

Model of C_{60} fullerene, $(H_2O)_{60}$ water, and other similar clusters

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An analytical calculation of the partition function for the lattice gas model of a finite fullerene type cluster and of an infinite nanotube type cluster is presented. The method of calculation is based on the Vdovichenko random walk approach. There appear to be two values of critical temperature, and the heat capacity in their vicinities is proportional to $(T - T_c)^{-1}$.

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I. INTRODUCTION

The lattice gas model is well known and is widely used in statistical mechanics [1]. It has a close relation to the Ising model for the phase transition in a ferromagnet [2]. If there is a system of spins interacting with nearest neighbors and located in the vortices of a lattice of a certain symmetry, then at a particular temperature spontaneous magnetization appears. Similarly, at a particular temperature an atomic structure consisting of the atoms interacting with nearest neighbors can appear. Analytical solutions for these models are known only for two-dimensional infinite planar structures such as the square, the triangle, and the honeycomb lattices. In three dimensions numerical methods are used.

In the field of material science two problems that attract the attention of researchers are the formation, structure, and properties of fullerenes and the properties of water in specific conditions when it demonstrates a kind of phase transition between a low-density liquid phase and a high-density liquid phase at low temperatures. Not to discuss these questions in detail, we address the reader to such reviews as [3,4] and to the great number of references mentioned there. The common feature for both of these phenomena could be the symmetry of the corresponding atomic (molecular) clusters.

The simplest fullerene (not to mention nanotubes yet) presents a cluster of 60 carbon atoms coordinated like the vertices of a soccer ball with 12 pentagons and 20 hexagons as facets. This conformation is possible because of the four chemical bonds characterizing a carbon atom. But this is not the only atom (or molecule) with four bonds. A water molecule, for example, is able to create a tetrahedrally coordinated open network with the help of four hydrogen bonds attached to every oxygen atom. When simulated on a computer [6] in two dimensions, the “water molecules” aggregated in groups that demonstrated a fivefold orientational order, while hexagonal symmetry was in a sense also present. This result suggests the idea that, if the two-dimensional surface had a curvature, then the water molecules could form a soccer-ball type structure having the oxygen atoms in the vertices. The recent results [7] of a numerical investigation of a microscopicspherical pore containing water molecules on its inside surface confirms such a possibility, at least in the case when there is an external field of the pore’s walls. But the existence of C_{60} clusters challenges one to think that $(H_2O)_{60}$ clusters could also form in certain thermodynamic conditions in the absence of any ad-

ditional field. In this case, if these conditions are fulfilled and such clusters start to form, the density of water will become much less than that of bulk water, and a low-density liquid phase could appear.

The goal of this paper is to analyze the symmetry properties of an A_{60} cluster and to present a calculation of the partition function for the corresponding lattice gas model (here A is an arbitrary atom or molecule initially able to form a tetrahedral network, and hence potentially able to form a soccer-ball cluster). We are going to apply the Vdovichenko method for solution of the Ising problem. A detailed description of this method can be found in [5]. The method is based on the calculation of the number of random walk loops on an infinite flat plane with a certain symmetry type of the distribution of vertices. In the problem under discussion here, there is a finite set of vertices, but it can be shown that the method remains valid for this case too. Extending the result obtained to an infinite cluster (see below), we will be able to describe such an interesting physical system as the carbon nanotube. It will be shown that not only is the method used here applicable to this system, but it is also free from certain approximations used when dealing with finite A_{60} clusters.

II. CALCULATION OF THE PARTITION FUNCTION

In the further analysis we are going to consider a random walk on a finite lattice that presents a set of vertices on a soccer-ball cluster surface. Every step of this walk covers a single bond and leads to one of the neighboring vertices. Every bond of the soccer-ball cluster has one and the same length and every vertex has three nearest neighbors. The symmetry of the surface is rather complicated due to the existence of both hexagons and pentagons as facets.

Thus, first of all, we have to topologically transform the soccer-ball surface lattice in such a way that a convenient procedure for the random walk calculation can be developed. Let us assume that the bonds connecting the vertices are elastic and can expand, although every single step in the future random walk will still cover the whole bond between the neighboring vertices. The topological transformation goes in two stages. In the first stage we “pass a cylinder” through the opposite pentagons of the soccer ball and let the elastic bonds with vertices stick around the cylinder. In the second stage we “inflate” this cylinder radially and obtain the lattice structure shown in Fig. 1(a) (points i and i' coincide, $i = 1, \dots, 5$). Now instead of a ball’s surface we obtain a

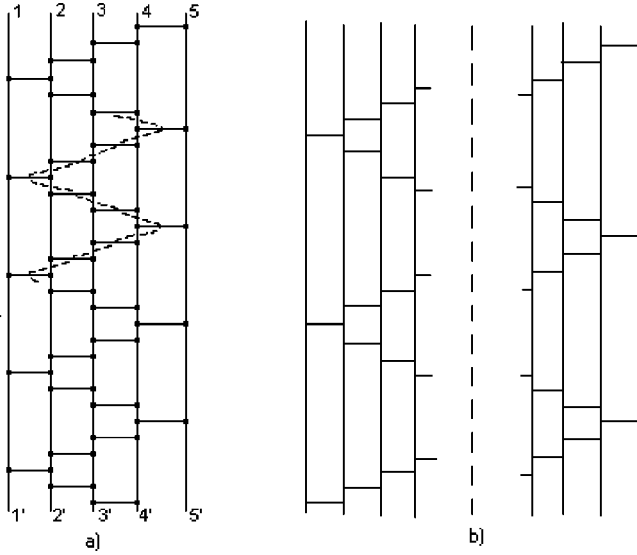


FIG. 1. View of the soccer-ball lattice after topological transformation. Points i and i' coincide for $i=1, \dots, 5$.

cylinder side surface and a finite ‘‘square’’ lattice with true (physical) periodic conditions. Every vertex has three nearest neighbors as initially, and every bond will be covered by a single step of a random walk, according to our assumption. There is an apparent division of vertices into two sets R and L : R set contains the vertices having right nearest neighbors, and L contains the vertices having left nearest neighbors [part of the border between the sets is shown in Fig. 1(a) by the dashed line]. The structure obtained suggests the idea of passing to a similar infinite structure following the same rule [Fig. 1(b)]. This new structure obviously represents a nanotube whose wall atoms are organized in a lattice with the same type of symmetry. One can see that the majority of the polygons in such a lattice are hexagons, which is in agreement with the known structure of carbon nanotubes. In the following calculations we will discuss simultaneously both the finite and the infinite lattices.

The next step is to find an expression for the partition function and calculate it. To have a clearer understanding of the following, see the corresponding chapter in [5]. Let J be the nearest neighbor interaction energy; then the expression for the partition function can be written

$$Z = \sum_{\{\sigma\}} \exp \left\{ -\Theta \left[\sum_{\{k,l \in R\}} (\sigma_{k,l} \sigma_{k,l+1} + \sigma_{k,l} \sigma_{k+1,l}) + \sum_{\{k,l \in L\}} (\sigma_{k,l} \sigma_{k,l+1} + \sigma_{k,l} \sigma_{k+1,l}) \right] \right\} = S(1-x^2)^{-N}, \quad (1)$$

where $\sum_{\{\sigma\}}$ means the summation over all possible configurations, $\Theta = J/2kT$, k is the Boltzmann constant, T is the absolute temperature, the factor $\frac{1}{2}$ is due to the double counting of each pair of vertices while summing over both sets, $x = \tanh \Theta$, and N is the number of vertices. Here we preserve for convenience the notation characteristic of a magnetic system [the obvious correlation between the magnetic

variables $\sigma^{(m,1)} = 1$, $\sigma^{(m,2)} = -1$ and the lattice gas variables $\sigma^{(l,1)} = 0$, $\sigma^{(l,2)} = 1$ is $\sigma^{(l,1)} = \frac{1}{2} (\sigma^{(m,1)} + \sigma^{(m,2)})$, $\sigma^{(l,2)} = \frac{1}{2} (\sigma^{(m,1)} - \sigma^{(m,2)})$]. The expression for S has the form

$$S = \sum_{\{\sigma\}} \left[\prod_{\{k,l \in R\}} (1 + x \sigma_{k,l} \sigma_{k,l+1}) (1 + x \sigma_{k,l} \sigma_{k+1,l}) \times \prod_{\{k,l \in L\}} (1 + x \sigma_{k,l} \sigma_{k,l+1}) (1 + x \sigma_{k,l} \sigma_{k+1,l}) \right]. \quad (2)$$

To calculate the polynomial in Eq. (2), a diagram technique developed by Vdovichenko and discussed in [5] can be used. If x corresponds to a bond between two neighbor vertices, the polynomial will correspond to the number of loops.

Remark 1. It is important to emphasize that this technique is designed in such a way that the loops containing the superposed bonds vanish. That is why this technique remains valid for the case of the finite lattice discussed here. (This also means that the same technique will apply for various nanotubes of the same symmetry type.) Notice also that the summation over k and l here is different from what it is in the case of an infinite planar lattice. Equations (1) and (2) give the exact value of the partition function.

With regard to Remark 1, the result of the calculation can be written

$$S = \exp \left(- \sum_{r=1}^{\infty} x^r f_r \right), \quad (3)$$

where f_r stands for the sum over single loops of r steps each. Now let us introduce $W_r(k, l, \nu)$ —the sum over all possible paths of r steps starting from the given vertex (k_0, l_0, ν_0) to the vertex (k, l, ν) in such a way that the last step to the vertex (k, l, ν) does not take place from the direction ν [$\nu = 1$ (right), 2 (up), 3 (left), 4 (down)]. According to the obtained symmetry structure (Fig. 1), $\nu = 3$ is forbidden for $(k, l) \in R$, and $\nu = 1$ is forbidden for $(k, l) \in L$. Then, as in [5], we get

$$S = 2^N \exp \left[- \sum_{r=1}^{\infty} \sum_{k_0 l_0 \nu_0} \frac{x^r}{2r} W_r(k_0, l_0, \nu_0) \right]. \quad (4)$$

It is possible to get the recurrence relations between W_{r+1} and W_r from the definition of $W_r(k, l, \nu)$. For R they can be written as

$$W_{r+1}(k, l, 1) = 0 + \exp(i\pi/4) W_r(k+1, l, 2) + 0 + \exp(-i\pi/4) W_r(k-1, l, 4), \quad (5)$$

$$W_{r+1}(k, l, 2) = \exp(-i\pi/4) W_r(k+1, l, 1) + 0 + 0 + W_r(k-1, l, 4),$$

$$W_{r+1}(k, l, 3) = 0 + 0 + 0 + 0,$$

$$W_{r+1}(k, l, 4) = \exp(i\pi/4) W_r(k, l+1, 1) + W_r(k+1, l, 2) + 0 + 0.$$

Similarly, for L we get

$$\begin{aligned}
 W_{r+1}(k,l,1) &= 0+0+0+0, \\
 W_{r+1}(k,l,2) &= 0+0+\exp(i\pi/4)W_r(k,l-1,3)+W_r(k \\
 &\quad -1,l,4), \\
 W_{r+1}(k,l,3) &= 0+\exp(-i\pi/4)W_r(k+1,l,2)+0 \\
 &\quad +\exp(i\pi/4)W_r(k-1,l,4), \\
 W_{r+1}(k,l,4) &= 0+W_r(k+1,l,2) \\
 &\quad +\exp(-i\pi/4)W_r(k,l-1,3)+0.
 \end{aligned} \tag{6}$$

The exponential factors correspond to the turns needed to complete the loops. In a compact form Eqs. (5) and (6) can be expressed as

$$W_{r+1}(k,l,\nu) = \sum_{k',l',\nu'} \Lambda(kl\nu|k'l'\nu') W_r(k',l',\nu'),$$

where the matrix Λ elements can be associated with a ‘‘transition probability’’ per step for a randomly walking point. The probability of having a path of r steps will thus be given by Λ^r . The diagonal elements of this matrix present the probability that the randomly walking point will return to its original position after r steps, and thus

$$\text{Tr}(\Lambda^r) = \sum_{k_0 l_0 \nu_0} W_r(k_0, l_0, \nu_0)$$

and

$$f_r = \frac{1}{2^r} \sum_i \lambda_i^r, \tag{7}$$

where λ_i are the eigenvalues of the matrix. Substituting Eq. (7) into Eq. (3), we get

$$S = 2^N \prod_{i=1}^8 \sqrt{1-x\lambda_i}. \tag{8}$$

Now we come to the direct calculation of the partition function and, consequently, we need the form of the Λ matrix.

Remark 2. In our case there are two sets of vertices and, consequently, there are two systems of equations. This means that the matrix of coefficients must have a Jordan (normal) form.

To diagonalize the matrix Λ with respect to indices k and l , the Fourier transformation is most convenient. Although according to the type of structure presented in Fig. 1 k and l vary in different ways, we will approximate the Fourier transform of Λ by a common expression,

$$W_r(p,q,\nu) = \sum_{k,l} \exp\left(-\frac{2\pi i(pk+ql)}{L}\right) W_r(k,l,\nu),$$

where $L = \sqrt{N}$. Therefore, the matrix of coefficients (i.e., random walk transition probabilities) will have the form

$$\Lambda(p,q,\nu|p',q',\nu') = \begin{pmatrix}
 0 & \alpha\varepsilon^p & 0 & \alpha^{-1}\varepsilon^{-p} & 0 & 0 & 0 & 0 \\
 \alpha^{-1}\varepsilon^{-q} & 0 & 0 & \varepsilon^{-p} & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 \alpha\varepsilon^q & \varepsilon^p & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & \alpha\varepsilon^{-q} & \varepsilon^{-p} \\
 0 & 0 & 0 & 0 & 0 & \alpha^{-1}\varepsilon^p & 0 & \alpha\varepsilon^{-p} \\
 0 & 0 & 0 & 0 & 0 & \varepsilon^p & \alpha^{-1}\varepsilon^{-q} & 0
 \end{pmatrix}$$

where $\alpha = \exp(i\pi/4)$ and $\varepsilon = 2\pi i/L$. For the given p and q a simple calculation gives

$$\begin{aligned}
 \prod_{i=1}^8 (1-x\lambda_i) &= \text{Det}(\delta_{\nu\nu'} - x\Lambda_{\nu\nu'}) = (1-x^2)^2 \\
 &\quad - 2x^2(1-x^2) \left[1 + \cos\frac{2\pi(p-q)}{L} \right. \\
 &\quad \left. + \cos\frac{2\pi(p+q)}{L} \right] + 2x^4 \cos\frac{4\pi p}{L}. \tag{9}
 \end{aligned}$$

Finally, the substitution of Eq. (9) into Eq. (8) and then into Eq. (1) gives the expression for the partition function Z :

$$\begin{aligned}
 Z &= 2^N (1-x^2)^{-N} \prod_{p,q=0}^L \left\{ (1-x^2)^2 - 2x^2(1-x^2) \left[1 \right. \right. \\
 &\quad \left. \left. + \cos\frac{2\pi(p-q)}{L} + \cos\frac{2\pi(p+q)}{L} \right] + 2x^4 \cos\frac{4\pi p}{L} \right\}^{1/2}. \tag{10}
 \end{aligned}$$

This expression is a finite polynomial in the case of an A_{60}

model cluster, but for the infinite structure presented in Fig. 1(b) this polynomial is infinite.

III. DISCUSSION

In order to describe the critical behavior of the system and to find the corresponding characteristics, a calculation of the thermodynamic potential $\Phi = -kT \ln Z$ should be performed. It should be mentioned here that, every time we speak of the exact results or of the critical features of the system's behavior, one should note that in the true sense this can be applied only to nanotubes with infinite length, while for finite-length nanotubes or for A_{60} model clusters the results are approximate.

The logarithm of the product gives the sum. Passing from summation to integration is the next approximation: in the case of the finite A_{60} model cluster lattice, the sum is neither infinite nor even very large, although in the case of an (infinite) nanotube this approximation can lead to an exact result. Proceeding with the calculation, we obtain

$$\begin{aligned} \Phi = & -NkT \ln 2 + NkT \ln(1-x^2) \\ & -NkT \frac{1}{2 \times 2\pi} \int_0^{2\pi} \int_0^{2\pi} \ln\{(1-x^2)^2 - 2x^2(1-x^2) \\ & \times [1 + \cos(\omega_1 - \omega_2) + \cos(\omega_1 + \omega_2)] \\ & + 2x^4 \cos 2\omega_1\} d\omega_1 d\omega_2. \end{aligned} \quad (11)$$

The formation of the soccer-ball structure corresponds to a phase transition, and the Φ function has a singularity at this point. Notice that, when applied to the finite A_{60} model cluster, the last (approximate) expression will not indicate a true singularity but a sharp transition. In our case the singularity corresponds to zero value of the logarithmic expression in the integral in Eq. (11). As a function of ω_1 and ω_2 this expression has a minimum when $\omega_1 = \omega_2 = 0$. If this condition is satisfied, the expression in the logarithm in Eq. (11) is equal to $(1-x^2)^2 - 6x^2(1-x^2) + 2x^4$. The last polynomial is a biquadratic equation with two positive roots

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

The last fact suggests that there are two critical temperatures corresponding to the formation of the soccer-ball structure. Analysis of the integral in Eq. (11) shows that in the vicinity of $(x_c)_2 = 0.39$ the integral is always positive, while in the vicinity of $(x_c)_1 = 0.86$ it can take both signs. The corresponding values of x_c for the square, the triangle, and the honeycomb infinite lattices are [1] 0.44, 0.27, and 0.66. It is interesting to note that a direct numerical calculation [8] of x_c for the soccer-ball structure provides $(x_c)_{\text{num}} = 0.628$, which is equal to $\frac{1}{2} [(x_c)_1 + (x_c)_2]$ of the analytical result obtained here.

Remark 3. Here we would like to underline that the well known result [9] suggests that a phase transition can occur only in an infinite system (the thermodynamic limit). Thus, at first glance it seems doubtful that critical behavior can be

obtained on a lattice with only 60 vertices. The important particular feature of the system under discussion is the true (physical) periodic conditions, which appear to lead to a ‘‘critical’’ behavior in this finite system. As we see from all the arguments and calculations given above, we get the same result for the infinite cluster, and this result does not contradict [9]. But the character of the calculation that leads to the partition function expression is the same. This means that the possibility of critical behavior here is due not to the infinite number of counted loops, but to the fact that the majority of these loops cancel out because of the superposition or intersection of the loops' bonds. Although further calculations based on the expression for the partition function are exact only for the infinite system and are approximate for the finite system, the character of the results must remain the same. A rigorous mathematical treatment of the role of true periodic conditions in the description of the critical behavior of a system constitutes a separate and wider problem.

Now we can get an expansion of the thermodynamic potential Φ in powers of t ($t = T - T_c$), where T_c is a critical temperature related to x_c ($x_c = \tanh J/2kT_c$). The regular part of this expansion can be simply replaced by its value for $t = 0$, while for its singular term we get

$$\int_0^{2\pi} \int_0^{2\pi} \ln(c_1 t + c_2 \omega_1^2 + c_3 \omega_2^2) d\omega_1 d\omega_2,$$

where c_1, c_2, c_3 are constants and $c_1 > 0$. Carrying out the integration, we obtain the singular term of the thermodynamic potential near the transition point in the form

$$\Phi \sim -c_1 t \ln t. \quad (12)$$

The thermodynamic potential appears to be continuous near the transition point, but the heat capacity C becomes infinite and is proportional to t^{-1} ,

$$C \sim \frac{1}{T - T_c}, \quad (13)$$

which differs from the known logarithmic singularity. In a recent paper [10] there is a plot of the heat capacity vs temperature for C_{60} and C_{70} fullerenes, and the text near it reads: ‘‘It is interesting to notice that contrary to the majority of organic substances the fullerenes' heat capacity dependence on temperature has two inflection points.’’ This result based on analysis of experimental data supports the theoretical result obtained here.

In conclusion, we can state the following. In this paper theoretical models of an A_{60} soccer-ball type finite structure and of a similar symmetry type infinite nanotube structure [Fig. 1 (b)] were discussed in the framework of the lattice gas model. To apply the Vdovichenko method for the partition function calculation, the soccer-ball lattice was topologically transformed into a lattice on a side surface of a cylinder. Since the vertices of this lattice fall into two sets, it is essential to present the matrix of coefficients in a Jordan form. After that, the analytical form of the partition function for this model was found directly. In the case of the infinite lattice the expression for the partition function led to exact

results, while for the finite A_{60} clusters these results are approximate. The thermodynamic potential for this model appears to have two critical temperatures, corresponding to the lattice formation. This is in accord with experimental data for the dependence of the fullerenes' heat capacity on temperature [10]. The arithmetic mean of the analytically found critical parameters ($x_c = \tanh J/2kT_c$) coincides with the value of the same critical parameter for a soccer-ball cluster found numerically [8] with the help of a computer. The heat capacity singularity appears to be not logarithmic but inversely proportional to the first power of $T - T_c$.

This model can be used to describe the formation of such physical systems as carbon fullerenes from the gaseous phase, or the formation of $(H_2O)_{60}$ -ice clusters from liquid water, or the formation of other similar clusters consisting of other atoms or molecules able to form a tetrahedrally coordinated network. In addition, this model is applicable for description of the formation not only of the classical

fullerene, but of various nanotubes of similar symmetry also. Strictly speaking, a regular nanotube of a certain type already presents the lattice on a side surface of a cylinder that was discussed above. In the case of long tubes there is no direct contradiction of the statement made in [9], but as we have shown clusters with true (physical) periodic conditions can demonstrate such "critical" behavior also. The expression obtained for the partition function provides the possibility of calculating various thermodynamic parameters of interest.

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