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Quasi-one-dimensional system of molecules inside carbon nanotubes: Exact solution for the lattice gas model and its application to fullerene-filled nanotubes

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The statistical mechanics of a system of molecules encapsulated inside a carbon nanotube was analyzed using a one-dimensional lattice gas model. Both open and closed tubes were studied and both the grand-canonical and the canonical partition functions were evaluated exactly. The formulas for the frequency of occurrence of clusters of various sizes were also derived. The model was applied to a (10,10) nanotube containing C_{60} molecules. The calculations gave detailed information on the clustering of molecules in both open and closed nanotubes. Analysis of the open system yields information on the conditions under which the nanotubes can be filled when they are in equilibrium with an external gas. The results show that an open nanotube can be filled very efficiently at room temperature provided there are enough external fullerenes in the gas phase. For a closed system at room temperature, we found a high degree of clustering that decreases with increasing temperature. Because of the strong interaction between fullerenes, the system is far from its random state even at the highest temperatures studied. For both cases, linear equations of state were determined as well. Obtained results are in accord with the experimental observations.

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I. INTRODUCTION

A system is called quasi-one-dimensional (1D) when its geometry is characterized by one macroscopic and two microscopic spatial dimensions. These conditions are satisfied for molecules moving inside a long narrow cylinder. Recently, this type of cylindrical environment has become experimentally available with the discovery of carbon nanotubes. Quasi-one-dimensional systems provide an opportunity to test 1D models, which are usually much simpler than those formulated in three dimensions. One of the most interesting features of 1D systems with short-range interactions is that they do not possess a phase transition except at $T=0$ K.[1]

Attempts to experimentally observe one-dimensional phenomena using carbon nanotubes have recently met with success. Teizer *et al.*[2] have measured the desorption of ^{4}He from interstitial regions between closed carbon nanotubes in bundles. The data can be understood only when ^{4}He is assumed to be a one-dimensional adsorbate. Predictions based on 2D adsorption underestimate the experimental results by more than five orders of magnitude. Kuznetsova *et al.*[3] have investigated the adsorption of Xe into nanotubes with both closed and open ends. The measured desorption data show that a quasi-one-dimensional confined Xe phase is established inside nanotubes with open ends and this phase desorbs via an equilibrium involving the 2D gas phase on the outer nanotube surface. Also, Smith *et al.*[4] have observed chains of C_{60} molecules (fullerenes) encapsuled in carbon nanotubes using high-resolution transmission electron microscopy (HRTEM). This system is usually called a peapod. Because of the appropriate size of the (10,10) nanotube (which is the most abundant in nanotube samples), this system provides a nearly ideal realization of a one-dimensional system. These experiments have stimulated many Monte Carlo simulation studies on adsorption of simple fluids such as hydrogen, nitrogen, methane, and carbon dioxide into carbon nanotubes.[5–15] These studies analyze the conditions at which nanotubes can be filled and estimate the adsorption capacity of carbon nanotubes for various species. However, the important question of dimensionality is not addressed in these studies.

The importance of this topic was recognized by the group led by Cole from Pennsylvania State University. Their intensive research activity[16–24] presents a great contribution to the understanding of the behavior of quasi-one-dimensional systems of molecules confined inside a carbon nanotube. Their studies, which focused on rare gases and hydrogen, revealed that the effective dimensionality depends not only on molecular size relative to the nanotube radius but also on thermodynamic variables (number of atoms and temperature) and geometry (isolated tubes or ordered arrays of tubes). The full quantum-mechanical treatment of one-dimensional ^{4}He was recently investigated by Krotscheck and Miller.[25,26]

In all these theoretical studies, little attention has been paid to the clustering of adsorbed molecules. Also, these studies did not compare the closed system with one interacting with its enviroment. It is reasonable to consider both cases. An example of an open system is the nanotube with open ends or with wall defects. Synthesized nanotubes typically have their ends closed, but various techniques have been developed to open them.[27–29]

In this paper, we use the lattice gas model to study 1D systems of molecules adsorbed inside a nanotube. This is a simple model in which molecules are attached to lattice sites and move around on the vertices of the lattice. Confining the particles to a lattice in this way makes the model considerably simpler to deal with than a true gas model in which molecules can take any position in space, although it makes the model somewhat less realistic. However, lattice gases give a good deal of insight into the general behavior of real gases. This model has proven useful to study various physi-

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cal phenomena such as diffusion, adsorption, interfaces, phase transformations, equilibrium crystal shapes, and even fragmentation in heavy ion collisions. Young and Lee[30] have shown that the grand-canonical ensemble in the lattice gas model is equivalent to an Ising model. Using this, the grand-canonical ensemble can be solved by mapping onto the Ising model, which is exactly solvable in one dimension. This procedure, however, does not work for the case of the canonical ensemble, which corresponds to the Ising model with fixed magnetization, known as the Kawasaki model.[31] Because of the restriction on the number of molecules (fixed magnetization), this model is more difficult to solve than the Ising model.

In this paper, we present an exact solution for both canonical and grand-canonical lattice gas models for a 1D array of molecules of arbitrary linear density. We also derive formulas for the frequency of occurrence of clusters of various sizes. The 1D lattice gas model is then applied to a system of C_{60} molecules inside a (10,10) nanotube. The recent theoretical treatment of interactions between fullerenes and nanotubes[32] shows that the C_{60} molecule is in a deep potential well at the center of a (10,10) tube and its motion perpendicular to the tube axis is highly restricted. This means that this system is quasi-one-dimensional. Since HRTEM images[4,33] provide information on the arrangement of C_{60} molecules, the computed distribution of fullerenes can be compared to experiment. The frequency of occurrence of molecular clusters of various sizes is computed for both open and closed nanotubes as a function of linear density and temperature. The linear equation of state is obtained, and for open tubes, the efficiency of filling is also computed as a function of temperature and pressure.

II. THE MODEL

A. Canonical ensemble—The cluster method

In our lattice gas model, we divide a nanotube into a chain of L lattice sites such that each lattice site can be either empty or occupied by one molecule. A site is characterized by the occupation number e_j, which is either 1 if the jth site is occupied or 0 if the jth site is empty. Only nearest-neighbor (NN) interactions are considered, so that the potential energy of the closed system is

$$H=-\epsilon\sum_{\text{NN pairs}} e_i e_j\,, \tag{1}$$

where $-\epsilon$ is the energy of interaction of a nearest-neighbor pair and the sum is over all nearest-neighbor pairs. The corresponding partition function Z is

$$Z(L,N,T)=\sum_{\sum_j e_j=N} e^{\beta\epsilon(e_1e_2+e_2e_3+\cdots)}, \tag{2}$$

where $\beta=(k_BT)^{-1}$, k_B being the Boltzmann constant, and the sum is taken over all states with a total number of molecules equal to N. To evaluate it, we use the cluster method[34] developed by Vavro, which is based on the fact that because of nearest-neighbor interactions, the energy depends only on the number of clusters (a cluster is defined as an array of sites in which all sites are occupied and the sites adjacent to the chain ends are either empty or are at a tube end). Then the sum over states can be replaced by the sum over all possible numbers of clusters, that is,

$$Z(L,N,T)=\sum_{k=1}^{\min(L-N+1,N)} Z_{\text{cl}}(L,N,k,T)e^{\beta\epsilon(N-k)}, \tag{3}$$

where k denotes the number of clusters, $\min(L-N+1,N)$ gives the maximum number of clusters that N molecules can form in L sites, which is the minimum of $L-N+1$ and N, and $Z_{\text{cl}}(L,N,k)$ gives the partition function for the system of length L with N molecules arranged into k clusters. We will consider the case in which the molecules in the first and the last site interact with the system's boundaries. This corresponds to the nanotube with capped ends. Binding energies for these interactions are denoted as ϵ_L (first site) and ϵ_R (last site). Obviously, taking both these energies to be zero yields the case of free ends. Three separate cases have to be considered: both sites 1 and L are occupied, one of the sites is occupied, and both sites are empty. Accordingly, $Z_{\text{cl}}(L,N,k,T)$ is written as the sum of three parts,

$$\begin{aligned}Z_{\text{cl}}(L,N,k,T)=&W_2(L,N,k,T)e^{\beta(\epsilon_L+\epsilon_R)}+W_1(L,N,k,T)\\&\times(e^{\beta\epsilon_L}+e^{\beta\epsilon_R})+W_0(L,N,k,T),\end{aligned} \tag{4}$$

where $W_i(L,N,k,T)$ $(i=0,1,2)$ gives the number of states in which N molecules are arranged into k clusters in L sites with i clusters attached to the ends of the system. These numbers have to account for two things: the number of ways to arrange molecules into a given number of clusters and the number of ways to arrange clusters of given lengths into the available sites. The first number is given by the binomial coefficient $\binom{N-1}{k-1}$ for N molecules in k clusters. To calculate the latter, we realize that arranging k clusters with given lengths into L sites is equivalent to arranging $L-N$ vacant sites into k' clusters. This number has three possible values: $k-1$, k, and $k+1$, so that the number of possible arrangements is found to be $\binom{L-N-1}{k'-1}$. Obviously, considering $W_i(L,N,k,T)$ (i clusters attached to the ends), $k'=k+1-i$, and so

$$W_i(L,N,k,T)=\binom{N-1}{k-1}\binom{L-N-1}{k-i} \tag{5}$$

for $i=0,1,2$. Here we take any binomial coefficient equal to zero whenever any of its arguments is negative. Also, we define $W_2(L,L,k,T)=1$. These assumptions allow the same expression to be used for special cases such as $L=N$ or $L=0$. Equation (3) in conjunction with Eqs. (4) and (5) gives the partition function.

The Helmholtz free energy F is given by

$$F=-k_BT\ln Z(L,N,T). \tag{6}$$

From the free energy, any thermodynamic quantity of interest can be computed.

To evaluate the probability $P_p(L,N,x)$ that a cluster has a length x, let us first find the total number of clusters with the length x, when N molecules are distributed into k clusters. Using the same ideas as before, we find this number to be

$$W_p(L,N,k,k',x,T)=k\binom{N-x-1}{k-2}\binom{L-N-1}{k'-1} \tag{7}$$

for $k\geqslant 2$ and for $k=1$,

$$W_p(L,N,1,k',x,T)=\delta_{N,x}\binom{L-N-1}{k'-1}+\delta_{L,N}, \tag{8}$$

$\delta_{x,y}$ being the Kronecker delta defined as 1 for $x=y$ and 0 otherwise. Summing over all possible numbers of clusters and expressing $W_p(L,N,k,k',x)$ in terms of the partition function $Z(L,N,T)$, the probability can then be expressed as follows:

$$\begin{aligned}P_p(L,N,x,T)=\frac{1}{Z_p(L,N,T)}\Bigg[&Z_{\mathrm{cl}}(L,N,1,T)\,\delta_{N,x}e^{-\beta\epsilon}\\&+\sum_{k=2}^{\min(L-N+1,N)}kZ_{\mathrm{cl}}(L,N,k,T)\binom{N-x-1}{k-2}\\&\times\binom{N-1}{k-1}^{-1}e^{-\beta\epsilon k}\Bigg],\end{aligned} \tag{9}$$

where $Z_p(L,N,T)$ is the normalization factor needed to satisfy $\Sigma_{x=1}^{N}P_p(L,N,x,T)=1$. The mean size of the cluster is then

$$\langle x\rangle=\sum_{x=1}^{N}P_p(L,N,x,T)x \tag{10}$$

and the mean number of all clusters is

$$\langle k\rangle=\frac{N}{\langle x\rangle}. \tag{11}$$

Now the mean number of clusters of various sizes can be written as

$$n(x)=P_p(L,N,x,T)\langle k\rangle. \tag{12}$$

The sum in the partition function (3) can be evaluated in terms of the hypergeometric function ${}_2F_1(a,b;c;z)=\Sigma_{n=0}^{\infty}[(a)_n(b)_n/(c)_n n!]z^n$, where $(a)_n=a(a+1)\cdots(a+n-1)$ and $(a)_0=1$, $a\neq 0$. For the case of open ends, the partition function then reads

$$Z(L,N,T)=e^{\beta\epsilon N}(L-N+1)\,\frac{{}_2F_1(1-N,-L+N;2;e^{-\beta\epsilon})}{e^{\beta\epsilon}}. \tag{13}$$

B. Grand-canonical ensemble

The partition function for the grand-canonical ensemble can easily be written from the canonical partition function as

$$Q_L=1+\sum_{N=1}^{L}Z(L,N,T)e^{\beta N(\epsilon_0+\mu)}, \tag{14}$$

where ϵ_0 is the binding energy of a molecule to a site and μ is the chemical potential.

The grand-canonical case with free ends can be solved more efficiently when the transfer matrix method is used. Let us write the grand-canonical partition function as the sum over all possible values of occupational numbers $\{e_n\}$,

$$Q_L=\sum_{\{e_n\}}e^{\beta\epsilon(e_1e_2+e_2e_3+\cdots)}e^{\beta(\epsilon_0+\mu)(e_1+e_2+\cdots)}. \tag{15}$$

To evaluate this partition function, we define the quantities $Z_k(0)$ and $Z_k(1)$ that give the grand partition function for the system of k sites in which the last site is empty $[Z_k(0)]$ or occupied $[Z_k(1)]$. Let us compute these quantities for the one-site system,

$$Z_1(0)=1 \quad\text{and}\quad Z_1(1)=e^b. \tag{16}$$

Here we have defined $a=\beta\epsilon$ and $b=\beta(\epsilon_0+\mu)$. For the two-site system,

$$Z_2(0)=\sum_{e_1=0,1,e_2=0}e^{a(e_1e_2)}e^{b(e_1+e_2)}=\sum_{e_1=0,1}e^{be_1}=1+e^b, \tag{17}$$

$$\begin{aligned}Z_2(1)=\sum_{e_1=0,1,e_2=1}e^{a(e_1e_2)}e^{b(e_1+e_2)}=\sum_{e_1=0,1}e^{ae_1}e^{be_1+1}\\=e^b+e^ae^{2b}.\end{aligned} \tag{18}$$

We can write this as

$$\begin{pmatrix}Z_2(1)\\Z_2(0)\end{pmatrix}=\begin{pmatrix}e^ae^b & e^b\\1 & 1\end{pmatrix}\begin{pmatrix}Z_1(1)\\Z_1(0)\end{pmatrix}. \tag{19}$$

This relation holds for any Z_L,Z_{L-1}, and so for a system of L sites

$$\begin{pmatrix}Z_L(1)\\Z_L(0)\end{pmatrix}=\begin{pmatrix}e^ae^b & e^b\\1 & 1\end{pmatrix}^{L-1}\begin{pmatrix}Z_1(1)\\Z_1(0)\end{pmatrix}. \tag{20}$$

Obviously, the total grand parttion function is

$$Q_L=Z_L(1)+Z_L(0). \tag{21}$$

Expanding the vector $\binom{Z_1(1)}{Z_1(0)}$ into eigenvectors of the matrix in Eq. (20), the grand partition function can be written as

$$\begin{aligned}Q_L&=Z_L(1)+Z_L(0)\\&=\lambda_1^{L-1}\left[a_1x_{11}+a_1x_{12}+\left(\frac{\lambda_2}{\lambda_1}\right)^{L-1}(a_2x_{21}+a_2x_{22})\right],\end{aligned} \tag{22}$$

where a_1,a_2 are constants and x_{11}, x_{12}, x_{21}, x_{22} are the components of the eigenvectors $\vec{x}_1$ and $\vec{x}_2$ corresponding to the eigenvalues λ_1 and λ_2 $(\lambda_1>\lambda_2)$. The eigenvalues and eigenvectors are found to be

$$\lambda_{1,2}=\frac{e^{a+b}+1\pm\sqrt{(e^{a+b}-1)^2+4e^b}}{2}, \tag{23}$$

$$\vec{x}_1=\begin{pmatrix}\lambda_1-1\\ 1\end{pmatrix},\quad \vec{x}_2=\begin{pmatrix}\lambda_2-1\\ 1\end{pmatrix}. \tag{24}$$

The constants a_1 and a_2 are

$$a_1=\frac{e^b-\lambda_2+1}{\lambda_1-\lambda_2},\quad a_2=\frac{\lambda_1-e^b-1}{\lambda_1-\lambda_2}. \tag{25}$$

Equation (22) in conjunction with Eqs. (23), (24), and (25) gives the exact expression for the grand partition function. For large L, the third and fourth term in Eq. (22) can be neglected so that the partition function reads

$$Q_L=\lambda_1^{L-1}(a_1x_{11}+a_1x_{12}) \tag{26}$$

and the thermodynamic potential $\Omega=-kT\ln Q$ is

$$\Omega=-kT(L-1)\ln\lambda_1. \tag{27}$$

To get the probability that a given site is occupied, we first write the probability that a given site is empty. This is easy to get, since when a site is empty, the tube can be described as two independent noninteracting tubes. That is, when l_1 is the position of an empty site from the left, the grand partition function is $Q_{l_1-1}\times Q_{L-l_1}$. Then the probability that this site is empty is

$$p_{\text{empty}}=\frac{Q_{l_1-1}Q_{L-l_1}}{Q_L}. \tag{28}$$

Here and below we assume $Q_l=1$ for any $l\leqslant 0$. The probability that the site is occupied is $1-p_{\text{empty}}$.

To get the probability of occurrence of clusters, let us note that a cluster effectively gives three noninteracting tubes. For the molecules inside the cluster of length x, the partition function is $e^{a(x-1)}e^{xb}$. Multiplying the partition functions for configurations outside the cluster gives

$$Q(l_1,x)=Q_{l_1-2}e^{a(x-1)}e^{bx}Q_{L-l_1-x}, \tag{29}$$

here we assume that the first occupied site in the cluster starts at position l_1. Then the probability that a cluster of n molecules occurs at given sites is

$$p(l_1,x)=\frac{Q_{l_1-2}e^{a(x-1)}e^{bn}Q_{L-l_1-x}}{Q_L}. \tag{30}$$

Using this probability, the mean number of clusters of various sizes is

$$n(x)=\sum_{l_1=1}^{L-x+1}p(l_1,x). \tag{31}$$

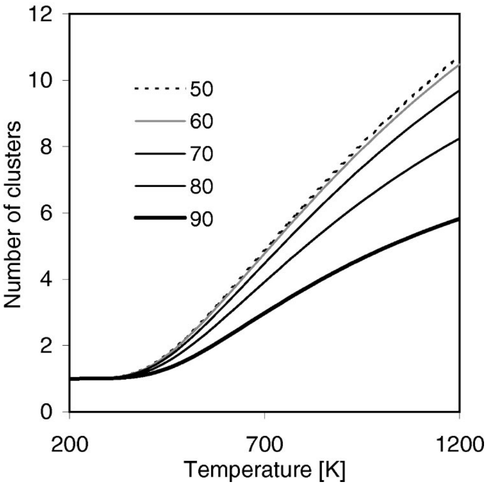

FIG. 1. The mean number of clusters vs temperature for 90, 80, 70, 60, and 50 C_{60} molecules in 100 sites (from bottom to top).

III. APPLICATION OF THE MODEL TO THE PEAPODS: CLOSED SYSTEM

For C_{60} molecules inside a (10,10) nanotube, the interaction energy ϵ is 0.278 eV,[35] whereas the binding energy to the nanotube ϵ_0 is 3.26 eV.[32]

Two types of boundary conditions are applied: free ends and spherically capped ends. The number of sites in the nanotube is taken to be 100. Using a higher number of sites does not affect results for given linear density N/L significantly. The number of internal molecules studied ranges from 50 to 90 in steps of 10. An important thing to note is that the system with $L-N$ molecules behaves just like the one with N molecules. The reason for this is the fact that the energy depends only on the number of clusters the system forms and this number is the same for both N and $L-N$ molecules in L sites.

For the free ends, the total number of clusters in the system as a function of temperature is displayed in Fig. 1. For temperatures up to 300 K, the system is frozen and all molecules form one cluster. As the temperature is increased, the number of clusters rises rapidly, depending on the linear density. The typical distribution of clusters of various sizes is shown for 80 fullerenes at temperatures 300 K, 600 K, and 1000 K in Fig. 2. At room temperature, the system is an almost perfect 1D solid. The different behavior for the single cluster is a consequence of the fact that the state at which all molecules form a single cluster has a different entropy than all the others. As the temperature is increased, smaller clusters start to form and the single large cluster gradually disappears. Figure 3 shows the decay of the probability of occurrence of the single cluster for all studied linear densities as a function of temperature. Clearly, there is no phase transition. The decreasing occurrence of the single cluster can be described as a ‘‘quasimelting’’ taking place over an extended temperature change. As expected, the rate of quasimelting is lower the higher the linear density is (for $N\geqslant L/2$), and at 1000 K the single cluster disappears even for the highest linear density.

The approach of the system to a quasigas state can be

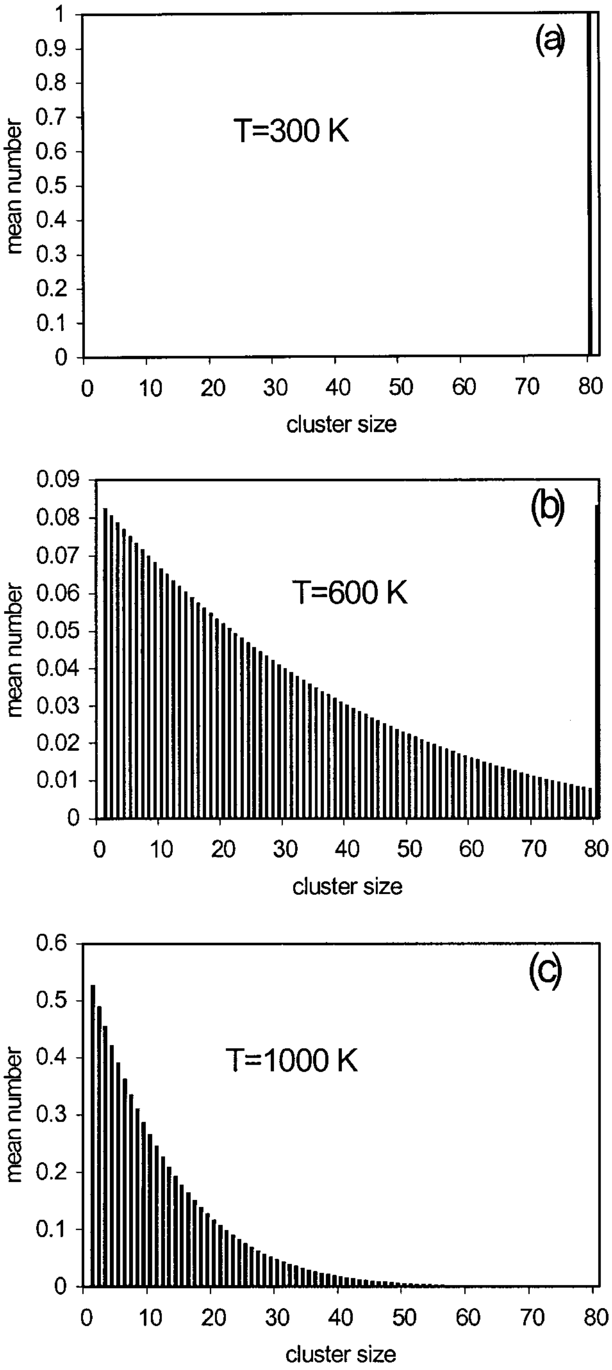

FIG. 2. Mean numbers of clusters of various sizes for 80 C_{60} molecules inside a (10,10) nanotube with 100 sites for temperatures (a) 300 K, (b) 600 K, and (c) 1000 K.

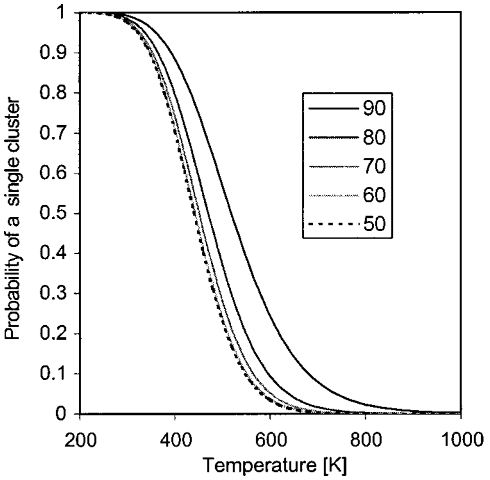

FIG. 3. Probability of occurrence of a single cluster as a function of temperature computed for 90, 80, 70, 60, and 50 C_{60} molecules in 100 sites (from top to bottom).

determined by comparing the properties of the system to those at very high temperature. This can be easily obtained, since at high temperatures the binding energy is negligible compared to the thermal energy and so one can simply use zeros for binding energies in the derived formulas to determine the high-temperature behavior. Computing the mean number of clusters for the high-temperature regime, we find that the system is far from the random state even at 1200 K, the highest temperature studied here, since the system forms about twice as many clusters at the high-temperature regime: 25.5 clusters for $N/L=0.5$ and 9.9 clusters for $N/L=0.9$.

Figure 4 shows the mean potential energy E normalized to the potential energy of the largest cluster E_0 as a function of temperature. As the temperature is increased, the single cluster decays, smaller clusters are formed, and subsequently the number of pair interactions decreases. Figure 5 displays the heat capacity as a function of temperature. As shown before, the number of clusters increases with temperature and the peak in the plot corresponds to the highest rate of cluster formation. Note that the position of the maximum is rather insensitive to the linear density.

The cluster distribution is dramatically changed when capped ends are used as boundary conditions. The binding energy of the fullerene to the hemisphere at the end of the tube is 1.14 eV.[32] This energy is more than four times higher than that between two fullerenes. Therefore, the energetically most favorable state is that in which the molecules form two clusters attached to the ends of the nanotube. Figure 6 shows

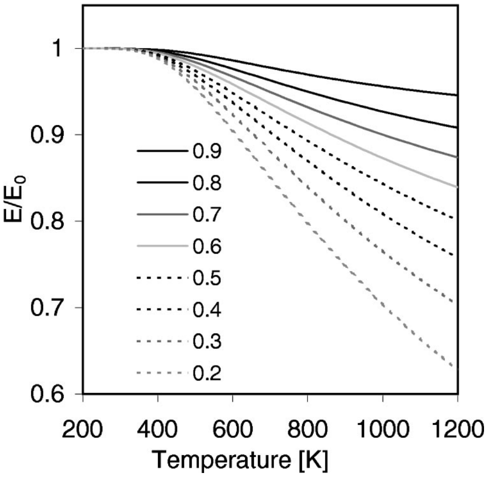

FIG. 4. Mean potential energy as a function of temperature for different linear densities N/L. E_0 is the potential energy at 0 K.

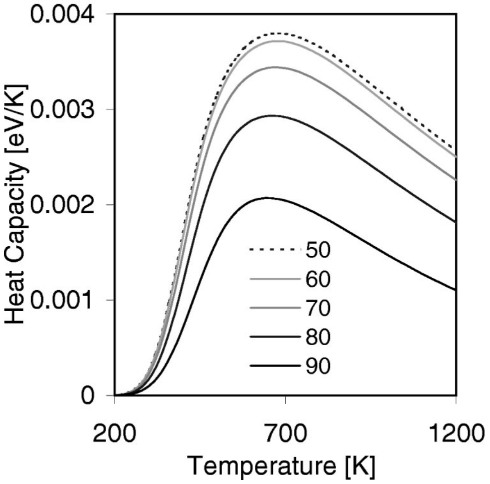

FIG. 5. Heat capacity vs temperature for 90, 80, 70, 60, and 50 C_{60} molecules in 100 sites (from bottom to top).

the cluster distributions for 300 K, 500 K, and 1000 K. At 300 K, the system forms two clusters attached to the nanotube ends. Because of the nearest-neighbor interactions between C_{60} molecules, the system is frustrated at this state, since its energy is the same for all possible cluster sizes. As a result, all clusters (except the one that contains all molecules) are observed with equal frequency. As the temperature is increased, this feature gradually disappears and at about 600 K the cluster distribution shape is similar to that with free ends, with the mean numbers of small clusters being slightly higher. The difference persists as the temperature is further increased up to 1000 K. This comes from the high binding energy to a cap, which is significant even at high temperatures; we find that for all studied temperatures the probability that a site next to the cap is occupied is close to 100%.

The ''quasimelting'' phenomenon in this case can be studied in terms of the probability of finding two clusters in the system. Plotting this quantity with respect to temperature for different linear densities, we get very nearly the same plot as for the melting in the free ends case (Fig. 3). Also, other characteristics of this system give the same behavior compared to the free ends case: the heat capacity as a function of temperature yields the same plot as for the free ends case (Fig. 5). Plotting E/E_0 for different densities as a function of temperature gives a slightly different plot (not shown), but the difference comes from using a different normalization constant (E_0, the energy at 0 K, is different for free and capped ends) whereas the actual behavior of the system is the same.

The mean number of clusters is shown in Fig. 7. Note that the only notable difference from Fig. 1 is that for temperatures up to 300 K, two clusters are formed instead of one.

IV. APPLICATION OF THE MODEL TO PEAPODS: OPEN SYSTEM

For an open system, the properties are controlled by values of the chemical potential μ and temperature T. In this section, all the results we report were obtained by the matrix method. The exact expression for the grand partition function given by Eq. (22) is used. In fact, both cluster and matrix methods could be used, but the latter method is more useful, since the derived formulas are simpler and require less computational effort.

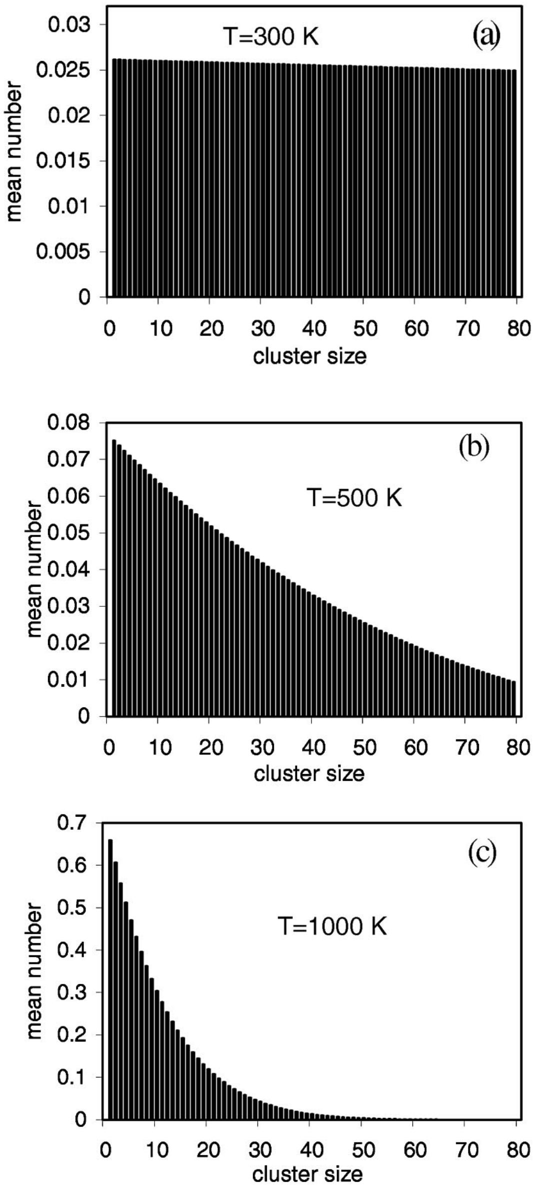

FIG. 6. Mean number of clusters of various sizes for 80 C_{60} molecules inside a spherically capped nanotube with 100 sites for temperatures (a) 300 K, (b) 500 K, and (c) 1000 K.

It is of importance to compare the results obtained for open and closed systems. The major difference between the two systems comes from the fact that the number of molecules is fixed in the closed system, whereas it is given by the distribution of probabilities of having various numbers of molecules in the open system. In general, quantities that depend linearly on the number of molecules in the system give the same results for both cases. This can be shown as follows: Let us consider a quantity G, linear in N:$G(N) = CN$, C being a constant and the probability distribution P_N. Let us choose any number of molecules N^* and any

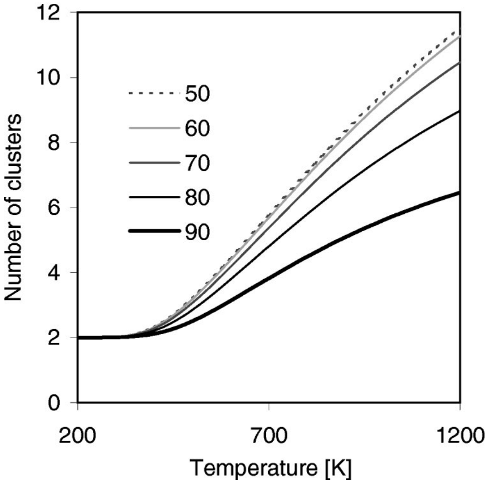

FIG. 7. The mean number of clusters vs temperature for 90, 80, 70, 60, and 50 C_{60} molecules inside a spherically capped nanotube with 100 sites (from bottom to top).

distribution P_N, for which $\langle N\rangle = N^*$, and let us compare the values for the quantity G in the open and closed systems. For the closed system,

$$G(N^*) = CN^*. \tag{32}$$

For the open system,

$$\langle G(N)\rangle = \sum_N G(N)P_N = C\sum_N NP_N = CN^*, \tag{33}$$

which is the same as for the closed system. Clearly, this is not true for nonlinear dependent quantities.

For our system, the probability distribution function P_N is given as

$$P_N = \frac{Z(L,N)e^{\beta N(\epsilon_0+\mu)}}{Q_L}. \tag{34}$$

Clearly, P_N is a nonlinear function of N, so we expect some differences in the behavior of closed and open systems. This can be demonstrated by computing the equation of state, which relates one-dimensional pressure to the temperature and linear density. The one-dimensional pressure is a force acting in the linear array of molecules, and for the grand-canonical ensemble it is given as

$$p_{1\mathrm{D}} = -\left(\frac{\partial \Omega}{\partial L}\right)_{T,\mu}. \tag{35}$$

In the case of the canonical ensemble, pressure can be determined by using a similar expression replacing Ω by the free energy F,

$$p_{1\mathrm{D}} = -\left(\frac{\partial F}{\partial L}\right)_{T}. \tag{36}$$

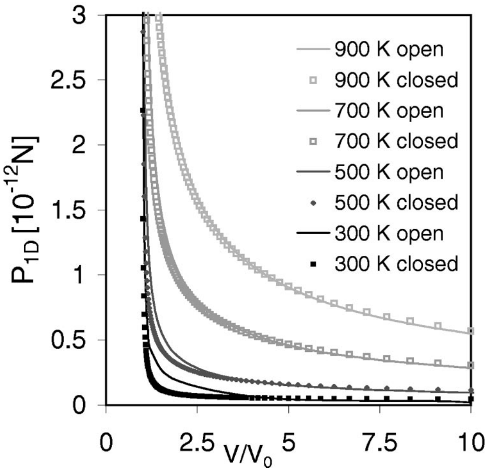

FIG. 8. The equation of state for C_{60} molecules inside a (10,10) nanotube for temperatures 300 K, 500 K, 700 K, and 900 K (from bottom to top) for both open (lines) and closed (points) systems.

The results are shown in Fig. 8, in which the force (linear pressure) is plotted against the 1D ''volume'' $V = Ld$, in units of $V_0 = \langle N\rangle d$ (for closed systems we use $V_0 = Nd$), $d = 10.05$ Å being the length of one site, so that V/V_0 gives the reciprocal linear density L/N. The lines correspond to the open system, whereas the equation of state for the closed system is displayed as points. Note that the differences between the two cases are significant at low temperatures, while at high temperatures the behavior of the two systems is very close. As expected, the transition from the high to low compressibility regime is more rapid at lower temperatures as the system goes from a gaslike to a solidlike state, although there is no phase transition.

Similarly, for clustering in terms of the mean numbers of clusters of various sizes, we find different results for the two cases at low temperatures, while at high temperatures the clustering in the open system reproduces that of the closed system well.

From the mean number of molecules inside the nanotube,

$$\langle N\rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,L}, \tag{37}$$

the filling fraction $\langle N\rangle/L$ can be determined as a function of T and μ. It is found that filling varies from 0 to complete for chemical potentials in the range $-3.8\ \mathrm{eV} \leqslant \mu \leqslant -3.3$ eV for all temperatures studied. Using the expression for the chemical potential of an ideal gas,

$$\mu = -kT\ln\left(\frac{(2\pi mkT)^{3/2}}{h^3}\frac{kT}{p}\right), \tag{38}$$

we can express the fractional filling as a function of temperature T and outside pressure p. This is displayed in Fig. 9. The efficiency of filling depends on temperature, and as it is decreased the curves approach a step function. p_0 are the values of the pressure at which the filling of the nanotube is 50% complete for a given temperature. These values are found to be extremely small: p_0 at 300 K is of the order of 10^{-46} Pa. These values increase with increasing temperature, but they remain extremely low unless the filling occurs at high temperatures: $p_0 = 3.0\times 10^{-3}$ Pa for 1000 K. This

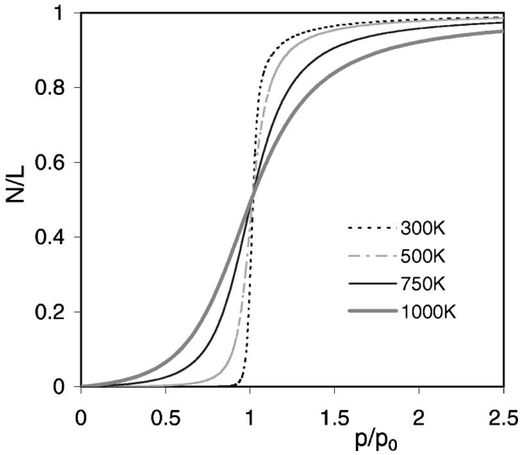

FIG. 9. Adsorption isotherms for an open nanotube for temperatures 300 K, 500 K, 750 K, and 1000 K.

means that, unless the filling takes place at high temperatures, an efficiency of almost 100% is expected. We have also investigated the effect of caps, which would correspond to filling nanotubes through wall defects, while the encapsulated ends are intact. We have found that neither of the two possible cases (caps on both ends or one cap and an open end on the other side of the nanotube) influences equilibrium filling substantially. The differences are well below 1%.

V. COMPARISON TO EXPERIMENTAL OBSERVATIONS

To prepare peapods experimentally, the sample containing closed nanotubes is annealed, typically for 2 h.[33] During the annealing process, the C_{60} molecules diffuse into nanotubes through wall defects and opened ends. Since they are allowed to diffuse only for a relatively short time, it is not likely that the whole system has reached its equilibrium state. Observation shows that many nanotubes are almost fully filled with C_{60}.[33] It is reasonable to expect that the equilibrium filling will be even higher, which agrees well with results of our calculations, from which almost 100% filling is expected at the experimental conditions.

For the clustering of fullerenes, it is important to note that all the experimental observations were made at room temperature. At these conditions no mobile external C_{60} molecules were detected [the mobility is only observed for temperatures exceeding 325 °C (Ref. 33)], so one can expect that the system behaves as closed and that clustering will be comparable to that of the closed system (which can be expected to reach equilibrium easier than the total system). The HRTEM observations show that the internal molecules prefer to form a single cluster,[36] which is in accord with our results.

VI. CONCLUSIONS

We have applied the lattice gas model with nearest-neighbor interactions to a quasi-one-dimensional system of molecules encapsulated inside a carbon nanotube. We have found an exact solution for both open and closed systems. The model was applied to the system of C_{60} molecules inside a (10,10) nanotube. We have computed the clustering of C_{60} molecules as a function of temperature for different linear densities of the internal molecules. We have found that C_{60} molecules form an almost perfect one-dimensional solid at room temperature. As the temperature is increased, quasimelting takes place over an extended temperature range, which depends on linear density. The effect of caps on clustering was also investigated. At low temperatures, the system was found to be in a frustrated state as two clusters attached to nanotube ends are formed. The clustering distribution approaches that for free ends with rising temperature. For the open system, we have computed the adsorption isotherms for different temperatures and found that nanotubes can be filled with C_{60} molecules very efficiently at room temperature. Differences between open and closed systems have also been studied. We have found differences between the two systems at low temperatures, while their behavior is close at high temperatures. Obtained results were compared with HRTM observations and showed good agreement.

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