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Ground-state configurations of the one-dimensional Falicov-Kimball model

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We consider the one-dimensional Falicov-Kimball lattice model as well as a continuum model, where the attractive potential between the electrons and the nuclei is a δ function, with an equal number N of classical "nuclei" and fermion "electrons." We find the exact leading behavior of the ground-state energy as a function of U for $U > U_c$. The error term is rigorously estimated. For fixed N the system forms "atoms" which have an effective repulsion between them. From this we argue that when N becomes infinite the ground-state configurations of the nuclei should be periodic. The low-temperature structure of the model is also discussed.

I. INTRODUCTION

The model discussed in this paper was considered in Refs. 1 and 2 as a mathematical simplification of the Hubbard model. It was introduced again by Falicov and Kimball (FK) in a different physical situation, namely to describe semiconductor-metal transitions[3] and to study ordering in mixed valence systems.[4,13] It can also be considered, as pointed out by Kennedy and Lieb,[5] as an extremely simplified model of real matter consisting of nuclei and electrons. The simplifications are the following. The nuclei are treated as classical particles occupying the sites of a lattice Z^d. The Coulombic repulsion between them is replaced by an on-site hard-core potential, i.e., a lattice site is empty or occupied by at most one nucleus. For the electrons, one retains the quantum kinetic energy, which is in this context just the lattice Laplacian, as well as the Fermi statistics. Apart from the effect of the Fermi statistics, which prevents them from being in the same state, the electrons do not interact. Their Coulombic repulsion is thus partially taken into account by an effective repulsive potential. In the same spirit, the electron-nucleus interaction is modeled by an on-site attractive potential.

Despite the simplifications, the FK model can provide some insight into the problem of the formation of atoms and of crystals in real matter. In particular by tracing out the electron coordinates, one obtains effective interactions between the nuclei, which determine the structure of the system. Indeed, it has been proved, in some cases, that at low temperatures the nuclei arrange themselves on a periodic sublattice of Z^d.[5,6] For this to happen, it is crucial for the electrons to be fermions. Indeed, if they were bosons the nuclei would clump together. In fact, since in this model there is no *a priori* interaction between the nuclei, except for the hard core, the crystallization comes about from the effective potential between nuclei induced by the electrons. This produces an attraction if the wave function of a single electron is localized over several lattice sites. On the other hand, the Fermi statistics act in the opposite direction (unless the density of electrons is much less then the density of nuclei, a case we shall not consider here). In the case of Bose statistics, the effective potential is always attractive, so that the nuclei always clump together.

Let us define the model and fix our notation. For a given configuration of M nuclei in a region Λ of a d-dimensional simple cubic lattice, $\Lambda \subset Z^d$, containing $|\Lambda|$ sites, the single electron Hamiltonian, is given by a $|\Lambda| \times |\Lambda|$ matrix with entries

$$h_{ij}[\{n_k\}] = (-\delta_{|i-j|,1} + 2d\delta_{i,j}) - Un_i\delta_{i,j} , \qquad (1.1)$$

where $i,j \in \Lambda$ denote lattice sites, $n_i = 1,0$ is the occupation number of the nuclei, $\sum_{i\in\Lambda} n_i = M$, and U is the strength of the attractive on-site potential. The hopping constant (related to the inverse mass of the electron) in front of the kinetic-energy term has been set equal to 1. We shall usually take Λ to be a simple cube and consider free or periodic boundary conditions. The ground-state energy of N electrons in the presence of a fixed configuration n_i of nuclei is given by

$$\sum_{k=1}^{N} e_k(\{n_i\}) , \qquad (1.2)$$

where $e_1(\{n_i\}) \le e_2(\{n_i\}) \le \cdots \le e_N(\{n_i\})$ are the lowest N eigenvalues of (1.1). We are interested in the configurations of nuclei which minimize (1.2) under the condition that the number of nuclei is equal to the number of electrons. This neutral case will be the only case considered in this paper.

The half-filled case, where the electronic and nuclear densities are both $\frac{1}{2}$, was first discussed in Refs. 5 and 6, where it was shown that there are two configurations of nuclei minimizing (1.2). These are the two possible chessboard configurations on the cubic lattice (the results also cover more general bipartite lattices). Later it was argued in Ref. 7 that, in the case of a one-dimensional lattice, if the density is p/q, with p and q relative primes, the ground-state configuration has period q, and within

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each period the p nuclei tend to occupy a configuration which is "as homogeneous as possible." It was furthermore conjectured there that this should hold for all U and all densities. A partial proof of the conjecture was given in Ref. 8 for the case $U > U_{\min}(q)$, with a $U_{\min}(q) \rightarrow \infty$, when $q \rightarrow \infty$. In this paper, we derive a formula for the ground-state energy in one dimension and control the error term for $U > U_c$, U_c independent of the density, in a uniform way with respect to the configuration of the nuclei. In particular we show that a finite number of particles on the infinite lattice will form atoms interacting by a repulsive, exponentially decaying, two-body nearest-neighbor potential. Our results thus provide support for the claim of Ref. 7 that the nuclear configuration should be homogeneous for any density, at least as long as $U > U_c$.

The results for the ground state enable us to draw some conclusions about the low-temperature structure of the one-dimensional model. Calling μ_n, μ_e the chemical potentials of the nuclei and electrons, respectively, the grand-canonical partition function, after one traces out the electronic degrees of freedom, has the form

$$\Xi_\Lambda = \sum_{n_k=0,1} \exp\left[\beta\mu_n \sum_k n_k + \operatorname{tr}\ln[1+e^{-\beta(h[\{n_k\}]-\mu_e)}]\right] , \tag{1.3}$$

where $h[\{n_k\}]$ is the single-electron Hamiltonian with matrix elements (1.1). In the $d=1$ case considered here, Λ is just a line segment of length $|\Lambda|$. Expression (1.3) can be viewed as the partition function of a purely classical system of "c particles," the probabilities of configurations of the c particles on the lattice being determined by the complicated weight in the exponent which can be thought of as an effective potential energy depending on the temperature and chemical potential. Our interest is in finding the form of this effective potential in the limit $|\Lambda| \rightarrow \infty$. At the same time, we want to know whether it is meaningful to think of the c particles as either bound atoms (or molecules), i.e., bound states of electrons and nuclei, or as ionized atoms. We argue that if the chemical potentials are such that the system is neutral (equal densities of electrons and nuclei) and the temperature is low enough, then the partition function reduces approximately to that of a lattice gas of atoms interacting with the effective nearest-neighbor potential found in the ground state. At higher temperatures this picture is obviously wrong, but the characterization of the transition (which is presumably not sharp) between low and high temperatures remains an open problem. We note that for dimensions greater than or equal to 2, the same questions are relevant but the analysis will be more complicated because of the additional features of the Ising-like transition, which has been proven to exist for the half-filled case[5,6] and also near half-filling.[9]

The paper is organized as follows. In Sec. II, the main result is formulated and discussed for the FK model. There we also introduce a continuous model which has the same basic features as the FK model. The low-temperature structure is also discussed in this section. In the remainder of the paper we prove our main results. In Sec. III, we derive by the transfer-matrix method a polynomial equation for the eigenvalues of (1.1). This polynomial equation is then related in Sec. IV to the partition function of a classical lattice gas. Since the degree of our polynomial is much larger than the number N of electrons, we have to carefully isolate the roots corresponding to the lowest-N eigenvalues in the sum (1.2). This is the subject of Sec. V, where we also show that sum (1.2) is related to the free energy of the classical lattice gas. Section VI then combines the above results to give the proof of our main formula for the ground-state energy of the FK model.

II. MAIN RESULTS

We consider the Hamiltonian formally defined by (1.1) for an infinite one-dimensional lattice: it acts on wave functions $\psi(i)$, $i \in Z$, such that $\sum_{i\in Z}|\psi(i)|^2$ is finite. For a finite number M of nuclei in a specified configuration $\{n_j\}$, the spectrum of this Hamiltonian on the infinite lattice has the following properties (see Appendix A).

(i) There is a continuous part which spans the interval [0,4].

(ii) For $U > 4$, there are exactly M distinct negative eigenvalues, all located in the interval $[-U, -U+4]$.

Notice that these properties are independent of the configuration of the M nuclei. In the case $M=1$, the energy of the unique bound state (the atom) is

$$E_0 = 2-(U^2+4)^{1/2} , \tag{2.1}$$

while the wave function is given by

$$\psi_0(i) = (\coth|\ln\epsilon|)^{-1/2}\exp(|i|\ln\epsilon) , \tag{2.2}$$

where we have chosen the origin as the position of the nucleus, and the parameter ϵ is related to U by

$$\epsilon = \tfrac{1}{2}[(U^2+4)^{1/2}-U] \text{ or } E_0 = 2-\epsilon-\epsilon^{-1} , \quad 0<\epsilon<1 . \tag{2.3}$$

We now state our main result about the ground-state energy, which, in the case $U>4$, is just the sum of the N negative eigenvalues. It will be denoted by $E((l)_N, N)$ where $(l)_N = \{l_1, \ldots, l_{N-1}\}$ specifies the configuration of the nuclei by the successive distances between them. The distances are labeled from left to right, and l_i is defined as the number of empty sites between the ith and $(i+1)$th occupied sites.

Theorem 1

There exists a $U_c > 4$ (or $\epsilon_c < \sqrt{5}-2$) independent of N and the configuration of the nuclei such that, for $U > U_c$ (or $\epsilon < \epsilon_c$),

$$E((l)_N, N) = NE_0 + \left[\sum_{i=1}^{N-1} \phi(l_i)\right][1+R_N((l)_N, \epsilon)] , \tag{2.4}$$

with

$$\phi(l_i)=2(l_i+1)\epsilon^{2l_i+1} \qquad (2.5)$$

and

$$|R_N((l)_N,\epsilon)|=O(\epsilon) \qquad (2.6)$$

uniformly with respect to N, $(l)_N$.

It follows from (2.4) that the minimum of $E((l)_N,N)$ is attained when all nuclei are infinitely far apart from each other, the total energy being then equal to NE_0. Thus a finite equal number of electrons and nuclei will form atoms of energy E_0. The effective potential energy between these atoms is, to leading order, $\phi(l)$, which is repulsive.

We can also consider the problem of minimizing $E((l)_N,N)$ under the constraint

$$\sum_{i=1}^{N} l_i=L \ , \qquad (2.7)$$

which corresponds to having the nuclei confined to a region Λ, of length $|\Lambda|=L+N$, with one nucleus at each end, while the electrons are free to move in all of Z. To achieve this rigorously one would need more control on the remainder term (2.6). However, it is instructive to look at the leading term

$$\sum_{i=1}^{N-1} \phi(l_i) \ . \qquad (2.8)$$

It is easy to see that, if $L=(N-1)q$, q an integer, then the minimum is attained when $l_i=q$ for all i, i.e., the ground state consists of nuclei arranged in a periodic way with a period q.

We can also consider the thermodynamic limit obtained by letting $L\rightarrow\infty$ and $N\rightarrow\infty$ and keeping N/L fixed. Since (2.6) is uniform with respect to N, $(l)_N$, and $\phi(l)$ is a convex potential, we have

$$\lim_{N\rightarrow\infty}\frac{1}{N}E((l)_N,N)=E_0+\langle\phi(l)\rangle[1+O(\epsilon)]$$
$$\geq E_0+\phi(\langle l\rangle)[1+O(\epsilon)] \ , \qquad (2.9)$$

where $\langle\ \rangle$ is the average with respect to the distribution of lengths between the nuclei. Considering only the leading term, we see that if $\langle l\rangle=q$, an integer, then the minimum is attained for a distribution in which $l_j=q$ for all j. This corresponds to a crystalline ground state of period q. These results are in agreement with the conclusions of Ref. 7 at least for $U>U_c$, with U_c independent of the density.

We can use theorem 1 to derive the structure of the effective potential in the weight of the partition function (1.3) for low temperatures and chemical potential μ_e in the gap of the spectrum. The reason that we have to fix μ_e in the gap is that it enforces the neutrality for $\beta=\infty$. First we notice the following identities:

$$\mathrm{tr}\ln[1+e^{-\beta(h[\{n_k\}]-\mu_e}]=-\frac{\beta}{2}\mathrm{tr}(h[\{n_k\}]-\mu_e)+\mathrm{tr}\ln[e^{\beta/2|h[\{n_k\}]-\mu_e|}+e^{-\beta/2|h[\{n_k\}]-\mu_e|}]$$
$$=\frac{\beta}{2}[\mathrm{tr}|h[\{n_k\}]-\mu_e|-\mathrm{tr}(h[\{n_k\}]-\mu_e)]+\mathrm{tr}\ln[1+e^{-\beta|h[n_k]-\mu_c|}] \ . \qquad (2.10)$$

When μ_e is in the gap, i.e., $-U+4<\mu_e<0$, we have, for large enough β,

$$\mathrm{tr}\ln[1+e^{-\beta|h[n_k]-\mu_e|}]$$
$$=|\Lambda|O(e^{-\beta\min(|\mu_e+U-4|,|\mu_c|)}) \ . \qquad (2.11)$$

Moreover, one can see that

$$\mathrm{tr}|h[n_k']-\mu_e|-\mathrm{tr}(h[n_k]-\mu_e)$$
$$=-2\sum_{e_j<\mu_e}(e_j[\{n_k\}]-\mu_e)$$
$$=-2E((l)_N,N)+2\mu_e\sum_j n_j \ . \qquad (2.12)$$

In the last equality, we have used the fact that the number of negative eigenvalues is equal to $\sum_j n_j$. Combining (2.10)–(2.12) and the formula in theorem 1, we obtain the effective potential for large enough β and small enough ϵ, namely,

$$\beta\mu_n\sum_j n_j+\mathrm{tr}\ln[1+e^{-\beta/2|h[n_k]-\mu_e|}]$$
$$=\beta(\mu_e+\mu_n-E_0)\sum_j n_j$$
$$+\beta\left[\sum_j\phi(l_j)\right][1+O(\epsilon)]+|\Lambda|O(e^{-\beta C}) \ ,$$
$$C>0 \qquad (2.13)$$

When N/Λ is of order one, this effective potential thus corresponds to leading order in ϵ and $e^{-\beta C}$, to a system of atoms with an effective chemical potential $\mu_e+\mu_n-E_0$ and a repulsive two-body potential $\phi(l)$ between nearest-neighbor atoms.

In the high-temperature limit $\beta\rightarrow0$, the situation is of course very different. Developing the effective potential in (1.3) to first order in β, one finds

$$\Xi_\Lambda\approx e^{|\Lambda|[\ln2+\beta(\mu_e-1)]}\sum_{n_k=0,1}e^{\beta(\mu_n+U/2)\sum_k n_k} \ . \qquad (2.14)$$

This is the product of the partition functions of a gas of free nuclei and free electrons in the limit of small β. As mentioned in Sec. I, the characterization of the transition between low and high temperature is an open problem even for the one-dimensional FK model.

Continuum FK model

For the rest of this section, we discuss the continuous analog of the one-dimensional FK model. Consider N electrons and N nuclei moving on a one-dimensional line. The positions of the nuclei are denoted by $(r)_N = \{r_1 < \cdots < r_N\}$. For a given configuration of nuclei, the single-electron Hamiltonian is

$$-\Delta_x - \sum_{m=1}^{N} \gamma\delta(x-r_m) + \sum_{l<m}^{N} V(r_l - r_m) \ , \tag{2.15}$$

where $\gamma > 0$ and V is a hard-core potential

$$V(r)=0 \ \text{ if } |r|>h \ \text{ and } V(r)=\infty \ \text{ if } |r|<h \ . \tag{2.16}$$

The electrons do not interact with each other but are subject to the Fermi statistics. The relevant dimensionless parameter is $\gamma h = b$. For $N=1$, the Hamiltonian (2.15) has, for any value of b, exactly one bound state, the atom, of energy $-\gamma^2/4$. When b is large enough the Hamiltonian (2.15) has exactly N nondegenerate bound states with negative energies $\tilde{e}_1((r)_N) < \cdots < \tilde{e}_N((r)_N)$, in addition to the continuous part of the spectrum which for every b and N spans $[0,\infty]$ (see Ref. 10). In this case the ground-state energy is given by the sum

$$\tilde{E}((r)_N, N) = \sum_{k=1}^{N} \tilde{e}_k((r)_N) \ . \tag{2.17}$$

Because of the hard-core potential, the only allowed configurations for the nuclei satisfy $|r_l - r_m| > h$, for $l,m = 1,\dots,N$. For such configurations we can prove the following.

Theorem 2

There exists a constant $b_c > 1$, independent of the number and configuration of the nuclei, such that for $b > b_c > 1$, and for every $(r)_N$ such that $\gamma |r_l - r_{l+1}| > b$, we have

$$\tilde{E}((r)_N, N) = -N\frac{\gamma^2}{4} + \left[\sum_{l=1}^{N-1} \tilde{\phi}(r_{l+1} - r_l)\right] \times [1 + \tilde{R}_N((r)_N, \gamma)] \ , \tag{2.18}$$

with

$$\tilde{\phi}(r) = \frac{\gamma^2}{2}[\gamma|r| - 1]e^{-\gamma|r|} \tag{2.19}$$

and

$$\tilde{R}_N((r)_N, N) = O(e^{-a}) \tag{2.20}$$

uniformly in N, $(r)_N$,

From this theorem one can draw the same conclusions as for the lattice model. Namely, the ground state of N nuclei and N electrons on the infinite line will consist of atoms infinitely far apart from each other, the effective interaction between atoms being purely repulsive. The minimum of the leading term in (2.18) under the constraint $\sum_{l=1}^{N-1} |r_{l+1} - r_l| = L$, $L > Nh$ is attained for $|r_{l+1} - r_l| = L/N$ for $l = 1,\dots,N$. This is also true in the thermodynamic limit $N,L \to \infty$, with $N/L = \rho$ fixed, since the statement of the theorem is uniform with respect to N. Thus we expect that the system forms a crystal in the ground state with a period $1/\rho$. However, a rigorous proof of this statement would require a more detailed control of the error term (2.20).

The above statements hold for $b > b_c$. For sufficiently small values of b, the structure of the ground state can be very different. An analysis of the case of two electrons and two nuclei is already instructive. We find that there exist $0 < b_1 < b_2$ such that for $b < b_1$ one electron binds with the two nuclei while the other one is in a scattering state; for $b_1 < b < b_2$, both electrons are bound to a pair of nuclei; for $b > b_2$, we have two atoms infinitely far apart from each other.

The rest of the paper is devoted to a proof of theorem 1. The proof of theorem 2 is similar, and we explain the modifications in Appendix B.

III. POLYNOMIAL EQUATION FOR THE ENERGIES OF THE BOUND STATES

In this section, we use the transfer-matrix method to derive a polynomial equation for the energies of the bound states of the Hamiltonian (1.1). These are solutions of the Schrödinger equation

$$-[\psi(i-1) - 2\psi(i) + \psi(i+1)] - Un_i\psi(i) = e\psi(i) \ . \tag{3.1}$$

For simplicity, we do not label ψ and e by their quantum number, and we do not write explicitly their dependence on n_i. Let $i_1, i_2, \dots, i_N$ denote the positions of the N nuclei on the lattice and set $i_0 = -\infty$, $i_{N+1} = +\infty$. In the region $i_k \le i \le i_{k+1}$, $k = 0,\dots,N$ the solutions of (3.1) are of the form

$$\psi_k(i) = A_k(\epsilon y)^i + B_k(\epsilon y)^{-i} \ , \tag{3.2}$$

where y is related to the eigenenergy by

$$e = 2 - ey - \frac{1}{\epsilon y}, \quad 0 < \epsilon y < 1 \ . \tag{3.3}$$

The solutions (3.2) must satisfy the matching conditions $\psi_k(i_{k+1}) = \psi_{k+1}(i_{k+1})$ for $k = 0,\dots,N-1$. This leads to

$$\begin{bmatrix} A_{k+1} \\ B_{k+1} \end{bmatrix} = [1 - (\epsilon y)^2] T_k \begin{bmatrix} A_k \\ B_k \end{bmatrix} \ , \tag{3.4}$$

where the transfer matrix T_k can be cast in the factorized form $T_k = V_k H V_{-k}$, with

$$H = \begin{bmatrix} 1 - (1-\epsilon^2)y - \epsilon^2 y^2 & -(1-\epsilon^2)y \\ (1-\epsilon^2)y & 1 + (1-\epsilon^2)y - \epsilon^2 y^2 \end{bmatrix} \ ,$$
$$V_k = \begin{bmatrix} (\epsilon y)^{-k} & 0 \\ 0 & (\epsilon y)^k \end{bmatrix} \ . \tag{3.5}$$

To have bound-state solutions clearly requires that

$A_0=B_N=0$. This condition and (3.4) lead to the equation

$$[T_0T_1\cdots T_N]_{11}=0\ . \tag{3.6}$$

Using the factorized form of T_k together with the property $V_kV_{k'}=V_{k+k'}$, (3.6) can be put in the equivalent form

$$P_N(y,(l)_N)\equiv[Q(l_1)\cdots Q(l_{N-1})Q((l_N))]_{11}=0\ , \tag{3.7}$$

with the matrix $Q(l)$ given by

$$Q(l)=\begin{bmatrix}(1-y)(1+\epsilon^2y) & -\epsilon^{-2}(1-\epsilon^2)^2(\epsilon y)^{2l+4}\\ 1 & (1+y)(1-\epsilon^2y)(\epsilon y)^{2l+2}\end{bmatrix}\ . \tag{3.8}$$

In (3.7), l_N is an arbitrary number and the product does not depend on it. P_N is a polynomial in the variable y and has degree $\sum_{i=1}^{N-1}(2l_i+4)$. The number of roots of P_N (in the complex plane) is equal to its degree and thus is always greater than N. From property (ii) in Sec. II and relation (3.3), there must be, for $U>4$, N distinct roots located in the interval $[\frac{2}{3},4]$, which correspond to the energies of the N bound states. These roots will be called the "physical roots." We are thus faced with the problem of extracting the physical roots from all the other ones. This will be done rigorously after we obtain some intuition into the structure of this polynomial and the location of the roots in the complex plane.

The atomic polynomial

For $N=1$, the polynomial defined by (3.7) is simply

$$P_1(y)=(1-y)(1+\epsilon^2y)\ . \tag{3.9}$$

The root $y=1$ corresponds, via (3.3), to the energy (2.3) of the atom. The other root $y=-1/\epsilon^2$ is unphysical. Note that it tends to $-\infty$ when $\epsilon\to0$ (or $U\to\infty$).

The molecular polynomial

For two nuclei separated by a fixed distance l, the polynomial (3.7) is

$$P_2(y,l)=(1-y)^2(1+\epsilon^2y)^2-(1-\epsilon^2)^2y^2(\epsilon y)^{2l+2}\ , \tag{3.10}$$

which has $2l+4$ roots. The two physical roots (they satisfy $0<\epsilon y<1$) should tend to $y=1$ (which corresponds to the atom) as $\epsilon\to0$ or as $l\to\infty$. Moreover, in this limit $P_2(y,l)$ tends to $P_1(y)^2$, for $\epsilon y<1$, which suggests that all other roots tend to infinity in the complex plane. This is confirmed by looking at the special case $l=0$ (the two nuclei are on nearest-neighbor sites) where we can determine exactly the four roots of P_2:

$$y_\pm=\pm\frac{1}{\epsilon},\quad y'_\pm=\frac{1}{1\pm\epsilon-\epsilon^2}\ . \tag{3.11}$$

For $0<\epsilon<\sqrt{2}-1$ (or $U>2$), two of them correspond to the bound states, namely $y'_\pm$. These tend to one as $\epsilon\to0$ while $y_\pm$ tends to $\pm\infty$. Note that for $\sqrt{2}-1<\epsilon<1$ (or $U<2$), only one root corresponds to a bound state, namely y'_+. So for $U<2$ and $l=0$, there is only one bound state. For $\epsilon=\sqrt{2}-1$ (or $U=2$), two of the solutions become degenerate: $y'_-=y_+=\sqrt{2}+1$. These values of y and ϵ correspond to $e=0$ by (3.3). Physically this means that as $\epsilon\to\sqrt{2}-1$ from below, one of the two bound states merges in the continuum. For general l, we know from property (ii) in Sec. II that there are two nondegenerate bound states for $U>4$. To find their behavior for small ϵ, we look for roots of the form

$$y=1+\sum_{n=1}^{\infty}c_n\epsilon^n\ . \tag{3.12}$$

This yields to leading order

$$y_\pm=1\pm\epsilon^{l+1}+(l+2)\epsilon^{2l+2}+\cdots\ . \tag{3.13}$$

Adding the corresponding eigenenergies given by (3.3), we find that the energy of the molecule is to leading order equal to $2E_0+\phi(l)$, in agreement with theorem 1.

Factorization property for general N

For any $0<L<N$, we can write

$$\left[\prod_{i=1}^{N}Q(l_i)\right]_{11}=\left[\prod_{i=1}^{L}Q(l_i)\right]_{11}\left[\prod_{i=L+1}^{N}Q(l_i)\right]_{11}+\left[\prod_{i=1}^{L}Q(l_i)\right]_{12}\left[\prod_{i=L+1}^{N}Q(l_i)\right]_{21}\ . \tag{3.14}$$

An inspection of the second product on the right-hand side of (3.14) shows that it is equal to $(\epsilon y)^{2l_L+4}$ multiplied by a polynomial $S(y,l_1,\ldots,l_{L-1},l_{L+1},\ldots,l_{N-1})$ which is independent of l_L. So

$$P_N(y,(l)_N)=P_L(y,l_1,\ldots,l_{L-1})P_{N-L}(y,l_{L+1},\ldots,l_{N-1})+(\epsilon y)^{2l_L+4}S(y,l_1,\ldots,l_{L-1},l_{L+1},\ldots,l_{N-1})\ . \tag{3.15}$$

For $0<\epsilon y<1$, the second term on the right-hand side of (3.15) vanishes when we let $l_L\to\infty$. P_N then factorizes into the product of two polynomials associated with the two separate clusters of nuclei. As a consequence of this factorization property, P_N tends to $P_1(y)^N$ in the limit where all $l_k\to\infty$. This suggests that in this limit there are exactly N physical roots close to $y=1$, while all the others tend to infinity in the complex plane. The same is true when $\epsilon \to 0$, as can be seen directly from (3.7) and (3.8); i.e., the N physical roots branch off from the N-fold degenerate root $y=1$ at $\epsilon=0$.

IV. MAPPING TO A ONE-DIMENSIONAL LATTICE GAS

The key observation which enables us to deal with the polynomial P_N for general $(l)_N$ is the realization that it is closely related to the partition function of a one-dimensional lattice gas. To see this, we first note that if we write out the product of the matrices in (3.7), the symbols Q_{12} and Q_{21} will appear the same number of times. Furthermore, $P_1(y)=(1-y)(1+\epsilon^2 y)$ is independent of $(l)_N$. Thus (3.7) will remain unchanged if we replace Q_{21} by $Q_{21}P_1(y)$ and Q_{12} by $Q_{12}/P_1(y)$. Finally we can extract an overall factor $(P_1(y))^N$. Thus the polynomial P_N can be written as

$$P_N(y,(l)_N) \equiv (P_1(y))^N [\bar{Q}(l_1)\cdots\bar{Q}(l_{N-1})\bar{Q}((l_N))]_{11} , \tag{4.1}$$

where $\bar{Q}(l)$ is the new matrix

$$\begin{bmatrix} 1 & -\epsilon^{-2}(1-\epsilon^2)^2 \dfrac{(\epsilon y)^{2l+4}}{(1-y)^2(1+\epsilon^2 y)^2} \\ 1 & \dfrac{(1+y)(1-\epsilon^2 y)}{(1-y)(1+\epsilon^2 y)}(\epsilon y)^{2l+2} \end{bmatrix} . \tag{4.2}$$

We now define "activities" $\zeta(y,l)$ and a "weight" $w(y)$ independent of l by

$$\zeta(y,l)=\bar{Q}_{12}(l), \quad \zeta(y,l)w(y)=\bar{Q}_{22}(l) . \tag{4.3}$$

With these definitions, the matrix $\bar{Q}$ is the transfer matrix associated with the "partition function"

$$\bar{Z}_N(y,(l)_N)= \sum_{n_i=0,} \sum_{i=1}^{N-1} (\zeta(y,l_i))^{n_i} \prod_{i=1}^{N-2} (w(y))^{n_i n_{i+1}} . \tag{4.4}$$

$\bar{Z}_N(y,(l)_N)$ can formally be considered as the partition function of a lattice gas on the sites $i=1,\dots,N-1$, with an activity $\zeta(y,l_i)$ depending on the site i, and nearest-neighbor interaction $\ln(w(y))$. From (4.1)–(4.4), we have

$$P_N(y,(l)_N)=(P_1(y))^N \bar{Z}_N(y,(l)_N) . \tag{4.5}$$

It will turn out to be more convenient to work with a slightly different partition function. For $i=1,\dots,N-1$, we define the "normalized free measures"

$$d\mu_i(n)=\frac{1}{[1+\zeta(y,l_i)]}[\delta_0(n)+\zeta(y,l_i)\delta_1(n)] , \tag{4.6}$$

where $\delta_\alpha(n)=1$ are the Dirac measures centered at $\alpha=0,1$. The new partition function is

$$Z_N(y,(l)_N) = \int d\mu_1(n_1)\cdots \int d\mu_{N-1}(n_{N-1}) \prod_{i=1}^{N-2} (w(y))^{n_i n_{i+1}} . \tag{4.7}$$

In terms of (4.7), relation (4.5) becomes

$$P_N(y,(l)_N) = (P_1(y))^N \left[\prod_{i=1}^{N-1} [1+\zeta(y,l_i)] \right] Z_N(y,(l)_N) . \tag{4.8}$$

Our interest is then in obtaining the zeros of $Z_N(y,(l)_N)$ which lie on the real axis "close" to $y=1$. It will turn out that for small ϵ this corresponds to finding a low activity expansion of the free energy

$$F_N(y,(l)_N)=\ln Z_N(y,(l)_N) . \tag{4.9}$$

In this context it is a "polymer expansion,"[11] which we briefly review in the rest of this section.

Polymer expansion

We will denote by G the connected graphs consisting of bonds connecting nearest-neighbor points on the one-dimensional finite lattice $1,\dots,N-1$. We will say that $i \in G$ (resp$i \in G$) if the site i belongs at least to one bond of the graph (resp if it does not belong to any of the graph's bonds). Thus a graph G contains at least two sites and at most $N-1$ sites; the number of sites of a graph will be denoted by $|G|$. Two graphs G,G' are said to be disjoint if they do not have any common site. In such a case we will write $G \cap G' = \varnothing$. One can think of these graphs as "polymers." With each polymer G we associate an activity given by

$$K(y,G)=\int \prod_{i\in G} d\mu_i(n_i) \prod_{(i,i+1)\in G} [(w(y))^{n_i n_{i+1}}-1] . \tag{4.10}$$

Then by a standard calculation,[11] one can rewrite (4.7) as

$$Z_N(y,(l)_N) = \sum_{M=0}^{\infty} \frac{1}{M!} \sum_{(G_1,\dots,G_M),G_i\cap G_k=\varnothing} \prod_{i=1}^{M} K(y,G_i) . \tag{4.11}$$

The term $M=0$ in the sum is set equal to 1. The disjointness condition $G_i \cap G_k = \varnothing$ implies that there are, in fact, only a finite number of terms in the sum. Indeed, for $M > \frac{1}{2}(N-2)$ the disjointness condition cannot be satisfied and it is understood that the corresponding terms of the sum vanish. One can view (4.11) as the partition function of a system of polymers interacting by a two-body hard-core potential

$$V(G,G')=\infty \quad \text{if } G\cap G'\neq\varnothing$$

and (4.12)

$$V(G,G')=0 \quad \text{if } G\cap G'=\varnothing \ .$$

Starting from the representation (4.11) for the partition function, one can make a formal low activity expansion for the free energy (4.9). The result is

$$F_N(y,(l)_N)=\sum_{s=1}^{N-1} F_{N,s}(y,(l)_N) \ , \tag{4.13}$$

with

$$F_{N,s}(y,(l)_N)=\sum_{M=1}^{\infty}\frac{1}{M!}\sum_{(G_1,\ldots,G_M),s\in G_1}\left[\prod_{i=1}^{M}K(y,G_i)\right]\Phi_T(G_1,\ldots,G_M) \ , \tag{4.14}$$

where $\Phi_T(G_1,\ldots,G_M)$ are the Ursell functions corresponding to the hard-core potential (4.12). For each s (4.14) has a limit as $N\to\infty$, where the polymers G now contain sites belonging to all of Z. To prove convergence properties of the series which are uniform with respect to $N,(l)_N$, we will use the following bound (see Refs. 11 and 12 for reviews).

Tree graph bound

Suppose there exists a function $\omega(G)$, independent of y, and a domain D of the complex y plane such that

$$|K(y,G)|\le\omega(G) \quad \text{for } y\in D \tag{4.15}$$

and

$$c_s\equiv\sum_{G,s\in G}\omega(G)e^{|G|}<\infty \ . \tag{4.16}$$

Then

$$\frac{1}{M!}\sum_{(G_1,\ldots,G_M),s\in G_1}\left[\prod_{i=1}^{M}|K(y,G_i)|\right]|\Phi_T(G_1,\ldots,G_M)|\le c_s^M \ . \tag{4.17}$$

Furthermore, if $c_s<1$, the right-hand side of (4.14) converges uniformly with respect to $y\in D$ and $F_{N,s}(y,(l)_N)$, $s=1,\ldots,N-1$ are analytic functions of $y\in D$. This remains true for the limit $N\to\infty$.

V. LOCATION OF THE ROOTS OF $P_N(y,(l)_N)$

As was discussed in Sec. III, the N distinct physical roots must be located near $y=1$ on the real axis for large enough U. The following lemma gives some more detailed information about these roots. In particular, it proves that there exists a neighborhood of $y=1$ in the complex y plane where there are no other roots.

Lemma 5.1

Let $m=\min((l)_N)$. There exists $\epsilon_c<\sqrt{5}-2$ (or $U_c>4$), independent of N, $(l)_N$, such that for $\epsilon<\epsilon_c$ (or $U>U_c$), $P_N(y,(l)_N)$ has (with y a complex variable) the following characteristics.

(i) There are exactly N roots in the disk $|y-1|<\epsilon^{(m/2)+(1/4)}$. These are necessarily located on the real axis and are the physical roots.

(ii) No roots in the annulus $A(m)=\{y|\epsilon^{(m/2)+(1/4)}<|y-1|<\frac{1}{2}\}$.

(iii) All remaining roots are outside the disk $|y-1|<\frac{1}{2}$.

Let r be a number satisfying $\epsilon^{(m/2)+(1/4)}<r<\frac{1}{2}$. Let C_r be the circle centered at $y=1$ with radius r. Denoting the derivatives of P_N, Z_N, and F_N with respect to y by P'_N, Z'_N, and F'_N, we will prove that

$$\int_{C_r}\frac{dy}{2\pi i}\frac{P'_N(y,(l)_N)}{P_N(y,(l)_N)}=N \tag{5.1}$$

for $\epsilon<\epsilon_c$. Clearly results (i), (ii), and (iii) of the lemma all follow from (5.1).

We first prove (5.1) for $N=2$.

Proof of (5.1) for $N=2$

Using (3.8) and (3.9), one can easily check that

$$\frac{P'_2(y,l)}{P_2(y,l)}=2\frac{P'_1(y)}{P_1(y)}+\sum_{k=1}^{\infty}q_k(y,l) \ , \tag{5.2}$$

with

$$q_k(y,l)=\frac{1}{k}(1-\epsilon^2)^{2k}e^{(2l+2)k}\frac{d}{dy}\left[\frac{y^{(2l+4)k}}{(P_1(y))^{2k}}\right] \ . \tag{5.3}$$

Let us estimate (5.3) for y belonging to the circle C_r. Setting $y=1+re^{i\theta}$, we have

$$\begin{aligned}|P_1(y)|^2&=r^2[(1+\epsilon^2+\epsilon^2 r\cos\theta)^2+(\epsilon^2 r\sin\theta)^2]\\&\ge r^2[(1+\epsilon^2)[1+\epsilon^2(1-2r)]+\epsilon^4r^2]\\&\ge r^2(1+\epsilon^4r^2) \ ,\end{aligned} \tag{5.4}$$

where we have used $r<\frac{1}{2}$ for the second inequality. For $r<\frac{1}{2}$ and $\epsilon<\epsilon_c<\sqrt{5}-2$, we also have

$$\begin{aligned}|P'_1(y)|&=|\epsilon^2-1-2\epsilon^2y|\\&\le 1+\epsilon^2+2\epsilon^2r\le 2 \ .\end{aligned} \tag{5.5}$$

From (5.4) and (5.5), we get

$$\begin{aligned}\left|\frac{d}{dy}\left[\frac{y^{(2l+4)k}}{(P_1(y))^{2k}}\right]\right| &= \left|(2l+4)k\frac{y^{(2l+4)k-1}}{(P_1(y))^{2k}}-2k\frac{P_1'(y)}{(P_1(y))^{2k+1}}y^{(2l+4)k}\right| \\ &\leq (2l+4)k\frac{(1+r)^{(2l+4)k-1}}{r^{2k}}+4k\frac{(1+r)^{(2l+4)k}}{r^{2k+1}} \\ &\leq 2(2l+4)k\frac{(1+r)^{(2l+4)k}}{r^{2k+1}} \ . \end{aligned} \tag{5.6}$$

This implies

$$\left|\int_{C_r}\frac{dy}{2\pi i}q_k(y,l)\right| \leq 4(l+2)\left[(1-\epsilon^2)\epsilon^{l+1}\frac{(1+r)^{l+2}}{r}\right]^{2k} . \tag{5.7}$$

Using $\epsilon^{(m/2)+(1/4)}<r<\frac{1}{2}$ with $m=l$ for $N=2$, estimate (5.7) becomes

$$\left|\int_{C_r}\frac{dy}{2\pi i}q_k(y,l)\right| \leq 4(l+2)[(\tfrac{3}{2}\sqrt{\epsilon})^{l}\tfrac{9}{4}\epsilon^{3/4}]^{2k} . \tag{5.8}$$

For $\epsilon<\sqrt{5}-2$, the right-hand side of (5.8) is smaller than $4(l+2)c_l^{2k}$ for some constant $c_l<1$ depending only on l. Thus for $\epsilon<\sqrt{5}-2$ we can integrate (5.2) around the circle C_r and interchange the integral and the sum on the right-hand side there. To obtain (5.1), we note that from (3.8),

$$\int_{C_r}\frac{dy}{2\pi i}\frac{P_1'(y)}{P_1(y)}=1 , \tag{5.9}$$

and that

$$\int_{C_r}\frac{dy}{2\pi i}q_k(y,l)=0 , \tag{5.10}$$

since $q_k(y,l)$ is the derivative of a function which is analytic in $A(m)$.

Proof of (5.1) for $N>2$

Using (4.8), we find

$$\frac{P_N'(y,(l)_N)}{P_N(y,(l)_N)}=N\frac{P_1'(y)}{P_1(y)}+\sum_{i=1}^{N-1}\frac{\zeta'(y,l_i)}{1+\zeta(y,l_i)} +\frac{Z_N'(y,(l)_N)}{Z_N(y,(l)_N)} , \tag{5.11}$$

which, using (3.8), (3.9), (4.3), and (4.9), gives

$$\frac{P_N'(y,(l)_N)}{P_N(y,(l)_N)}=N\frac{P_1'(y)}{P_1(y)}+\sum_{i=1}^{N-1}\left[\frac{P_2'(y,l_i)}{P_2(y,l_i)}-2\frac{P_1'(y)}{P_1(y)}\right] +F_N'(y,(l)_N) . \tag{5.12}$$

The next step is to integrate both sides of (5.12) along a circle $C_r\subset A(m)$. The integral of the first term on the right-hand side of (5.12) is equal to N because of (5.9). The integral of the sum on the right-hand side vanishes for $N=2$ because of relation (5.1). So (5.1) will be true for $N>2$ if and only if

$$\int_{C_r}\frac{dy}{2\pi i}F_N'(y,(l)_N)=0 . \tag{5.13}$$

To prove (5.13), we use the following lemma.

Lemma 5.2

For $\epsilon<\epsilon_c$ (or $U>U_c$), $F_N(y,(l)_N)$ is an analytic function of $y\in A(m)$, where ϵ_c, U_e and m are the same as in lemma 5.1.

Proof of Lemma 5.2

We will use the low activity expansion (4.13) and (4.14) and the "tree graph bound" to prove that the lemma 5.2 holds for all $F_{N,s}(y,(l)_N)$, $s=1,\ldots,N-1$. From (4.2) and (4.3), we have

$$\zeta(y,l_i)=-(1-\epsilon^2)^2y^2\frac{(\epsilon y)^{2l_i+2}}{(1-y)^2(1+\epsilon^2y)^2} \tag{5.14}$$

and

$$w(y)=-\frac{1}{(1-\epsilon^2)^2}\frac{1}{y^2}(1-y^2)(1-\epsilon^4y^2) . \tag{5.15}$$

We need to estimate (5.14) and (5.15) for $y\in A(m)$. Using (5.4), we get

$$\begin{aligned}|\zeta(y,l_i)| &\leq \frac{(1+r)^2[\epsilon(1+r)]^{2l_i+2}}{r^2} \\ &\leq \tfrac{9}{4}(\tfrac{3}{2}\epsilon)^{2l_i+2}\epsilon^{-m-1/2} \\ &\leq \tfrac{9}{4}(\tfrac{3}{2}\sqrt{\epsilon})^{2l_i+2}\epsilon^{l_i-m}\epsilon^{1/2} \\ &=(\tfrac{3}{2}\sqrt{\epsilon})^{2l_i}\tfrac{81}{16}\epsilon^{3/2}\leq\tfrac{81}{16}\epsilon^{3/2} . \end{aligned} \tag{5.16}$$

For the last two inequalities, we used $l_i\geq m$ and $\epsilon<\sqrt{5}-2$. This implies

$$\left|\frac{\zeta(y,l_i)}{1+\zeta(y,l_i)}\right|\leq c_1e^{3/2} \tag{5.17}$$

for a positive constant c_1 (one can take $c_1=16$). To estimate (5.15), we use $|y|^2>(1-r)^2$, $r<\frac{1}{2}$, and $\epsilon<\sqrt{5}-2$, which leads to

$$|w(y)|\leq\frac{[1+(1+r)^2][1+\epsilon^4(1+r)^2]}{(1-\epsilon^2)^2(1-r)^2}\leq c_2 \tag{5.18}$$

for a positive constant c_2 (one can take $c_2=15$). With the help of (4.6) and (4.10), the activity of a polymer G can be expressed as

$$K(y,G)=\prod_{i\in G}\left[\frac{\zeta(y,l_i)}{1+\zeta(y,l_i)}\right][w(y)-1]^{|G|-1}\ , \tag{5.19}$$

and using (5.17) and (5.18) we can estimate it for $y\in A(m)$ as

$$\begin{aligned}|K(y,G)|\le&(c_1\epsilon^{3/2})^{|G|}(c_2+1)^{|G|-1}\\&\times[c_1(c_2+1)e^{3/2}]^{|G|}(c_2+1)^{-1}\ .\end{aligned}\tag{5.20}$$

So we have obtained a bound of type (4.15) with $D=A(m)$ and $\omega(G)$ given by the last member of (5.20). Thus c_s defined in (4.16) is estimated as

$$c_s=(c_2+1)^{-1}\sum_{G,s\in G}[c_1(c_2+1)\epsilon^{3/2}]^{|G|}e^{|G|}\ . \tag{5.21}$$

We notice that the number of polymers G (they are connected) that contain a given site s, and such that $|G|=n$, is at most n. Thus

$$c_s\le(c_2+1)^{-1}\sum_{n=2}^{\infty}n[ec_1(c_2+1)\epsilon^{3/2}]^{n+1}\ , \tag{5.22}$$

so $c_s<1$ for $\epsilon<\epsilon_c<\sqrt{5}-2$ (where ϵ_c depends only on c_1 and c_2), which implies the analyticity of $F_{N,s}(y,(l)_N)$ for $y\in D=A(m)$ and $\epsilon<\epsilon_c$.

VI. EXPANSION OF THE GROUND-STATE ENERGY

The ground state-energy is given by the eigenvalue sum (1.2). Using (3.3), we have

$$E((l)_N,N)=\sum_{k=1}^{N}\left[2-y_k-\frac{1}{y_k}\right]\ , \tag{6.1}$$

where y_k, $k=1,\dots,N$ are the physical roots of the polynomial $P_N(y,(l)_N)$. From lemma 5.1, we see that this sum can be represented by an integral around a circle C_r as in (5.1),

$$E((l)_N,N)=\int_{C_r}\frac{dy}{2\pi i}\left[2-\epsilon y-\frac{1}{\epsilon y}\right]\frac{P_N'(y,(l)_N)}{P_N(y,(l)_N)}\ . \tag{6.2}$$

From (4.8) and (4.9), we get

$$\begin{aligned}E((l)_N,N)=&N\int_{C_r}\frac{dy}{2\pi i}\frac{P_1'(y)}{P_1(y)}\\&+\sum_{i=1}^{N}\int_{C_r}\frac{dy}{2\pi i}\left[2-\epsilon y-\frac{1}{\epsilon y}\right]\frac{\zeta_i'(y,l_i)}{1+\zeta_i(y,l_i)}\\&+\int_{C_r}\frac{dy}{2\pi i}\left[2-\epsilon y-\frac{1}{\epsilon y}\right]F_N'(y,(l)_N)\ .\end{aligned}\tag{6.3}$$

Let us cast this expression in a more transparent form. The first integral on the right-hand side of (6.3) is equal to E_0. For the terms in the sum, we use

$$\frac{\zeta'(y,l_i)}{1+\zeta(y,l_i)}=\frac{P_2'(y)}{P_2(y)}-2\frac{P_1'(y)}{P_1(y)}\ . \tag{6.4}$$

Moreover, because of lemma 5.2, we can integrate by parts the last term on the right-hand side of (6.3) to obtain

$$\begin{aligned}E((l)_N,N)=NE_0+&\sum_{i=1}^{N-1}\int_{C_r}\frac{dy}{2\pi i}\left[2-\epsilon y-\frac{1}{\epsilon y}\right]\\&\times\left[\frac{P_2'(y,l_i)}{P_2(y,l_i)}-2\frac{P_1'(y)}{P_1(y)}\right]\\&+\int_{C_r}\frac{dy}{2\pi i}\left[\epsilon-\frac{1}{\epsilon y^2}\right]F_N(y,(l)_N)\ .\end{aligned}\tag{6.5}$$

For $N=2$, we have to replace F_N by 1, and the last integral does not contribute. For $N>2$, our expansion for the ground-state energy is obtained by inserting into (6.5) the low activity expansion (4.14) for F_N. It can be shown, using the tree graph bound and estimates similar to those in the proof of lemma 5.2, that the expansion for the ground-state energy converges uniformly with respect to N, $(l)_N$ for $\epsilon<\epsilon_c$. Let us first consider the case where $N=2$.

Ground-state energy for $N=2$

Using formulas (5.3) and (5.4), we have

$$\begin{aligned}\int_{C_r}\frac{dy}{2\pi i}&\left[2-\epsilon y-\frac{1}{\epsilon y}\right]\left[\frac{P_2'(y,l)}{P_2(y,l)}-2\frac{P_1'(y)}{P_1(y)}\right]\\&=\sum_{k=1}^{\infty}\frac{1}{k}(1-\epsilon^2)^{2k}\epsilon^{(2l+2)k}\\&\qquad\times\int_{C_r}\frac{dy}{2\pi i}\left[2-\epsilon y-\frac{1}{\epsilon y}\right]\frac{d}{dy}\left[\frac{y^{(2l+4)k}}{(P_1(y))^{2k}}\right]\ .\end{aligned}\tag{6.6}$$

The permutation of the sum and integral can be justified by estimates similar to (5.6). The computation of the contour integral in (6.6) is outlined in Appendix C and yields the result (C6). Combining (6.5), (6.6), and (C6), we obtain a series expansion [see (C7)] for the ground state of a molecule with two nuclei separated by a distance l. The sum on the right-hand side of (C7) is the effective potential two-body potential discussed in Sec. II. We can check that the leading correction to $2E_0$ is

$$\phi(l)[1+O(\epsilon)]\ , \tag{6.7}$$

where $O(\epsilon)$ is uniform with respect to l, in agreement with (2.5).

Ground-state energy for $N>2$

As a consequence of (6.5), (6.6), and (6.7), we see that to obtain the result of theorem 1 it is sufficient to show that

$$\left|\int_{C_r}\frac{dy}{2\pi i}\left[\epsilon-\frac{1}{\epsilon y^2}\right]F_N(y,(l)_N)\right|<c\epsilon\sum_{i=1}^{N-1}\phi(l_i) \tag{6.8}$$

for a positive number c. The estimate (6.8) is based on the following lemma.

Lemma 6.1

For a given collection of polymers $G_1, \ldots, G_M$, let $k^*(G_1, \ldots, G_M)$ be an integer among all $k \in G_1 \cup \ldots \cup G_M$ such that

$$l_{k^*(G_1,\ldots,G_M)} \leq l_k \quad \text{for } k \in G_1 \cup \cdots \cup G_M \ . \tag{6.9}$$

Then there exist two positive numerical constants κ_1 and κ_2, for which the following estimate holds:

$$\left| \int_{C_r} \frac{dy}{2\pi i} \left[\epsilon - \frac{1}{\epsilon y^2} \right] \prod_{i=1}^{M} K(y, G_i) \right| \leq \kappa_1 \phi(l_{k^*(G_1,\ldots,G_M)}) (\kappa_2 \epsilon)^{|G_1| + \cdots + |G_M| - M + 1} \ . \tag{6.10}$$

The proof of this lemma will be given later. First we show why it implies (6.8). From the polymer expansion (4.14) and (6.10), we have

$$\begin{aligned} &\left| \int_{C_r} \frac{dy}{2\pi i} \left[\epsilon - \frac{1}{\epsilon y^2} \right] F_{N,s}(y, (l)_N) \right| \\ &\quad \leq \kappa_1 \sum_{M=1}^{\infty} \frac{1}{M!} \sum_{(G_1,\ldots,G_M), s \in G_1} \phi(l_{k^*(G_1,\ldots,G_M)})(\kappa_2 \epsilon) \left[\prod_{i=1}^{M} (\kappa_2 \epsilon)^{|G_i| - 1} \right] |\Phi_T(G_1, \ldots, G_M)| \\ &\quad \leq \kappa_1 \sum_{M=1}^{\infty} \frac{1}{M!} \sum_{U, s \in U} (\sqrt{\kappa_2 \epsilon})^{|U|} \sum_{G_1 \cup \cdots \cup G_M = U, s \in G_1} \phi(l_{\kappa^*(G_1,\ldots,G_M)}) \left[\prod_{i=1}^{M} (\sqrt{\kappa_2 \epsilon})^{|G_i|} \right] |\Phi_T(G_1, \ldots, G_M)| \ . \end{aligned} \tag{6.11}$$

In the last member of inequality (6.11), the only graphs U that contribute are the connected graphs U. Indeed if $G_1 \cup \cdots \cup G_M$ is not connected, then the Ursell function $\Phi_T(G_1, \ldots, G_M)$ associated to the hard-core potential (4.12) vanishes. Also, notice that we have used $|U| \leq |G_1| + \cdots + |G_M| - M + 1$ to obtain the second inequality. The inequality (6.11) is preserved if we replace $\phi(l_{k^*(G_1,\ldots,G_M)})$ by $\sum_{k \in U} \phi(l_k)$ and then release the constraint $G_1 \cup \cdots \cup G_M = U$. This leads to

$$\begin{aligned} &\left| \int_{C_r} \frac{dy}{2\pi i} \left[\epsilon - \frac{1}{\epsilon y^2} \right] F_{N,s}(y, (l)_N) \right| \\ &\qquad \leq \kappa_1 \left[\sum_{U, s \in U} (\sqrt{\kappa_2 \epsilon})^{|U|} \sum_{k \in U} \phi(l_k) \right] \sum_{M=1}^{\infty} \frac{1}{M!} \sum_{(G_1,\ldots,G_M), s \in G_1} \left[\prod_{i=1}^{M} (\sqrt{\kappa_2 \epsilon})^{|G_i| - 1} \right] |\Phi_T(G_1, \ldots, G_M)| \ . \end{aligned} \tag{6.12}$$

The sum over M in (6.12) can be estimated by applying the tree graph bound [see (4.15)–(4.17)] with $\omega(G) = \sqrt{\kappa_2 \epsilon}^{|G|-1}$. We then find that the sum over M is smaller than a constant times $\sqrt{\epsilon}$. Thus performing the sum over $s = 1, \ldots, N-1$ on both sides of (6.12) gives (c' is a numerical constant)

$$\left| \int_{C_r} \frac{dy}{2\pi i} \left[\epsilon - \frac{1}{\epsilon y^2} \right] F_N(y, (l)_N) \right| \leq c' \sqrt{\epsilon} \sum_{s=1}^{N-1} \sum_{U, s \in U} (\sqrt{\kappa_2 \epsilon})^{|U|} \sum_{k \in U} \phi(l_k) \ . \tag{6.13}$$

Let us estimate the sum over U in (6.13). Since only the graphs U which are connected contribute, there are n of them which contain the site s and such that $|U| = n$. Thus

$$\begin{aligned} \sum_{U, s \in U} (\sqrt{\kappa_2 \epsilon})^{|U|} \sum_{k \in U} \phi(l_k) &= \sum_{n=2}^{N-2} (\sqrt{\kappa_1 \epsilon})^n \sum_{|U| = n, s \in U} \sum_{k \in U} \phi(l_k) \\ &\leq \sum_{n=2}^{N-2} n (\sqrt{\kappa_1 \epsilon})^n \sum_{k = \max(1, s-n)}^{\min(N, s-n)} \phi(l_k) \ . \end{aligned} \tag{6.14}$$

Finally, combining (6.13) and (6.14), we find

$$\begin{aligned} &\left| \int_{C_r} \frac{dy}{2\pi i} \left[\epsilon - \frac{1}{\epsilon y^2} \right] F_N(y, (l)_N) \right| \\ &\quad \leq c' \sqrt{\epsilon} \sum_{n=2}^{N-2} n^2 (\sqrt{\kappa_1 \epsilon})^n \sum_{i=1}^{N-1} \phi(l_i) \\ &\quad \leq c \epsilon \sum_{i=1}^{N-1} \phi(l_i) \ . \end{aligned} \tag{6.15}$$

To complete the proof of theorem 1, it remains to prove lemma 6.1.

Proof of lemma 1.6

The value of the integral in (6.10) is determined by the location of the poles of $K(y, G_i)$, $i = 1, .., M$ inside the circle C_r. We recall that from (4.6) and (4.10),

$$K(y, G) = \prod_{i \in G} \left[\frac{\zeta(y, l_i)}{1 + \zeta(y, l_i)} \right] [w(y) - 1]^{|G|} \ . \tag{6.16}$$

We see on (5.15) that the only pole of $w(y)$ is $y = 0$ and it lies outside C_r. So we have to consider the poles of

$$\frac{\zeta(y,l_i)}{1+\zeta(y,l_i)}=-\frac{(1-\epsilon^2)^2y^2(\epsilon y)^{2l_i+2}}{P_2(y,l_i)} . \tag{6.17}$$

Applying lemma 5.1 to the case $N=2$, we see that the poles of $K(y,G)$ which are located inside C_r are in fact inside a circle of radius $e^{(1/2)l_{k^*(G_1,\ldots,G_M)}+1/4}$ and center $y=1$. Since $e^{(l/2)+(1/4)}<(2l+2)^{-1}<\frac{1}{2}$, for any $l\geq 0$, all the poles that contribute to the integral in (6.10) are also located inside a circle $C^*(G_1,\ldots,G_M)$ of center $y=1$ and radius

$$r^*(G_1,\ldots,G_M)=\frac{1}{2l_{k^*(G_1,\ldots,G_M)}+2} . \tag{6.18}$$

In what follows, for simplicity we write C^*, r^*, and k^*. Note that $r^*\leq r$. We have

$$\int_{C_r}\frac{dy}{2\pi i}\left[\epsilon-\frac{1}{\epsilon y^2}\right]\prod_{i=1}^{M}K(y,G_i)$$
$$=\int_{C^*}\frac{dy}{2\pi i}\left[\epsilon-\frac{1}{\epsilon y^2}\right]\prod_{i=1}^{M}K(y,G_i) . \tag{6.19}$$

We now have to bound the integrand of the right-hand side of (6.19). For $y\in C^*$ and $i\in G_1\cup\cdots\cup G_M$, we have the estimate [see (5.16)]

$$|\zeta(y,l_i)|\leq[\epsilon(1+r^*)]^{2l_i+2}\frac{(1+r^*)^2}{r^{*2}} . \tag{6.20}$$

For $i=k^*$, this implies

$$|\zeta(y,l_{k^*})|$$
$$\leq 9(l_{k^*}+1)^2\epsilon^{2l_{k^*}+2}\left[1+\frac{1}{2l_{k^*}+2}\right]^{2l_{k^*}+2}$$
$$\leq 9e(l_{k^*}+1)^2\epsilon^{2l_{k^*}+2} , \tag{6.21}$$

and, for $i\neq k^*$, $\epsilon<\sqrt{5}-2$,

$$|\zeta(y,l_i)|\leq 9e(l_i+1)^2\epsilon^{2l_i+2}\leq 9e\epsilon . \tag{6.22}$$

We will also have

$$\left|\epsilon-\frac{1}{\epsilon y^2}\right|\leq\epsilon+\frac{2}{\epsilon} . \tag{6.23}$$

Combining (6.21), (6.22), and (5.18) we get, for $y\in C^*$ and $\epsilon<\epsilon_c$,

$$\left|\prod_{i=1}^{M}K(y,G_i)\right|$$
$$\leq\kappa_1'(l_{k^*}+1)^2\epsilon^{2l_{k^*}+2}(\kappa_2'\epsilon)^{|G_1|+\cdots+|G_M|-M+1} \tag{6.24}$$

for two numerical constants κ_1',κ_2'. With (6.19), (6.23), and (6.24), we conclude

$$\left|\int_{C_r}\frac{dy}{2\pi i}\left[\epsilon-\frac{1}{\epsilon y^2}\right]\prod_{i=1}^{M}K(y,G_i)\right|$$
$$\leq\kappa_1'(\epsilon^2+2)(l_{\kappa^*}+1)$$
$$\times e^{2l_{k^*}+1}(\kappa_2'\epsilon)^{|G_1|+\cdots+|G_M|-M+1} , \tag{6.25}$$

which is identical to (6.10).

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APPENDIX A

The single-particle Hamiltonian can be written in the form

$$h[\{n_i\}]=h_0-UD , \tag{A1}$$

where h_0 is the kinetic-energy part and D is the diagonal (infinite matrix) with entries n_i on the diagonal. The spectrum of h_0 spans the interval [0,4] and if $\sum_i n_i=M<\infty$, D is a finite rank operator. Thus $h[\{n_i\}]$ has the same continuous spectrum as h_0. This proves (i) in Sec. II.

The lowest eigenvalue of $-UD$ is $-U$, and it is M-fold degenerate. Since $0\leq h_0\leq 4$, the discrete part of the spectrum of h is necessarily located in the interval $[-U,-U+4]$. Now we show that there are exactly M eigenfunctions corresponding to this discrete spectrum if $U>4$. Consider the Hamiltonians $h(\gamma)=\gamma h_0-UD$, where $\gamma>0$. Notice that (i) $h(0)$ has M degenerate eigenvalues equal to $-U$, and an infinitely degenerate eigenvalue equal to 0; (ii) $h(0)<h(1)$; and (iii) $h(1)=h[\{n_i\}]$. From (i), (ii), and (iii) and the minimax principle, it follows that $h[\{n_i\}]$ has at most M negative eigenvalues. Now suppose that $h[\{n_i\}]$ has M' negative eigenvalues with $M'<M$. Let $\psi_1,\ldots,\psi_N$ be the corresponding eigenvectors. Since $M'<M$, it is possible to find at least one normalized vector ϕ such that $(\phi,\psi_k)=0$, $k=0,\ldots,N$, and $\phi(k)=0$ if $n_k=0$. Then

$$\sum_{k:n_k=1}|\phi(k)|^2=\sum_{k}|\phi(k)|^2=1 \tag{A2}$$

and

$$(\phi,h[\{n_i\}]\phi)=(\phi,h_0\phi)-U\sum_{k:n_k=1}|\phi(k)|^2$$
$$=(\phi,h_0\phi)-U<0 \tag{A3}$$

for $U>4$. Inequality (A3) shows that the number of negative eigenvalues must be at least equal to M for $U>4$ and thus there are exactly M of them.

To finish the proof of (ii) from Sec. II, it remains to see that the corresponding M eigenvalues cannot be degenerate. In the one-dimensional case, the eigenfunctions decay like $\exp(-|i||\ln y_k|)$ for $|i|\to\infty$, and y_k is related to the energy by $\epsilon_k=2-y_k-y_k^{-1}$. Since the whole eigenfunction can be built up by the transfer-matrix method, two degenerate eigenvalues would lead to the same eigenfunctions. Since there are M orthogonal eigenfunctions, this is clearly impossible.

APPENDIX B

Here we outline the proof of theorem 2. The method is an adaptation of that for the discrete case. We look for bound states of the Hamiltonian (2.15), of the form $\psi(x)=Ae^{-\kappa x}+Be^{\kappa x}$, with different A and B in each region between the scattering centers $r_1,\ldots,r_N$. The parameter κ is related to the energy by $\tilde{e}=-\kappa^2$. We define the dimensionless parameter $y=2\kappa/\gamma$, so that $\tilde{e}=-(\gamma^2/4)y$, and $y=1$ corresponds to the energy of the atom. The matching conditions between the different regions lead to Eq. (3.6), with T_i replaced by

$$\tilde{T}(r_i)=\tilde{V}(r_i)\tilde{H}\,\tilde{V}(-r_i),$$

$$\tilde{H}=\begin{bmatrix}(y-1)y^{-1} & -y^{-1}\\ y^{-1} & (1+y)y^{-1}\end{bmatrix}, \qquad \tilde{V}(r_i)=\begin{bmatrix}e^{(1/2)y\gamma r_i} & 0\\ 0 & e^{-(1/2)y\gamma r_i}\end{bmatrix}. \tag{B1}$$

Setting $|r_2-r_1|=d_1,\ldots,|r_N-r_{N-1}|=d_{N-1}$, this leads to the analog of equation (3.7), namely

$$\tilde{P}_N(y,(l)_N)=[\tilde{Q}(d_1)\cdots\tilde{Q}(d_{N-1})\tilde{Q}(d_N)]_{11}=0\ , \tag{B2}$$

$$\tilde{Q}(d)=\begin{bmatrix}(y-1) & -e^{-yd\gamma}\\ 1 & (y+1)e^{-yd\gamma}\end{bmatrix}. \tag{B3}$$

From (B2) and (B3), we see that the atomic and molecular polynomials are, respectively,

$$\tilde{P}_1(y)=(y-1)\ , \tag{B4}$$

$$\tilde{P}_2(y,d)=(y-1)^2-e^{-yd\gamma}\ . \tag{B5}$$

Note that, in the continuous case, $\tilde{P}_N(y,(r)_N)$ is not a polynomial but a transcendental function of y. The factorization property (3.14) still holds. Also, as $\gamma h=b(d_i>h)$ tends to ∞, $\tilde{P}_N(y,(d)_N)\rightarrow(y-1)^N$, so that all the physical roots become concentrated around $y=1$.

It is again possible to relate $\tilde{P}_N$ to the partition function of a one-dimensional lattice gas on $N-1$ sites. Formulas (4.6), (4.7), and (4.8) still hold with $P_N\rightarrow\tilde{P}_N$ and the following definitions for $\tilde{\zeta}(y,d)$ and $\tilde{w}(y)$:

$$\tilde{\zeta}(y,d)=-e^{-yd\gamma}(y-1)^{-2}\ , \tag{B6}$$

$$\tilde{\zeta}(y,d)\tilde{w}(y)=\frac{y+1}{y-1}e^{-yd\gamma}\ . \tag{B7}$$

The corresponding free energy $\tilde{F}_N(y,(d)_N)$ has a formal polymer expansion which is identical to that of the discrete case and which can also be controlled using the tree graph bound. With the help of this representation, we can prove properties similar to those in lemmas 5.1 and 5.2. Let $d_{\min}=\min((d)_N)$ and $A(d_{\min})=\{y|e^{-(1/4)d_{\min}\gamma}<|y-1|<\frac{1}{2}\}$. There exists b_c such that for $b>b_c$, we have for y a complex variable.

(i) $\tilde{P}_N$ has exactly N zeros inside the inner circle of $A(d_{\min})$. They are located on the real axis.

(ii) $\tilde{P}_N$ has no zeros in $A(d_{\min})$.

(iii) All the remaining zeros are located outside the outer circle of $A(d_{\min})$.

(iv) The free energy $F_N(y,(l)_N)$ is an analytic function of y for $y\in A(d)$.

The ground-state energy can be computed as in (6.2):

$$\tilde{E}((r)_N,N)=-\frac{\gamma^2}{4}\int_{C_r}\frac{dy}{2\pi i}y^2\frac{\tilde{P}'_N(y,(d)_N)}{\tilde{P}_N(y,(d)_N)}\ , \tag{B8}$$

where C_r is a circle, $y=1+re^{i\theta}$, contained in $A(d)$. Using the mapping to the one-dimensional lattice gas, we have

$$\tilde{E}((r)_N,N)=-\frac{\gamma}{4}N-\frac{\gamma^2}{4}\sum_{i=1}^{N-1}\int_{C_r}\frac{dy}{2\pi i}y^2\left[\frac{\tilde{P}'_2(y,d_i)}{\tilde{P}_2(y,d_i)}-2\frac{\tilde{P}'_1(y,d_i)}{\tilde{P}_1(y,d_i)}\right]-\frac{\gamma^2}{4}\int_{C_r}\frac{dy}{2\pi i}y\tilde{F}_N(y,(d)_N)\ . \tag{B9}$$

Using (B4) and (B5), we can compute the terms in the sum of the right-hand side of (B9). To leading order this yields the effective two-body potential (2.19). The last term is estimated as in the discrete case by using the polymer expansion and the tree graph bound.

APPENDIX C

First we outline the computation of the contour integral in (6.6). An integration by parts gives

$$I_k(\epsilon,l)=\int_{C_r}\frac{dy}{2\pi i}\left[\epsilon y^{(2l+4)k}-\frac{1}{\epsilon}y^{(2l+4)k-2}\right]\frac{1}{(P_1(y))^{2k}}\ . \tag{C1}$$

Since

$$\frac{1}{(P_1(y))^{2k}}=\frac{(-1)^{2k}}{(1+\epsilon^2y)^{2k}}\frac{d^{2k-1}}{dy^{2k-1}}\frac{1}{y-1}\ , \tag{C2}$$

by Cauchy's theorem we find

$$I_k(\epsilon,l)=-\frac{1}{\epsilon}\frac{d^{2k-1}}{dy^{2k-1}}A(y)B(y)|_{y=1}\ , \tag{C3}$$

where

$$A(y)=\epsilon^2 y^{(2l+4)k}-y^{(2l+4)k-2} \tag{C4}$$

and

$$B(y)=\frac{1}{(1+\epsilon^2 y)^{2k}}\ . \tag{C5}$$

Performing the derivatives in (C3) yields

$$I_k(\epsilon,l)=-\frac{1}{\epsilon}\sum_{p=0}^{2k-1}(-1)^{2k-1-p}\frac{(2k-1)!}{p!(2k-1-p)!}\frac{(4k-2-p)!}{(2k-1)!}\frac{[(2l+4)k-2]!}{[(2l+4)k-p]!}$$
$$\times\frac{\epsilon^{2(2k-1-p)}}{(1+\epsilon^2)^{4k-1-p}}\{\epsilon^2(2l+4)k[(2l+4)k-1]-[(2l+4)k-p][(2l+4)k-p-1]\}\ . \tag{C6}$$

The series expansion for the ground state of a molecule with two nuclei separated by a distance l is

$$E_2(l,2)=2E_0+\sum_{k=1}^{\infty}\frac{1}{k}(1-\epsilon^2)^{2k}\epsilon^{(2l+2)k}I_k(\epsilon,l)\ . \tag{C7}$$

By inspection, we see that the leading term of the sum in (C7) is given by $k=1$ and $p=2k-1=1$. This term is exactly $\phi(l)=2(l+1)\epsilon^{2l+1}$.

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