al.* [12], and also Abramo and Caccamo [13] have utilized the Girifalco potential (2, 3) for the orientationally disordered modification of C_{70}, with the same A and B as in the case of C_{60} (4). This corresponds to the approximation of the shape of the C_{70} molecule by a sphere. Its radius $a(a^{(1)} < a < a^{(3)})$ has been determined by fitting the calculated lattice constant to its experimental value. Such an approach yields reasonable results for the equation of state and bulk modulus at moderate temperatures [13], for the thermal expansion, the Gruneisen parameter and the enthalpy of sublimation [12].

The intermolecular forces in the high-temperature modifications of C_{60} and C_{70} (2) are somewhat more short-range than in simple van der Waals crystals. Therefore, they can be classified as van der Waals crystals [11] with a great number of intramolecular degrees of freedom [14].

The use of the same values of the parameters A and B for various fullerenes reflects the commonness of van der Waals atom-atom interactions in carbon. But the necessity of fitting the radius of the approximant sphere (effective radius) to the experimental lattice parameter renders this method unsuitable in the case of fullerenes for which hitherto there are no experimental data. We can avoid these difficulties by using simple topological considerations. Since the atoms of the fullerene molecules are situated on their surfaces, *i.e.* on two-dimensional manifolds one can concede that the effective radii of such molecules are proportional to the square root of the ratio between the numbers of atoms in the molecules:

$$a_m = a_n\sqrt{m/n}. \quad (5)$$

Because of this, using the known value of a_n for anyone fullerene, for instance for C_{60}, it is easy to obtain the effective radius for any other fullerene. (Note that for C_{70} it coincides with those derived from experimental data for the lattice constant [12,13] within $0.6 - 0.8\%$). Substituting it into formulae (3) gives the coefficients α and β of the Girifalco potential for the latter.

We have calculated the parameters of this potential for two higher fullerenes – C_{76} and C_{84}. They are listed in Table 1 together with those for C_{60} [11] and C_{70} [12,13]. In particular, one can see that the parameters for C_{70} calculated in [12,13] are very close to each other. In Figure 1, we plot the dependence of the Girifalco potential on the intermolecular distance for the four fullerenes, for C_{70} only the curve with parameters from [12] being shown.

Table 1. Parameters of the Girifalco potential for the four fullerenes: the effective molecular diameter $2a$, the coefficients α and β, the minimum point r_0, and the depth of the potential well ε.

	C_{60} [a]	C_{70} [b]	C_{70} [c]	C_{76} [d]	C_{84} [d]
$2a(10^{-8}$ cm)	7.100	7.600	7.620	7.991	8.401
$\alpha(10^{-14}$ erg)	7.494	6.781	6.670	5.920	5.356
$\beta(10^{-17}$ erg)	13.595	8.176	7.913	5.287	3.542
$r_0(10^{-8}$ cm)	10.056	10.549	10.575	10.946	11.357
$-\varepsilon/k_B$ (K)	3218.4	3678.4	3653.0	3808.4	4081.5

[a] Girifalco [11]; [b] Kniaz', Girifalco and Fischer [12]; [c] Abramo and Caccamo [13]; [d] This work.

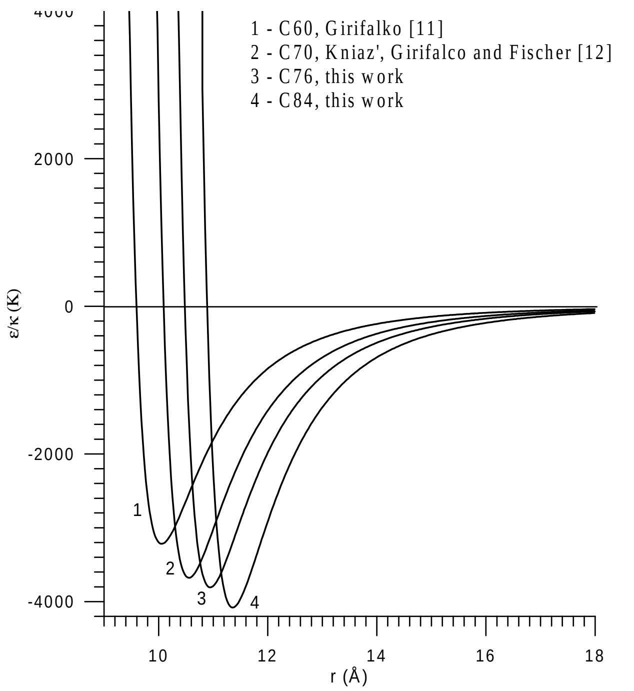

Fig. 1. The Girifalco intermolecular potential for four fullerenes.

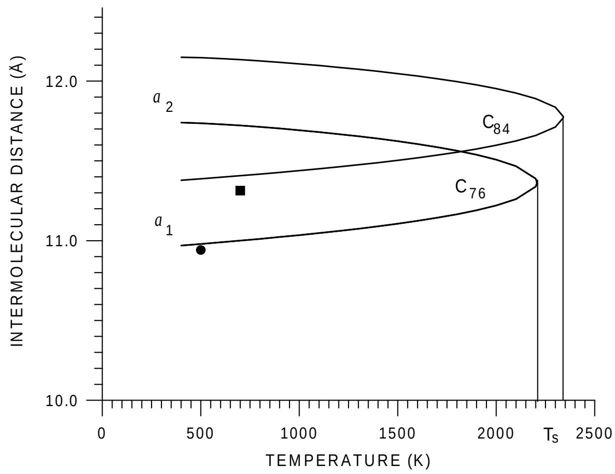

Fig. 2. Nearest-neighbor distances in C_{76} and C_{84} fullerites along their sublimation curves. Experimental data are from references [18] and [19].

We utilize the Girifalco potential with the coefficients from Table 1 in the investigation of the sublimation of C_{76} and C_{84} fullerites. Thermodynamic functions of the vapor are calculated employing the virial expansions up to the second terms. For the solid phase we use the correlative method of unsymmetrized self-consistent field (CUSF) [14–17]. It enables one to take into account the anharmonicity of lattice vibrations that is strong in fullerites above 700–800 K. The reliability of this method is confirmed by the results for C_{60} [14,16] and C_{70} [17] which are in good agreement with experiment. Note also that CUSF has been verified its results for the simple van der Waals crystals [15] with computer simulations.

The equilibrium between two phases is determined by the equality of their chemical potentials together with their equations of state. Including into the zeroth approximation of CUSF anharmonic terms up to the fourth order we have for the sublimation curve the set of equations [16]:

$$P = -\frac{a}{3\nu}\left[\frac{1}{2}\frac{\mathrm{d}K_0}{\mathrm{d}a} + \frac{\beta\Theta}{2K_2}\frac{\mathrm{d}K_2}{\mathrm{d}a} + \frac{(3-\beta)\Theta}{4K_4}\frac{\mathrm{d}K_4}{\mathrm{d}a}\right] + P^2 + P^{\mathrm{H}}; \quad (6)$$

$$P = P_{\mathrm{id}}(1 - BP_{\mathrm{id}}/\Theta);$$
$$P_{\mathrm{id}} = \Theta\left(\frac{K_4}{12\pi^2\Theta}\right)^{3/4} \times \exp\left[\frac{K_0}{2\Theta} - \frac{5}{24}\left(\frac{\beta}{X}\right)^2 - \frac{1}{4}\left(X + \frac{5\beta}{6X}\right)^2 + \frac{f^2 + f^{\mathrm{H}}}{\Theta}\right] \Big/ D_{-1.5}\left(X + \frac{5\beta}{6X}\right). \quad (7)$$

Here $\Theta = kT$ is the absolute temperature in energy units, P_{id} the saturated vapor pressure in the ideal gas approximation, $B(T)$ the second virial coefficient, a the nearest neighbor distance in the crystal, $\nu(a)$ the volume of its unit cell, $K_0/2$ the energy of the static lattice per molecule, K_2 and K_4 are the force coefficients of the second and fourth orders, β is the solution of the transcendental equation

$$\beta = 3X\frac{D_{-2.5}(X + 5\beta/6X)}{D_{-1.5}(X + 5\beta/6X)}; \quad X = K_2\sqrt{3/\Theta K_4}, \quad (8)$$

$D_\nu(Z)$ are the parabolic cylinder functions, f^2, f^{H}, P^2 and P^{H} the corrections by perturbation theory to the Helmholtz energy of the crystal per molecule and to its equation of state, they take into account, in particular, the higher-order anharmonicity.

Equations (7) and (8) with account of (9) determine the saturated vapor pressure $P_{\mathrm{sat}}(T)$ and the nearest-neighbor distance $a(T)$. We have solved them for C_{76} and C_{84} at $T \geq 400$ K because the potential (2) is inapplicable to orientationally ordered phases that exist in these fullerites at lower temperatures. In addition, the saturated vapor pressure is vanishingly small at such temperatures. The results for $a(T)$ are shown in Figure 2. The lower roots a_1 represent the stable thermodynamic states whereas the upper roots a_2 the absolutely unstable ones (for them the isothermal bulk modulus of the crystal is negative). The limiting temperature T_{S} is the point of loss of the thermodynamic stability (spinodal point) for the two-phase crystal - vapor system. One can see that the discrepancy between calculated and experimental values is 0.35% for C_{76} and 0.8% for C_{84}.

Figures 3 and 4 present the logarithm of the saturated vapor pressure for the two fullerites *versus* the inverse of temperature. Here, as in Figure 2, the lower branches correspond to stable states and the upper ones to unstable. For both branches the dependence $\log P(1/T)$ is almost linear. For the stable branches there is a good agreement with experiment. On the interval $800 \leq N \leq 1\,100$ K,

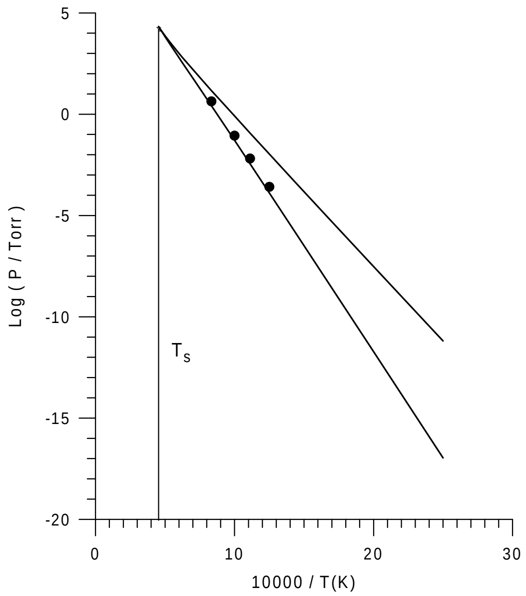

Fig. 3. Saturated vapor pressure of C_{76}. Experimental data are from reference [19].

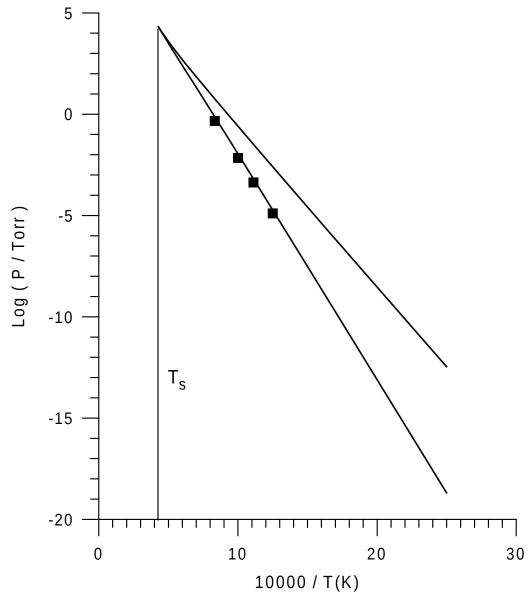

Fig. 4. Saturated vapor pressure of C_{84}. Experimental data are from reference [19].

Table 2. Coefficients of equation (9) for P_{sat} in Torr.

	A	B (K)	10^4C (K^{-1})
C_{76}	9.432	10525	1.9746
C_{84}	9.476	11238	1.9729

our results for these branches for C_{76} and C_{84} are approximated by the formulae $\log(P_{\text{sat}}/\text{Torr}) = (9.046 - 10\,340/(T/\text{K})$ and $\log(P_{\text{sat}}/\text{Torr}) = 9.094 - 11\,056/(T/\text{K})$, respectively. They practically coincide with those deduced from experiments for this temperature range $\log(P_{\text{sat}}/\text{Torr}) = (8.80 \pm 0.20) - (10\,150 \pm 150)/(T/\text{K})$ for C_{76} [18] and $\log(P_{\text{sat}}/\text{Torr}) = (9.11 \pm 0.30) - (10\,950 \pm 300)/(T/\text{K})$ for C_{84} [19]. Over more wide temperature limits, they are more accurately approximated by the equation

$$\log P_{\text{sat}} = A - \frac{B}{T} - CT \tag{9}$$

with the coefficients listed in Table 2. The last term in (9) has an anharmonic nature. Although the value of C is comparatively small, at high temperatures it gives an appreciable contribution. For instance, in the vicinity of the spinodal points it changes the results for P_{sat} in about 2.5 times. This testifies that at such temperatures the anharmonicity of the crystal lattice vibration is pronounced.

In Figure 5 is shown the temperature dependence of enthalpies of sublimation [16]

$$\Delta H_{\text{sub}} = -N\left[\frac{K_0}{2} + \frac{(\beta-1)\Theta}{4} + E^2 + E^{\text{H}} - BP_{\text{sat}}\right] \tag{10}$$

calculated for this fullerites along the stable branches $a_1(T)$ of their sublimation curves (E^2 and E^{H} are the cor-

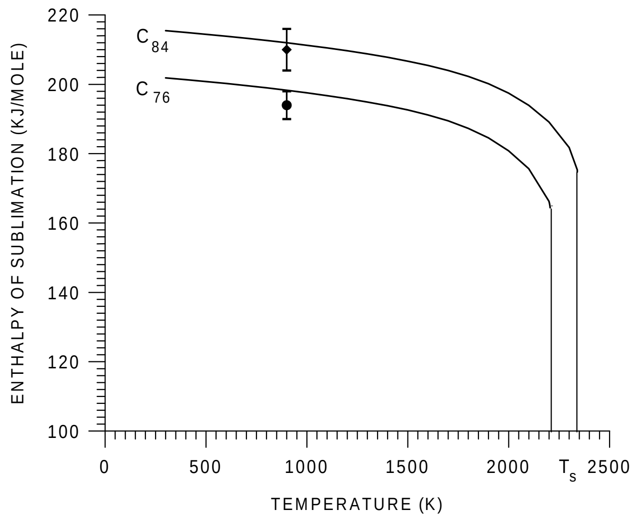

Fig. 5. Enthalpies of sublimation of C_{76} and C_{84}. Experimental data are from references [19] and [20].

rections to the molar internal energy of the crystal). One can see that the agreement with experiments is within their limits of error.

Unfortunately, there are experimental data for the intermolecular distances and the enthalpies of sublimation of these fullerites only at one temperature for each. Computer simulations for them are lacking at all. But a satisfactory test of variation trend of these quantities with the temperature for C_{60} [16] and C_{70} [17] provides reason to expect the correct prediction for C_{76} and C_{84}. In any case, a large-scale comparison with experimental data in the future would be of great interest.

Thus, we can recommend the Girifalco potential with the parameters from Table 1 for theoretical investigation of a wide set of thermodynamic properties for high-temperature modifications of C_{76} and C_{84} fullerites, as well as use the proposed method as a recipe for calculation of such parameters for other higher and smaller fullerenes [21]. Note also that on the basis of arguments like (5) it has been established the presence of giant fullerene molecules in a thick film of C_{60} [22].

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