Exact solution for the lattice gas model in one dimension

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A simple method to obtain a canonical partition function for a one-dimensional lattice gas model is presented. The simplification is based upon rewriting a sum over all possible configurations as a sum over all possible numbers of clusters in the system.

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I. CANONICAL ENSEMBLE

The behavior of a canonical ensemble is fully described by its canonical partition function. In the case of the lattice gas model the partition function can be written in the form

$$Z(L,N,\beta)=\sum_{\Sigma_{i=1}^{L} e_i=N,} \exp(-E[\{e_i\}]\beta), \tag{1}$$

where L is the number of sites in the system, N is the number of particles, $\beta=(k_BT)^{-1}$, k_B being the Boltzman constant, $E[\{e_i\}]$ is potential energy of the system, $e_i=1$ if the ith site is occupied, and $e_i=0$ otherwise. The main problem when calculating the canonical partition function is accounting only for states with total number of particles N, that is to calculate degeneracies of the energy levels.

Here I present a method for obtaining the partition function as well as clustering probability for one-dimensional (1D) lattice gas model, assuming that the interaction between molecules is only of nearest-neighbor type and that the binding energy ε_s is constant for each site except for the leftmost site $i=1$ and the rightmost site $i=L$, where the binding energies are equal to $\varepsilon_s+\varepsilon_L$ and $\varepsilon_s+\varepsilon_R$, respectively.

First, it is useful to realize, that in the case of nearest-neighbor interaction, the interaction energy depends only on the number of clusters, and not on their positions or lengths. Then, the problem of finding $Z(L,N,\beta)$ can be formulated as a problem of finding all possible configurations of k clusters. This is a unique property of one-dimensional systems and is based on the fact that the boundary of a 1D cluster always consists of two points. Two- and three-dimensional clusters do not possess this property; the boundary of two or three dimensional clusters depend not only on the cluster size but also on the configuration of particles within the cluster, i.e., the cluster shape.

In the following it will be assumed that $k\geqslant 1$, $L\geqslant N\geqslant 1$. It is suitable for further calculations to introduce a function $F(k,n)$, which counts the number of ways in which k integer numbers $a_i\geqslant 1$, $i=1,\ldots,k$ can be chosen such that $\Sigma_{i=1}^{k}a_i=n$. Thus, it is possible to write

$$F(k,n)=\sum_{\Sigma_{i=1}^{k} a_i=n} 1=\sum_{m=1}^{n-k+1} F(k-1,n-m). \tag{2}$$

This recurrent formula gives

$$F(k,n)=\begin{cases}\binom{n-1}{k-1} & \text{if} \quad k\geqslant 1\wedge n\geqslant k\\ 0 & \text{otherwise.}\end{cases} \tag{3}$$

Thus, the number of ways to distribute N particles among k clusters is given by $F(k,N)$ and the number of ways to distribute $(L-N)$ empty sites among k clusters is given by $F(k,L-N)$. So that the number of configurations of the system with N occupied sites arranged into k clusters and $(L-N)$ empty sites arranged into k can be expressed as $F(k,N)F(k,L-N)$.

Now it is suitable to express the canonical partition function $Z(L,N,\beta)$ as a sum over number of clusters $k=1,\ldots,k_{max}$, k_{max} being equal to $\min(L-N+1,N)$

$$Z(L,N,\beta)=\sum_{k=1}^{k_{max}} Z_{cl}(L,N,k,\beta)\exp[(N-k)\varepsilon\beta], \tag{4}$$

where $Z_{cl}(L,N,k,\beta)$ is the partition function for a system of length L with N particles in k clusters and k_{max} gives the maximum number of clusters the system can contain.

A. System with interaction between particles and boundaries

To calculate the canonical partition function of the system $Z(L,N,k,\beta)$ in the case of interaction of particles with the boundaries of the system, it is convenient to write the function $Z_{cl}(L,N,k,\beta)$ as a sum of three parts

$$Z_{cl}(L,N,k,\beta)=\sum_{i=0}^{2} W_i(L,N,k)\exp(\mathcal{E}_i\beta), \tag{5}$$

where

$$\mathcal{E}_2=\varepsilon_R+\varepsilon_L,$$

$$\mathcal{E}_1=\beta^{-1}\log[\exp(\varepsilon_R\beta)+\exp(\varepsilon_L\beta)],$$

$$\mathcal{E}_0=0, \tag{6}$$

and $\varepsilon_R(\varepsilon_L)$ is the nearest-neighbor interaction between right (left) end of the system and particle, and $W_i(L,N,k)$, $i=0,1,2$ are the numbers of realizations of system with the length L containing N particles arranged into k clusters and with i clusters attached to the ends of the system.

In the case when sites 1 and L are occupied (two clusters attached to the ends of the system, $i=2$), we have $k'=(k-1)$ clusters of $(L-N)$ empty sites and k clusters of N particles so that we can write

$$W_2(L,N,k)=\delta_{L,N}+F(k,N)F(k-1,L-N), \tag{7}$$

where

$$\delta_{n,m}=\begin{cases}1 & \text{if } n=m\\ 0 & \text{otherwise.}\end{cases} \tag{8}$$

When only one of the sites 1, L is occupied ($i=1$), then $(L-N)$ empty sites are arranged into $k'=k$ clusters and again we have k clusters of N particles and can write

$$W_1(L,N,k)=F(k,N)F(k,L-N). \tag{9}$$

When neither one of the sites 1, $L(i=0)$ is occupied, we are dealing with $k'=(k+1)$ clusters of $(L-N)$ empty sites and k clusters of N particles, so that it is possible to write

$$W_0(L,N,k)=F(k,N)F(k+1,L-N). \tag{10}$$

Thus, using Eq. (4) together with the Eqs. (5), (7), (9), and (10) we can calculate the partition function of the system together with all thermodynamic quantities such as the mean energy of the system $E(L,N,T)$, thermal capacity $C(L,N,T)$, pressure $p(L,N,T)$, and probability $P_{cl}(L,N,\beta,k)$ to find k clusters in the system, which can be written in the form

$$P_{cl}(L,N,\beta,k)=\frac{Z_{cl}(L,N,k,\beta)}{Z(L,N,\beta)}\exp[(N-k)\varepsilon\beta]. \tag{11}$$

To calculate the probability $P_p(N,L,\beta,x)$ to find a cluster of length x, we must start with $W_p(N,L,k,k',x)$, which is the number of clusters of the length x when taking into account all possible configurations of system of length L with N particles arranged into k clusters and with $(L-N)$ empty sites arranged into k' clusters. It can be shown that for $k\geqslant 2$

$$W_p(N,L,k,k',x)=kF(k-1,N-x)F(k',L-N), \tag{12}$$

and for $k=1$ we get

$$W_p(N,L,1,k',x)=\delta_{N,x}(F(k',L-N)+\delta_{L,N}). \tag{13}$$

Using the same arguments and method that were used to calculate $Z(L,N,\beta)$, it is possible to express $P_p(L,N,\beta,x)$ as

$$P_p(L,N,\beta,x)=\frac{1}{Z_p(L,N,\beta)}\Bigg[Z_{cl}(L,N,1,\beta)\,\delta_{N,x}\exp(-\varepsilon\beta)+\sum_{k=2}^{k_{max}}kZ_{cl}(L,N,k,\beta)\frac{F(k-1,N-x)}{F(k,N)}\times\exp(-k\varepsilon\beta)\Bigg]. \tag{14}$$

It is important to point out that $Z_p(L,N,\beta)$ and $Z(L,N,\beta)$ are different functions; $Z_p(L,N,\beta)$ is a normalization factor needed to satisfy the condition $\Sigma_{x=1}^{N}P_p(L,N,\beta,x)=1$, while $Z(L,N,\beta)$ is the partition function for the system of L sites containing N particles.

B. Periodic boundary conditions

The calculation of the canonical partition function $Z_{pbc}(L,N,\beta)$ in the case of the periodic boundary conditions is now very straightforward; it is enough to realize that this problem is equivalent to the case of ends interacting with particles with interaction energies $\varepsilon_R=\varepsilon_L=\varepsilon/2$ when both first and last site are occupied and $\varepsilon_R=\varepsilon_L=0$, if one of these sites is empty. It immediately yields the result

$$Z_{pbc}(L,N,\beta)=\sum_{k=1}^{k_{max}}Z_{cl}^{(pbc)}(L,N,k,\beta)\exp[(N-k)\varepsilon\beta], \tag{15}$$

where

$$Z_{cl}^{(pbc)}(L,N,k,\beta)=\delta_{L,N}\exp(\varepsilon\beta)+\frac{L}{k}F(k,L-N)F(k,N). \tag{16}$$

Due to the periodic boundary conditions, the maximum number of clusters k_{max} the system can contain is now equal to $\min(L-N,N)$.

Expression (16) can be easily understood. The first part $\delta_{L,N}\exp(\varepsilon\beta)$ is trivial and represents a special case when $L=N$, i.e., every site is occupied. If $L>N$, then due to the periodic boundary conditions, the number of clusters of particles is equal to the number of clusters of empty sites. Thus, $F(k,N)$ counts the number of ways to arrange N particles into k clusters and $F(k,L-N)$ does the same with $L-N$ empty sites. The factor L arises from the fact that there are L ways to position each arrangement of clusters, and the factor $1/k$ accounts for the fact that with periodic boundary conditions, we do not know which cluster is first—and there are exactly k ways to choose the first.

Calculating the probability $P_{cl}^{(pbc)}(L,N,\beta,k)$ to find k clusters in the system is now easy

$$P_{cl}^{(pbc)}(L,N,\beta,k)=\frac{Z_{cl}^{(pbc)}(L,N,k,\beta)}{Z_{pbc}(L,N,\beta)}\exp[(N-k)\varepsilon\beta], \tag{17}$$

and the probability $P_p^{(pbc)}(L,N,\beta,x)$ to find a cluster of length x can be written in the form

$$P_p^{(pbc)}(L,N,\beta,x)=\frac{\Sigma_{j=0}^{2}W_j^{(pbc)}(L,N,\beta,x)\exp(j\varepsilon\beta)}{Z_p^{(pbc)}(L,N,\beta)}, \tag{18}$$

where $Z_p^{(pbc)}(L,N,\beta)$ is normalization factor such that $\Sigma_{x=1}^{N}P_p^{(pbc)}(L,N,\beta,x)=1$ and W_j, $j=0,1,2$ can be expressed as

$$W_0^{(pbc)}(L,N,\beta,x)=L\Theta(L-N-1)\,\delta_{x,N}+\exp(\varepsilon)\,\delta_{x,L}, \tag{19}$$

$$W_1^{(pbc)}(L,N,\beta,x)=\sum_{k=2}^{k_{max}} kF(k-1,N-x) \times[F(k+1,L-N)+F(k,L-N)] \times\exp(-k\varepsilon\beta), \tag{20}$$

and

$$W_2^{(pbc)}(L,N,\beta,x)=\sum_{k=3}^{k_{max}} F(k-1,L-N) \times[(k-2)F(k-1,N-x)+(x-1) \times F(k-2,N-x)]\exp(-k\varepsilon\beta). \tag{21}$$

II. GRAND-CANONICAL ENSEMBLE

It is now possible to calculate properties of the open system (grand-canonical ensemble) since the grand-canonical partition function can be writen as a sum of canonical partition functions over the number of particles

$$Q(L,\beta,\mu)=1+\sum_{N=1}^{L} Z(L,N,\beta)\exp[N(\varepsilon_s+\mu)\beta],$$

where ε_s is an interaction energy between particle and site (in our 1D system) different from 1,L. However, in the case of the periodic boundary conditions or in the case of the noninteracting boundaries it is simpler to use the transfer-matrix method [1].

III. CONCLUSIONS

A simple method for calculating the properties of open and closed 1D systems with periodic boundary conditions, and with boundaries interacting with particles, was presented. Numerical values can be easily obtained, since the summations over all possible configurations of N particles on L sites were rewritten as summations over $k=1,\ldots,\min(L-N+1,N)$, where $\min(L-N+1,N)$ is the maximum number of clusters in the system, this number being considerably smaller than the number of all possible configurations of the system.

The method employs the fact that the boundary of each cluster consists of two points. This is a unique property of one dimension, so that it is not possible to generalize this method to higher dimensions.

The results can be used in the study of equilibrium properties of quasi-1D clusters. An ideal system on which it is possible to study low-dimensional physics is provided by single-walled carbon nanotubes (SWNT's). These can be filled with various molecules and atoms, and if the radius of a SWNT's is sufficiently small, the motion of trapped particles is confined along the tube axis. What makes SWNT's special is the possibility to open and close the ends of nanotubes [2], providing the opportunity to study both open and closed systems. Recently, the presented method was succesfully used by Hodak and Girifalco [3] for a theoretical study of clustering C_{60} molecules encapsulated in carbon nanotubes. This type of system, also called peapod, was experimentaly observed by Smith *et al.* [4].

Other interesting systems, which can be used to probe the physics of low-dimensional structures and for which the obtained results may be applicable are provided by the interstitial channels in ropes of SWNT's [5,6] and by the grooves on the external surface of the ropes [7], both of which can provide high-energy adsorption sites.

The presented method can also be useful in analysis of the stability of one-dimensional metals, which can be obtained for example by alkali-metal absorption on semiconductor surfaces [8], and in the study of the behavior of classical gases confined in nanopore materials [9] and zeolite materials [5].

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