ONE-DIMENSIONAL STATISTICAL MODELS

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The properties of one-dimensional statistical systems are studied. A consistent comparison of the values of the binary correlation function obtained from the configuration integral and from Bogolyubov chain equations in various approximations is presented. The results obtained here are discussed briefly.

The existing methods for studying the behavior of real statistical systems are usually based on perturbation theory, and the presence of small parameters characterizing the proximity of the system to an ideal system is assumed. Strongly interacting systems do not permit the isolation of small parameters; therefore, there are no effective methods for studying them at present. In this connection, it appears to be of interest to turn to one-dimensional systems which enable the investigation to be advanced much further and, in particular, permit a consideration of the case of strong interaction. Comparison of the exact results with approximate results obtained by methods for decomposing chains of recurrence equations for correlation functions [1] may be regarded as a qualitative criterion of the accuracy of the latter.

Configuration integrals for one-dimensional statistical systems were first obtained in reference [2]. Papers have recently appeared in which one-dimensional models are studied by methods of the theory of stochastic processes [3-6].

1. Consider one-dimensional equilibrium isothermal system consisting of N particles on a segment of the Ox-axis of length L. The statistical properties of the system can be studied by the Gibbs method. Let (p, q) be the set of N momenta and N coordinates of the particles in the system. As is known, the distribution function of such a system is of the form [7]

$$f = Z^{-1} \exp\left(-H(p, q) / kT\right).$$

Here H is the hamiltonian of the system, k is the Boltzmann constant, and T is the temperature. The constant Z is called the statistical integral of the system. From the normalization condition for the distribution function

$$Z = \int \exp\left(-\frac{H(p, q)}{kT}\right) dp\, dq.$$

It is not difficult to show that in the case under consideration

$$Z = \left(\frac{mkT}{2\pi h^2}\right)^{N/2} \frac{Q_N}{N!} \equiv$$

$$\equiv \left(\frac{mkT}{2\pi h^2}\right)^{N/2} \frac{1}{N!} \int_0^L \ldots \int_0^L \exp\left(-\frac{U_N}{kT}\right) dx_1 \ldots dx_N. \quad (1.1)$$

Here m is the particle mass, h is Planck's constant, and U_N the part of the function H depending only on the coordinates. Thus, we obtain full information on the system if we can calculate Q_N (the configuration integral).

If the particles are impenetrable, then

$$0 \leqslant x_1 < x_2 < \ldots < x_N \leqslant L. \quad (1.2)$$

In the approximation in which only closest neighbors interact,

$$U_N = \sum_{(1 \leqslant i \leqslant N-1)} \Phi\left(|x_{i+1} - x_i|\right) + U_L.$$

Here Φ is the particle interaction potential and U_L is the energy of interaction with the wall. If the wall consists of particles of the same nature, then

$$U_L = \Phi(x_1) + \Phi(L - x_N).$$

Employing the method of reference [2], with the aid of the Laplace transformation, the convolution theorem, and the method of steepest descent, we obtain an expression for the configuration integral

$$Q_N = e^{p\beta L} \{\varphi(p\beta)\}^{N+1}, \qquad \varphi = \int_0^\infty e^{-\beta[px + \Phi(x)]}\, dx. \quad (1.3)$$

Here p is the pressure.

Let us take a model of the system in which the particles are spheres of radius a, interacting with each other according to a law determined by choice of the potential

$$\Phi(|x_i - x_j|) = \Phi_{el}(|x_i - x_j|) + K(|x_i - x_j|).$$

Here Φ_{el} is the potential of the electric forces, which we take in the form

$$\Phi_{el}(x) = \infty \qquad (x < a),$$

$$\Phi_{el} = \Phi_{el}(a)(a / x) \exp\left[\gamma(a - x)\right] \qquad (x \geqslant a).$$

We take the potential K(x) in the form of a modified Lennard-Jones potential

$$K(x) = \infty \qquad (x < a),$$

$$K(x) = \delta\omega(\omega_2 / \omega_1)^{\omega}\left[(a / x)^{\omega_1} - (a / x)^{\omega_2}\right] \qquad (x \geqslant a).$$

Here δ is the depth of the potential well and $\omega = \omega_1/(\omega_2 - \omega_1)$. The first term characterizes the close-range repulsion, the second the attraction at greater distances. Usually, we take $\omega_1 = 12$ and $\omega_2 = 6$ [8].

Henceforth, we shall express all quantities in units of a (a = 1) and introduce for convenience the following notation

$$\mu = \beta\Phi_{el}(1), \qquad \chi = \beta\delta, \qquad \eta = \chi\omega(\omega_2 / \omega_1)^{\omega(\omega_2/\omega_1)}$$

According to (1.3),

$$\varphi(p\beta) = \quad (1.4)$$

$$= \int_1^\infty \exp\{-[\beta px + (\mu / x) e^{-\gamma(x-1)} + \eta (x^{-\omega_1} - x^{-\omega_2})]\} dx =$$

$$= \sum_{k=0}^\infty \sum_{n=0}^\infty \sum_{m=0}^\infty \frac{(-1)^{k+n}}{k!n!m!} \mu^k \eta^{m+n} e^{\gamma k} E_{k+\omega_1 n+\omega_2 n} (p\beta + \gamma k).$$

Here E_ν is an exponential integral function of ν-th order. In the purely electrostatic case (K = 0)

$$\varphi (p\beta) = (p\beta)^{-1} \exp (-p\beta) +$$
$$+ \sum_{n=1}^\infty \frac{(-1)^n}{n!} e^{\gamma n} \mu^n E_n (p\beta + n\gamma). \tag{1.5}$$

We note that the term preceding the sum in (1.5) is the result obtained for solid spheres [9].

For a "real" gas ($\Phi_{el} = 0$)

$$\varphi (p\beta) = (p\beta)^{-1} \exp (-p\beta) + \sum_{m,n=0}^{\infty'} \frac{(-1)^n}{m!n!} E_{\omega_1 n+\omega_2 m} (p\beta). \tag{1.6}$$

The prime means that a term is lacking in the sum when m = 0 and n = 0, simultaneously.

2. Now we shall consider the computation of the binary correlation function g(x) starting from the expression (1.3) for the configuration integral. Let

$$dW (\xi, m) = \psi_m (\xi)\, d\xi \qquad \left(\int_0^\infty \psi_m (\xi)\, d\xi = 1\right) \tag{2.1}$$

be the probability of discovering two specific particles of the system separated by (m − 1) others. obviously, $\xi = |x_k - x_{k\pm m}|$, where k is the number of the fixed particle. When m = 1 we find the distribution of the nearest neighbor, when m = 2, that of the second nearest neighbors, etc. We shall assign to the configuration integrals of the subsystems subscripts which indicate the number of particles in the subsystem. Setting $\xi = L - x_{N-m}$, it is not difficult to obtain

$$\psi_m (\xi) = \frac{Q_{m-1}(\xi)\, Q(L-\xi)}{Q_N(L)}. \tag{2.2}$$

Going over to the asymptotic values ($N \to \infty$, $L \to \infty$, $L/N \to l$, l is a constant) yields

$$\psi_m (\xi) = \{\varphi (p\beta)\}^{-m} Q_{m-1} (\xi) \exp (-p\beta\xi) \tag{2.3}$$

$$\psi_1 (\xi) = \frac{e^{-\beta(p\xi+\Phi(\xi))}}{\varphi (p\beta)} \text{ when } m = 1 \tag{2.4}$$

$$\psi_m (\xi) = \frac{e^{-p\beta\xi}}{\{\varphi(p\beta)\}^m} \frac{1}{2\pi i} \oint \{\varphi (s)\}^m e^{s\xi}\, ds \text{ when } m > 1.$$

The integration path includes all strips of the integrand. With one particle fixed, the probability of discovering any other particle at a distance of from x to x + dx from the first one is equal to

$$dW (x) = L^{-1} g (x)\, dx. \tag{2.5}$$

Here g(x) is the one-dimensional analog of the radial distribution function. It follows from (2.1) and (2.5) that

$$g (x) = l \sum_{m=1}^\infty \psi_m (x) =$$

$$= \frac{l e^{-p\beta x}}{2\pi i} \sum_m \{\varphi (p\beta)\}^{-m} \oint e^{sx} [\varphi (s)]^m\, ds. \tag{2.6}$$

We shall denote the sums in (1.4)—(1.6) by R(s). As can be seen from (2.6), in order to compute g(x), we must first find the residues at all poles of the function

$$e^{sx} \left\{\frac{e^{-sx}}{s} + R (s)\right\}^m \quad \text{for } m = 1, 2, \ldots$$

and then sum over m. Making use of the residue theorem, and considering only those singularities that make a basic contribution to (2.6), we finally get

$$g (x) = 0 \qquad (x < 1),$$

$$g (x) = \frac{e^{-p\beta x}}{l} \sum_m \frac{1}{[\varphi (p\beta)]^m} \sum_{\lambda=1}^m \frac{C_\lambda{}^m}{(\lambda-1)!} \times$$

$$\times \sum_{k=0}^{\lambda-1} C_k{}^{\lambda-1} (x-\lambda)^k [R^{m-\lambda} (0)]^{\{\lambda-k-1\}}$$

$$(x \geqslant 1). \tag{2.7}$$

Here C are the binomial coefficients , and $\{\lambda - k - 1\}$ denotes ($\lambda - k - 1$)-ple differentiation. The summation over m for fixed x is extended to values of m satisfying the inequality x > m. When m = λ = = k + 1 (solid noninteracting spheres), we get the result of reference [9].

3. We shall now compute the binary correlation function g(x), starting with the chain equations [1, 10], and making use of the approximations of reference [11]. The Kirkwood hypothesis permits us to express the triplet distribution function as a superposition of binary functions, that is, $F_3(123) = g(12)\,g(23)\,g(31)$.

We introduce the correlation coefficients $\varepsilon_{ij} = g_{ij} - 1$ and, for convenience, occasionally write $\Theta = kT = 1/\beta$.

Then we can obtain the following equations for ε_{12}:

$$\theta \frac{\partial}{\partial x_1} \ln (1 + \varepsilon_{12}) = F_{12} + \frac{1}{l} \int (1 + \varepsilon_{13})\, \varepsilon_{23} F_{13} dx_3,$$

$$\theta \frac{\partial}{\partial x_2} \ln (1 + \varepsilon_{12}) = F_{12} + \frac{1}{l} \int (1 + \varepsilon_{23})\, \varepsilon_{13} F_{23} dx_3,$$

$$\left(F (x) = -\frac{\partial \Phi (|x|)}{\partial x}\right).$$

The order of the particles is fixed; therefore $x_{13} = x_{12} + x_{23}$. We write $x_{12} = x$, $x_{23} = y$, and $x_{13} = x + y$; and obtain an equation for determining ε(x)

$$\theta \frac{d}{dx} \ln [1 + \varepsilon (x)] = F (x) + \tag{3.1}$$

$$+\frac{1}{l}\int_0^\infty F(x+y)\,\varepsilon(y)\,(1+\varepsilon(x+y))dy. \quad (3.1)$$
(cont'd)

We now make use of an approximation analogous to the approximation of reference [11],

$$\frac{1}{x_{13}}\approx\frac{1}{x_{23}}\left(1+\frac{x_{12}}{x_{23}}\right) \quad (x_{23}>x_{12}),$$

$$\frac{1}{x_{13}}\approx\frac{1}{x_{12}}\left(1+\frac{x_{23}}{x_{12}}\right) \quad (x_{23}<x_{12}).$$

By linearizing (3.1) and differentiating the result twice, we get the ordinary differential equation

$$\left(\frac{\varepsilon'}{\Phi'}\right)'+\frac{\alpha\beta\varepsilon}{l}=0, \quad (3.2)$$

Let us consider some special cases.

1°. Let $\Phi(x) = 1/x$. Then, on the basis of (3.2)

$$\frac{d}{dx}\left(x^2\frac{d\varepsilon}{dx}\right)-\frac{\alpha\varepsilon}{l\theta}=0.$$

This implies that

$$g(x)=1-\varepsilon(x)=1-(\varkappa x)^{-\varkappa},$$

$$\varkappa={}^1/_2\,(1+\sqrt{1+4\alpha/l\theta}). \quad (3.3)$$

It can be seen from (3.3) that, unlike the three-dimensional case, there is no exponential decay of g(x) with increasing x. This is connected with the longer-range character of the forces in the one-dimensional case.

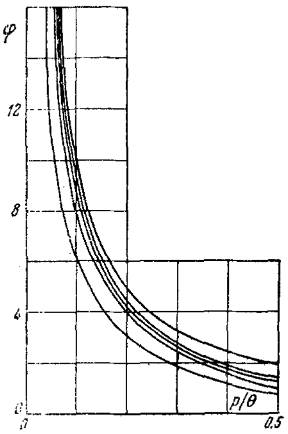

Fig. 1. From top to bottom: a) ideal gas; b) ω_2 = 6—attraction; c) solid spheres; d) ω_1 = 12—repulsion; e) ω_1 = 1.

2°. Let us consider $\Phi(x)\sim\pm x^{-\omega}$. Equation (3.2) takes the form

$$-\frac{1}{\omega}\left(x^{\omega+1}\frac{d\varepsilon}{dx}\right)'\pm\nu\varepsilon=0,\ \pm\nu\varepsilon(1)\frac{\omega-1}{\omega}\equiv K_1,\quad \nu=\frac{\delta}{l\theta}. \quad (3.4)$$

The plus and minus signs are associated with attraction and repulsion, respectively.

In the case of repulsion

$$\varepsilon(x)=\varepsilon(1)+C\sum_{n=0}^{\infty}\left\{a_k e^{-X(x)}+\frac{\vartheta+1}{\vartheta-1}(-1)^k b_k e^{X(x)}\right\}\frac{X}{k!}+$$

$$+\frac{K_1}{\vartheta-1}\sum_{k=0}^{\infty}(-1)^k b_k e^{X(x)}\frac{X^k(x)}{k!}. \quad (3.5)$$

$$\vartheta=\frac{\omega-1}{2\omega},\qquad X=\frac{1}{\vartheta}\frac{\sqrt{\nu}}{\sqrt{\omega}}x^{-1/2(\omega+1)},$$

$$\binom{a_0}{b_0}=1\pm\vartheta,\quad \binom{a_k}{b_k}=\prod_{j=1}^{k}\frac{(2j-1)\vartheta\mp1}{k\vartheta\mp1}.$$

The constants C and $\varepsilon(1)$ may be determined if we substitute x = 1 into (3.5) and (3.5) into (3.1), and consider the expressions obtained in this way simultaneously. The expressions obtained for C and $\varepsilon(1)$ are very cumbersome.

If we take only the attraction between particles into consideration, the solution of equation (3.4) is of the form

$$\varepsilon(x)=\frac{K_1}{\nu}+\frac{x^{-\omega/2}}{\nu}\left\{CJ_\sigma(Xx)-K_1\sin(\pi\sigma)\Gamma\left(\frac{2\omega-1}{\omega-1}\right)\times\right.$$

$$\left.\times\left(\sigma\sqrt{\frac{\nu}{\omega}}\right)^\sigma Y_\sigma(Xx)\right\} \quad (3.6)$$

$$(\sigma=1/2\vartheta).$$

Here J is a cylindrical function of the first kind and Y a cylindrical function of the second kind. The constant C is determined in the same way as for (3.5) and is again very cumbersome.

3°. Let $\Phi(x)=(\alpha/x)\exp(-\gamma x)$. The solution of the linearized equation, in the form of a Neumann series, is written

$$\varepsilon(x)=\beta\left\{-\alpha\frac{e^{-\gamma x}}{x}+\frac{1}{l}[E_1\{\gamma(1+x)\}-E_1(\gamma x)]-\right.$$

$$\left.-\alpha\sum_{m=1}^{\infty}\left(-\frac{\beta}{l}\right)^m\int_1^\infty K_m(x,s)\frac{e^{-\gamma s}}{s}ds\right\},$$

$$K_0=\frac{e^{-\gamma(x+s)}}{x+s},\qquad K_m=\int_1^\infty K_{m-1}(x,t)K_0dt. \quad (3.7)$$

Due to the rapid convergence of the series in (3.7), the expression for $\varepsilon(x)$ can be represented with good accuracy in the form

$$-\varepsilon(x)=\frac{1+x}{\theta l}\{E_1(\gamma x)-E_1[\gamma(1+x)]\}+$$

$$+\frac{\alpha}{\theta}\frac{e^{-\gamma x}}{x}\left\{1-\frac{(1+x)}{\theta l}x\sum_{k=0}^{\infty}(-1)^k\frac{E_{k+1}(2\gamma)}{(x+1)^{k+1}}+A(x)\right\}. \quad (3.8)$$

Here

$$A(x)=\int_1^\infty\frac{e^{-\gamma s}}{x+s}\{E_1[\gamma(1+s)]-E_1(\gamma s)\}ds$$

is a rapidly converging integral which can easily be calculated approximately. As before, $g(x) = 0$ ($x < 1$) and $g(x) = 1 + \varepsilon(x)$ ($x \geq 1$).

4°. In conclusion, let us consider the nonlinearized equation for g(x) in the Kirkwood approximation. Turning from (x) to g(x), we rewrite (3.1) in the form

$$\frac{d}{dx} \ln g(x) =$$

$$= \xi F(x) + \zeta \int_0^{\infty} g(x+s)\,[g(s) - 1]\,F(x+s)\,ds \qquad (3.9)$$

$$\left(F(x) = \left(\gamma + \frac{1}{x}\right)\frac{c^{-\gamma x}}{x} + \frac{\omega_2}{x^{\omega_2+1}} - \frac{\omega_1}{x^{\omega_1+1}} \right).$$

The equation was solved by successive approximation with the aid of a computer. The same variations were considered in this case as in the linearized case. The convergence of the solution was investigated by the fixed point principle. The investigation showed that there exists a region of values of the parameters ξ, ζ where the successive approximations converge. We note that by virtue of the fixed order of the particles, the value of the integral in equation (3.9) is smaller than in the corresponding three-dimensional equation. This leads to the lack of a clearly expressed short-range order in the structure of the system (absence of oscillations), that is, the nonlinearity of the equation has little effect.

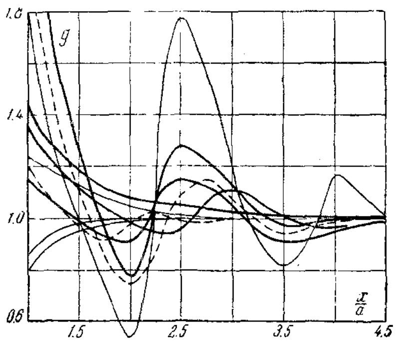

Fig. 2. From top to bottom: a) $\omega_1 = 12$, $l = 2$; b) solid spheres $l = 2$; c) $\omega_2 = 6$, $l = 2$; d) $\omega_2 = 6$, $l = 2$—equation linearized; e) $\omega_1 = 12$, $l = 8$; f) $\omega_2 = 6$, $l = 8$—equation linearized; g) solid spheres, $l = 8$; h) $\omega_2 = 6$, $l = 8$; i) $\omega_1 = 12$, $l = 8$—equation linearized; j) $\omega_1 = 12$, $l = 2$—equation linearized.

4. We have made a consistent comparison of the binary correlation functions of a one-dimensional system calculated with the aid of the configuration integral in the nearest-neighbor approximation and from chains of equations for the correlation functions.

Figure 1 shows the curves for $\varphi(p, T)$ determined in § 1. Curve 1 corresponds to an ideal gas, 2 to $\omega_2 = 6$ (attraction), 3 to solid spheres, 4 to $\omega_1 = 12$ (repulsion), and 5 corresponds to $\omega_1 = 1$. Different potentials with $\gamma \neq 0$ yield curves between 2 and 3. It can be seen from Fig. 1 that the maximum relative divergence of the graphs is about 200% for the largest p/Θ.

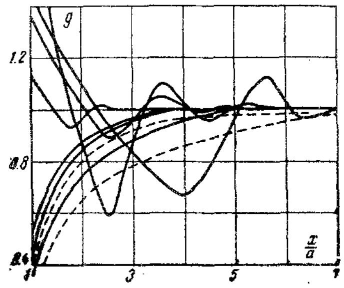

Fig. 3. From top to bottom: a) $\omega_2 = 6$, $l = 8$, $\alpha\beta = 0.25$; b) $\omega_2 = 6$, $l = 8$, $\alpha\beta = 1$; c) $\omega_2 = 6$, 12, $l = 2$, $\alpha\beta = 1$; d) $\omega_2 = 6$ and 12, $l = 16$, $\alpha\beta = 0.25$; e) $\omega_1 = 12$, $l = 2$, $\alpha\beta = 1$; f) $\omega_1 = 12$, $l = 8$, $\alpha\beta = 1$; g) $\gamma = 0.5$, $l = 8$, $\alpha\beta = 0.5$; h) $\gamma = 0.5$, $l = 16$, $\alpha\beta = 1$; i) $\gamma = 0.1$, $l = 8$, $\alpha\beta = 1$.

Figure 2 shows values of $g(x/a)$ for potentials of the Lennard-Jones type and solid spheres. Damped oscillations of the correlation functions calculated from the configuration integral can be seen; this is evidence of a clearly expressed short-range order. Compared with the three-dimensional model, the radius of the region of short-range order is significantly greater in the one-dimensional case. As the amplitude increases and the temperature decreases, the amplitudes of the oscillations increase and the region of oscillation occupies a larger area.

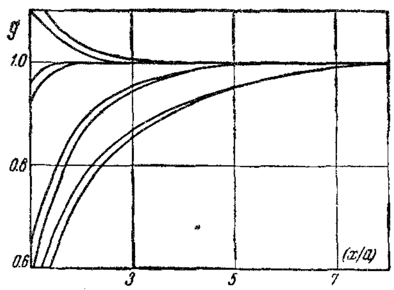

Fig. 4. (1)—$\gamma = 0.5$, $l = 2$; (2)—$\gamma = 0.1$, $l = 2$; (3)—$\gamma = 0.5$, $l = 4$; (4)—solid spheres, $l = 8$; (5)—$\gamma = 0.5$, $l = 8$; (6)—$\gamma = 0.1$, $l = 8$; (7)—Φ 1/x, $l = 8$; (8)—$\gamma = 0.5$, $l = 16$.

It can be seen from the curves in Fig. 3 that $g(x/a)$ calculated in the superposition approximation gives an asymptotically correct description of the properties of the system, differing materially from the exact value close to the boundary of the particle. The linearized superposition approximation gives an even greater divergence from the exact solution at small x/a and describes the asymptotic properties well. We note that the sharpness of the first peak is connected with the discontinous nature of the potential. For comparison, $g(x/a)$ for solid spheres calculated from the configuration integral are shown by a dashed line.

Figure 4 shows graphs of $g(x/a)$ for a purely electrical interaction. Analogous comparisons are made. The same conclusions can be drawn in regard to the general nature of the bahavior of the functions as in the preceding case. Also presented are graphs of $g(x/a)$ for the potential whose three-dimensional analogs are the correlation functions calculated in the Debye-Hückel approximation.

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