PHYSICAL REVIEW E **66**, 016109 (2002)

Structural phase transitions in the process of an A_{60} cluster formation

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(Received 2 January 2002; published 15 July 2002)

The explanation of the existence of the two critical parameters corresponding to the formation of an A_{60} fullerene cluster in the lattice gas model is given. The presented treatment suggests the possibility of the existence of the two phases of the same symmetry type—high-density phase and low-density phase. These theoretical results can be applied to the carbon fullerene or nanotube research.

DOI: 10.1103/PhysRevE.66.016109 PACS number(s): 05.50.+q

I. INTRODUCTION

The usual problems associated with the lattice gas (or ferromagnet) models [1] are to find the critical temperature T_c of the lattice formation (of the phase transition), to describe the behavior of some important thermodynamical values, for example, heat capacity, near the critical point, to find the critical indices, and so forth. In the absence of an external field in a real system, there are three parameters initially needed to construct such a model: J is the nearest-neighbor interaction energy, z is the number of nearest neighbors, and the type of symmetry. The analytical solutions of these problems were known only for the two-dimensional infinite planar structures such as the square, the triangle, and the honeycomb lattices. In three dimensions the numerical methods were used.

In a recent paper [2] an analytical calculation of the partition function for the lattice gas model of a finite A_{60}-type cluster was given. This type of cluster presents a fullerene with 12 pentagons and 20 hexagons as facets. It is characteristic, for example, for a fullerene molecule C_{60}. It could also be a model for a specific state of water or other matter consisting of atoms or molecules capable of forming a tetrahedrally coordinated network. It was also shown [2] that the obtained results could be used to describe such systems as carbon nanotubes. Contrary to the above mentioned models that are applicable mainly to describe the monolayer films (with account of the external field produced by the underlying surface), the model under discussion here is two dimensional only from the mathematical point of view and belongs to the real three-dimensional world.

Remark 1. Actually, what was calculated in [2] and in the analogous papers is the configurational part of the partition function. That is why the results following from such calculations should be regarded as complimentary to those of [3].

The expression for the thermodynamical potential obtained in [2] with the help of the partition function was

$$\begin{aligned}\Phi = & -NkT\ln 2 + NkT\ln(1-x^2)\\ & -NkT\frac{1}{2\times 2\pi}\int_0^{2\pi}\int_0^{2\pi}\ln\{(1-x^2)^2\\ & -2x^2(1-x^2)[1+\cos(\omega_1-\omega_2)+\cos(\omega_1+\omega_2)]\\ & +2x^4\cos 2\omega_1\}d\omega_1 d\omega_2 . \qquad (1)\end{aligned}$$

Here $x=\tanh\Theta$ is the traditional [4,1] parameter ($\Theta = J/2kT$, k is Boltzmann constant, T is the absolute temperature, $\frac{1}{2}$ follows here from the calculational reasons) used to search for the critical temperature T_c. In the process of deriving the analytical expression Eq. (1) presented in [2] one has to pass from summation to integration. Of course, for the 60-terms polynomial corresponding to the A_{60} fullerene cluster this is an approximation, and the possible singularity that could appear in the further analysis would be just the maximum. But for such system as a nanotube containing thousands of atoms the result becomes exact.

The corresponding values of x_c for the square, the triangle, and the honeycomb infinite planar lattices are known to be [1] 0.44, 0.27, 0.66. The surprising result [2] following from Eq. (1) is the existence of the two critical values of x:

$$(x_c)_{1,2} = \sqrt{\tfrac{1}{9}(4\pm\sqrt{7})} \approx \begin{cases} 0.86 \\ 0.39. \end{cases} \qquad (2)$$

The last fact treated traditionally suggests that there are two critical temperatures corresponding to the formation of an A_{60} cluster. The experimental data [5] discussed in [2] could be regarded as a support to such a treatment. On the other hand, it is hard to understand what the existence of the *two* critical temperatures physically means. Note, that the only three parameters of the model are J, z, and symmetry type.

II. HIGH-DENSITY PHASE AND LOW-DENSITY PHASE

The following approach reveals the possible physical meaning of this paradox. One can see that, strictly speaking, the expression Eq. (2) following from Eq. (1) means not the existence of the two critical temperatures, but the existence of the two critical values of $(x_c)_{1,2}$ pointing to the conditions of the phase transition, i.e., to the conditions of the A_{60} cluster formation.

These conditions include not only the temperature, but the density as well. If the temperature is sufficiently low and the density is increased, the atoms with the four tetrahedrally oriented bonds will be able to form the cluster with the due symmetry as soon as the density reaches the critical value. The existence of the two critical values $(x_c)_{1,2}$ suggests that this is not the end. If the density (i.e., external pressure) increases further and, consequently, the average distance between the atoms decreases, there will appear a situation when

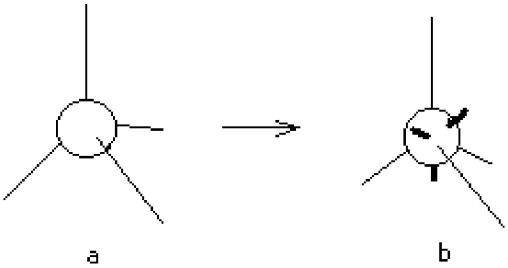

FIG. 1. Bonds characterizing the oriented double-well potential of an A_{60} cluster.

the cluster of the same symmetry type but of higher density is formed. Physically this corresponds to the double-well character of the atom's potential. The initial model did not specify the features of the potential, it was considered to be constant, but the obtained result points to the mentioned possibility. The described situation has a geometrical illustration.

An A atom is supposed to have four bonds oriented as the vortices of a tetrahedron, Fig. 1(a). Let us associate the interaction energy J with the length of a bond. This length as it is not a model's parameter, and there is no sign of it anywhere in the solution. It is only the symmetry and the nearest-neighbors number, z, that are taken into consideration while constructing the expression for the partition function leading to Eq. (1). If the two values of $(x_c)_{1,2}$ correspond to the existence of the two possible values of $J_{1,2}$ of the double-well potential, then there could be two possible lengths of the bonds causing the same symmetry type cluster to appear. In Fig. 1(b) the second set of the tetrahedrally oriented bonds is shown. One can easily imagine that such a set really provides another possibility to form the same type of cluster with the same number of nearest neighbors. The resulting second A_{60} fullerene is more compact and dense than the first one.

The two critical densities correspond to the well known phenomena of the structural phase transitions. This makes it possible to predict the existence of the two A_{60} phases—the high-density phase and the low-density phase. The phase transition under discussion is a second order one, which means that there can be no coexistence of phases in the critical region. (Compare to the situation corresponding to the horizontal part of the isotherm obtained from the van der Waals isotherm with the help of the Maxwell rule.) That is why the region between x_1 and x_2 must have no physical sense. As it can be seen from Fig. 2, it is really so because in this case the expression under logarithm in Eq. (1) becomes negative.

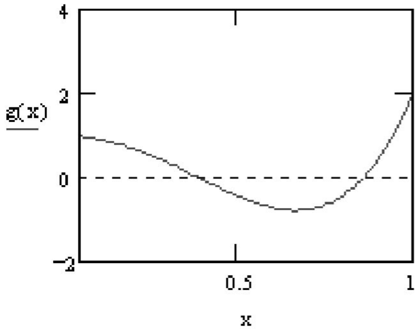

FIG. 2. Partition function containing x, $(x_1 < x < x_2)$ is negative, i.e., it has no physical sense.

Using the definition of x and Eq. (2) to calculate the interaction energy $J = kT \ln(1+x)/(1-x)$, one obtains

$$\frac{(J_c)_1}{(J_c)_2} \approx \frac{2.58}{0.82} \approx 3.15. \tag{3}$$

If J is proportional to the third power of the bond length, then the ratio between the specific volume of the low-density phase and the high-density phase is the same.

III. DISCUSSION

In the field of water research the existence of two [possibly $(H_2O)_{60}$] phases—high-density phase and low-density phase—is known [6] and corresponds to the difficult-to-reach conditions and instability. The double-well character of the potential is also discussed there in connection with this effect. The statistical approach presented here uses the fact that the hydrogen bonds in a water molecule provide the needed type of cluster symmetry. Carbon, and also the less investigated, in this sense other elements of the fourth group of the periodic table, could demonstrate the same property. One could say that the long covalent bonds are accompanied by their short opposite ends, the role of which is hardly discovered in the regular experimental conditions for similar reasons as for the water. If such dense systems do exist, they could demonstrate the exciting properties as well as the carbon fullerene or nanotube materials [7]. The experimental way to obtain them could be to start with the liquid phase of carbon at high pressures. The corresponding computer simulation could be, of course, the easiest way to get another proof of the existence of the phenomenon under discussion.

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