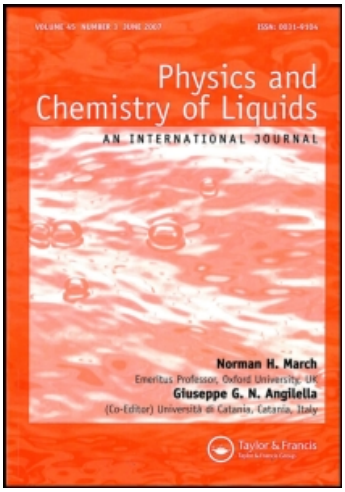

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W. Kunkin[a]; H. L. Frisch[a]
[a] Department of Chemistry State, University of New York at Albany Albany, New York

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Note on One-Dimensional Lattice Gas in External Fields‡

W. KUNKIN and H. L. FRISCH

Department of Chemistry
State University of New York at Albany
Albany, New York

Abstract—The fundamental equations of the scaled particle theory are derived for a one-dimensional lattice gas in an external potential. These equations relate the work required to add a particle, at a fixed point, to a $N-1$ particle system to the activity and to a series of coordinate distribution functions. The equations hold in any dimension, and replacing sums by integrals, describe continuum fluids. The rigid lattice gas is solved by these means. When nearest neighbors interact, in a positive, increasing external potential, a formal solution is obtained by a matrix method. The grand partition function, in the infinite length limit, depends only on a single eigenvalue of an infinite product of matrices. The one-particle distribution, in this limit, is reduced to a series of terminating continued fractions, which is readily approximated in the high coordinate or low activity limit. Lastly, it is shown that the zeros of the grand partition function lie on the negative real axis of the complex activity plane when the nearest-neighbor interaction is positive.

1. Rigid Lattice Gas

We consider a one-dimensional lattice gas of N particles distributed on M lattice sites in an external potential $U(k)$. We shall be interested in calculating the one-particle distribution function, $n_1(k)$, defined by

$$n_1(k_1) = (N/N!Z_N) \sum_{k_2, k_3, \ldots, k_N=0}^{M} \exp[-\beta \sum_{i<j}^{N} \phi(k_i - k_j) - \beta \sum_{i=1}^{N} U(k_i)] \quad (1.1)$$

and

$$Z_N = (1/N!) \sum_{k_1, k_2, \ldots, k_N=0}^{M} \exp[-\beta \sum_{i<j}^{N} \phi(k_i - k_j) - \beta \sum_{i=1}^{N} U(k_i)], \quad (1.2)$$

in the special case that no more than one particle can be placed on one site —there being no other interactions. (For convenience, the grid spacing and thermal wavelength have been chosen to be unity.)

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The calculation will be performed in an unorthodox way: the distribution will be related to the average, reversible work needed to add a (fixed) particle to a system of $N-1$ identical particles. We thereby generalize the basic equations of the scaled particle theory[1] to inhomogeneous fluids.

In general, an extra particle may be coupled into a system by a parameter λ, varying between zero and one, such that $\lambda = 0$ implies the particle is removed from the system and $\lambda = 1$ implies full coupling.[2] Writing the interaction energy between this particle and the others as $\lambda \sum_{i=2}^{N} \phi(k_i - k_1)$, the average work, $W(k;\lambda)$, needed to "turn on" a particle at site k up to λ-strength is

$$W(k;\lambda) = \sum_{k'} \int_0^\lambda d\lambda' \, \phi(k-k') n_1(k';\lambda' \mid k) = \sum_{k'} \int_0^\lambda d\lambda' \, \phi(k-k') \frac{n_2(k',k;\lambda')}{n_1(k;\lambda')}, \tag{1.3}$$

where $n_1(k';\lambda' \mid k)$ is a conditional density at k' in the presence of a particle at k.

The pair distribution in (1.3) is easily eliminated. Differentiating (1.1) with the added particle ("one") partially coupled, one obtains

$$\frac{\partial n_1(k_1;\lambda)}{\partial \lambda} = -\beta \frac{\partial W(k_1;\lambda)}{\partial \lambda} n_1(k_1;\lambda) - \frac{\partial \ln Z_N(\lambda)}{\partial \lambda} n_1(k_1;\lambda) \tag{1.4}$$

This integrates to

$$n_1(k_1) = z \exp[-\beta U(k_1)] \exp[-\beta W(k_1)], \tag{1.5}$$

at full coupling, where a well known identity for the activity, z, has been used:

$$z = N\left(\frac{Q_{N-1}}{Q_N}\right),$$

denoting the configurational sum in (1.2) by Q_N. Equation (1.5) is true also for continuum fluids.

An alternate representation of the work, in terms of distribution functions rather than activity, can be found by expanding (1.5), into

$$\exp[-\beta W(k_1)] = \left(\frac{1}{Q_{N-1}}\right) \sum_{k_2,\ldots,k_N} \exp\left[-\beta \sum_{2 \le i < j}^{N} \phi(k_i - k_j) - \beta \sum_{i=2}^{N} U(k_i)\right] \times \exp\left[-\beta \sum_{i=2}^{N} \phi(k_i - k_1)\right]. \tag{1.6}$$

Introducing the Mayer f-factor

$$f(k) = \exp[-\beta\phi(k)] - 1$$

into the last factor and expanding the resulting product, one finds

$$\exp[-\beta W(k_1)] = 1 + \sum_{m=1}^{N-1} \frac{1}{m!} \sum_{k_2,\ldots,k_{m+1}} \left[\prod_{i=2}^{m+1} f(k_i - k_1)\right] \times n_m(k_2,\ldots,k_{m+1}). \tag{1.7}$$

This holds for continuum fluids too, with the obvious modifications.

Let us specialize to the rigid gas. Since

$$\phi(k-k') = \begin{cases} 0 & (k \neq k') \\ \infty & (k = k') \end{cases},$$

while the mth order distribution vanishes for repeated arguments ($m \geqslant 2$) e.g.,

$$n_2(k,k) = 0,$$

only the first two terms in (1.7) survive, or,

$$\exp[-\beta W(k)] = 1 - n_1(k). \tag{1.8}$$

In a rigid gas we can derive (1.8) another way. When a particle is added to a system at a given lattice site, a hole is created with respect to the $N-1$ remaining particles since no other can occupy that site. It is generally true[3] that the work required to create a hole in a fluid is proportional to the negative logarithm of the probability, p, of observing a hole formed spontaneously in the fully coupled system. Here, these quantities depend on location in the external field, but we need not be concerned with the dependence on hole size which is the constant volume per site.

Explicitly,

$$p(k) = \exp[-\beta W(k)].$$

Since $n_1(k)$ is the probability of finding a particle at k,

$$p(k) = 1 - n_1(k)$$

and Eq. (1.8) follows. In any case, combining (1.8) with (1.5) leads to

$$n_1(k) = \frac{z\exp[-\beta U(k)]}{1 + z\exp[-\beta U(k)]} \tag{1.9}$$

where z is implicitly determined by

$$\sum_{k=0}^{M} n_1(k) = N \tag{1.10}$$

The density, not surprisingly, has the form of a Fermi-Dirac distribution.

If, in addition, particles on adjacent sites interact (nearest-neighbor interactions), the first four terms in (1.7) are non-vanishing. This equation then provides only a limited amount of information in the form of a functional relation between the singlet, pair, and triplet distributions. In the next section we formulate an exact approach to this interacting case. It remains an unanswered question whether Eqs. (1.5) and (1.7) or their continuum analogues can form the basis of a useful scaled particle theory of inhomogeneous fluids.

2. Rigid Lattice Gas with Nearest-Neighbor Interactions

We will describe the system by a set of numbers n_k, $k = 0, 1, \ldots, M$, which gives the number of particles at each site. The infinite contact potential is taken care of by permitting n_k to have only the values zero or one. In addition the particles interact by a constant nearest-neighbor potential i.e.,

$$\phi(k-k') = \begin{cases} 0 & |k-k'| \neq 1 \\ \phi & |k-k'| = 1. \end{cases}$$

The M-site grand partition function is

$$\mathfrak{Z}_M = \sum_{\{n_k\}} \prod_{k=0}^{M} z^{n_k} \exp[-\beta U(k) n_k - \beta\phi n_k n_{k+1}]. \tag{2.1}$$

We shall only consider external potentials which are positive and increasing functions; ϕ however may have either sign. Equation (2.1) also describes (when the external potential is harmonic) a system of fermions with the nearest-neighbor interaction in momentum space. The existence of one-particle energy states is maintained as the interaction clearly commutes with the free particle Hamiltonian.

We will employ an adaption of the matrix technique used, for example, in the Ising problem,[4] to calculate $\mathfrak{Z}_M$. Define a two-by-two matrix P_k with matrix elements

$$P_k = \begin{pmatrix} 1 & zx_k \\ 1 & zx_k\Phi \end{pmatrix}, \tag{2.2}$$

where $x_k = \exp[-\beta U(k)]$ and $\Phi = \exp[-\beta\phi]$. By the convenient choice of the periodic boundary condition

$$n_{M+1} = n_0,$$

$\mathfrak{Z}_M$ becomes

$$\mathfrak{Z}_M = \text{Trace} \prod_{k=0}^{M} P_k. \tag{2.3}$$

A matrix product containing $k+1$ factors obeys the recursion relation

$$\begin{pmatrix} a_{k+1} & b_{k+1} \\ c_{k+1} & d_{k+1} \end{pmatrix} = \begin{pmatrix} a_k & b_k \\ c_k & d_k \end{pmatrix} P_{k+1},$$

which is equivalent to four difference equations among the matrix elements:

$$a_{k+2} - (1 + zx_{k+1}\Phi)a_{k+1} + zx_{k+1}(\Phi - 1)a_k = 0, \tag{2.4a}$$

$$b_k = a_{k+1} - a_k, \tag{2.4b}$$

and a similar pair of relations obtained by replacing a_k by c_k and b_k by d_k. (The initial conditions, assuming $U(0) = 0$, are $a_0 = 1$ and $a_1 = 1 + z$.) If we define

$$v_k = \frac{a_{k+1}}{a_k}$$

the v_k satisfy the non-linear recursion relation

$$v_{k+1} = \frac{1 + zx_{k+1}\Phi - zx_{k+1}(\Phi - 1)}{v_k}, \tag{2.5}$$

which has the terminating continued fraction expansion

$$v_{k+1} = 1 + zx_{k+1}\Phi - \cfrac{zx_{k+1}(\Phi - 1)}{1 + zx_k\Phi - \cfrac{zx_k(\Phi - 1)}{1 + zx_{k-1}\Phi} - \cdots - \cfrac{zx_1(-\Phi 1)}{1 + z}}. \tag{2.6}$$

It follows therefore that the matrix element a_k is the product

$$a_{k+1} = \prod_{i=0}^{k} v_i. \tag{2.7}$$

If this product converges as k becomes infinite, the grand partition function in the limit $M \to \infty$ depends on a single matrix element by (2.4b). It is

$$\mathfrak{Z} = \prod_{k=0}^{\infty} v_k. \tag{2.8}$$

The convergence of (2.8) will be shown in Appendix A. It is brought about, of course, by the presence of the decaying exponential factor provided by the external potential. The grand potential per unit length, the quantity usually considered, vanishes in the semi-infinite system limit as do all other length averages. Nevertheless, *locally* dependent densities and pressures remain non-vanishing functions.

The one-particle distribution is found by inserting n_k inside the product of (2.1) and dividing by $\mathfrak{Z}$. It is therefore given by the formula (regarding the $\{x_k\}$ as a set of independent variables),

$$n_1(k) = x_k \frac{\partial \ln \mathfrak{Z}}{\partial x_k} = x_k \sum_{i=k}^{\infty} \frac{\partial \ln v_i}{\partial x_k}, \tag{2.9}$$

in the semi-infinite system. We observe that Eq. (1.10) is satisfied for interchanging the order of the sums

$$\sum_{k=0}^{\infty} n_1(k) = \sum_{i=0}^{\infty} \sum_{k=0}^{i} x_k \frac{\partial \ln v_i}{\partial x_k} = z \sum_{i=0}^{\infty} \frac{\partial \ln v_i}{\partial z} = \langle N \rangle.$$

To illustrate the complexity of the functions (2.9), assume $k \gg 1$ (or $z \ll 1$). Equation (2.5) implies that v_k approaches unity when k becomes large, so we define a y_k by

$$v_k = 1 + y_k.$$

If y_k is small it will approximately satisfy the first order difference equation

$$y_{k+1} - zx_{k+1}(\Phi - 1)y_k - zx_{k+1} = 0, \qquad (y_0 = z) \tag{2.10}$$

which can be exactly solved. When the solution of (2.10) is inserted into the linearized version of (2.9), we obtain the densities

$$n_1(k) = \left\{ \sum_{i=k}^{\infty} \prod_{j=1}^{i} z(\Phi - 1)x_j \right\} \times \left\{ z + \sum_{i=1}^{k} \left[zx_i \Big/ \left(\prod_{j=1}^{i} z(\Phi - 1)x_j \right) \right] \right\} \tag{2.11}$$

In the absence of the pair interaction, Eq. (2.11) reduces to a Boltzmann distribution.

Finally, we state a theorem about the matrix elements a_k. Inspection of Eq. (2.4a) shows that a_k is a polynomial in z of order k having positive coefficients, hence a_k has no zeros for real, positive z. If z is permitted to take on complex values, it can be shown that the $a_k(z)$ has all its zeros on the negative real axis, for arbitrary k, when the nearest-neighbor interaction is positive. We conclude that the zeros of the grand partition function, in the semi-infinite system, lie entirely on the negative real axis. The proof follows in Appendix B. We can to some extent characterize the complex zeros of $a_k(z)$ for negative potentials, but we have not been able to rule out the occurrence of non-analyticities on the positive real axis as $k \to \infty$ in this case. For a system which is finite in extent the grand partition function is analytic everywhere in the complex z plane. For such a system, there must also exist some external forces in the form of wall forces to confine it in space. We conjecture that the grand partition function will continue to be analytic in the limit of infinite volume in the presence of *any* external force of the kind considered here.

Appendix A. Convergence of Grand Partition Function

A necessary and sufficient condition that $\prod_{k=0}^{\infty} v_k$ converges, i.e., has a finite, non-zero value, is that $\sum_{k=0}^{\infty} y_k$ converges where

$$y_k = v_k - 1 = zx_k\left[\Phi + \frac{1-\Phi}{v_{k-1}}\right] \tag{A.1}$$

by Eq. (2.5). The proof is trivial: when the pair potential is positive ($0 < \Phi < 1$), it is obvious from (2.5) that all the v_k are greater than unity, while (2.10) indicates that the same is true when the potential is negative, ($1 < \Phi < \infty$). In both cases

$$y_k < zx_k,$$

and the series converges for all positive z.

Appendix B. Zeros of the Grand Partition Function

We will need some general theory of continued fractions.[5] One defines the kth *approximant* to a (possibly infinite) continued fraction, P_k/Q_k, to be

$$P_k/Q_k = q_0 + \cfrac{p_1}{q_1 + \cfrac{p_2}{q_2 + \cfrac{\ddots}{\cfrac{\ddots}{\cfrac{+p_k}{q_k}}}}}, \tag{B.1}$$

and one can show that

$$\frac{P_{k-1}}{Q_{k-1}} - \frac{P_k}{Q_k} = (-1)^k \frac{p_1 \cdots p_k}{Q_k Q_{k-1}}. \tag{B.2}$$

The v_k in the text terminates, thus it is equal to its own kth approximant.

Consider the fraction (B.1), with q_0 set to zero for convenience, in which the $\{p_i\}$ are real and positive and the $\{q_i\}$ are complex having positive real parts. The fraction v_k assumes this form, when the pair potential is positive, by making the substitutions

$$z = w^2$$
$$v_k(z) = v_k'(w)w,$$

into (2.5) and dividing by w. We may regard (B.1) as being generated by the sequence of transformations

$$t_1(s) = p_1/(q_1 + s), \qquad t_i(s) = p_i/(q_i + s), \qquad i = 1, 2, \ldots, k$$

so that

$$\frac{P_k}{Q_k} = t_1 t_2 \ldots t_k(0). \tag{B.3}$$

Since $\operatorname{Re} q_i > 0$ the transformation $t_i(s)$ maps the right half-plane of s into the right half-plane of t_i, in particular $t_1(s)$ maps $\operatorname{Re} s \geqslant 0$ upon the circular region

$$\left| t_1 - \frac{p_1}{2 \operatorname{Re} q_1} \right| \leqslant \frac{p_1}{2 \operatorname{Re} q_1}. \tag{B.4}$$

(The value of the first approximant lies on the circumference of this circle.) We conclude that the product of transformations (B.3) maps

$\mathrm{Re}\, s \geqslant 0$ into this same circular region i.e.,

$$\left| \frac{P_k}{Q_k} - \frac{p_1}{2\,\mathrm{Re}\, q_1} \right| \leqslant \frac{p_1}{2\,\mathrm{Re}\, q_1}, \tag{B.5}$$

or the fraction is bounded in a region in the complex activity plane equivalent to $\mathrm{Re}\, q_1 > 0$. This region is

$$\mathrm{Re}\left\{ \frac{1}{w} + w\Phi x_{k-1} \right\} > 0,$$

or

$$\mathrm{Re}\, w > 0 \tag{B.6}$$

Hence $v_k(z)$ is bounded in the full z plane with the exception of the negative real axis. Since, by (B.2), the numerator and denominator of any approximant cannot vanish simultaneously, $a_k(z)$ has all its zeros on the negative real axis.

Similar considerations for negative pair potentials (define $iv_k(z) = v_k'(w)w$) lead only to the inconclusive result that the complex zeros of $a_k(z)$ lie in the annular region

$$\mathrm{Min}\left\{ 1, \frac{1}{x_1 \Phi} \right\} \leqslant |z| \leqslant \frac{1}{x_{k-1}\Phi}.$$

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