

**BRIEF
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One-Dimensional Classical Model with Phase Transition

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This study is devoted to the investigation of phase transition (PT) in a one-dimensional classical system and to the determination of the dependence of the critical parameters on the characteristics of the model interaction potential. One of the approaches to the determination of the correlation between macroscopic properties of a substance and its microscopic characteristics is based on the calculation of the partition function Z . From this standpoint, this study is a further development of [1, 2]. For N monatomic particles of the system, the calculation of the kinetic part of Z presents no difficulties. As is known, the calculation or estimation of the configuration part of Z is a complex problem.

In [3], an expression for the logarithm of the configuration integral was found in the quadratic approximation of the saddle-point method,

$$\ln Z_c = \frac{N\beta}{2}(v(0) - nv(0)) - \frac{V}{2} \int_{\Omega} \frac{d^D \mathbf{k}}{(2\pi)^D} \ln(1 + n\beta \tilde{v}(\mathbf{k})),$$

where D is the dimensionality of space; $\beta = 1/T$ is the inverse temperature (Boltzmann constant $k_b = 1$); $n = N/V$ is the density; and $v(r)$ and $\tilde{v}(k)$ denote the pair central interaction potential and its Fourier transform, respectively. The calculation of thermodynamic functions is performed by standard methods using the free energy. Thus, the equation of state of the system being treated has the form

$$P = P_{id} + \frac{n^2 \tilde{v}(0)}{2} - \frac{T}{2} \int_{\Omega} \frac{dk}{2\pi} [\ln(1 + n\beta \tilde{v}(k)) - n \frac{\partial}{\partial n} \ln(1 + n\beta \tilde{v}(k))]. \quad (1)$$

The fundamental approximation, which may be used for any liquids, implies that their properties are largely defined by the repulsive part of the potential [4]. This assumption is supported by the results of [5] in

numerical simulation of a liquid, which agree with experimental data for real liquids. Therefore, for the sake of simplicity of the calculations, we will take into account only the repulsive forces, and the form of the interaction potential will be preassigned by a monotonically decreasing function of r ,

$$v(r) = \frac{A}{2a} \exp(-ar), \quad A > 0, \quad a > 0 \quad (2)$$

with a positive Fourier transform,

$$\tilde{v}(k) = A/(k^2 + a^2). \quad (3)$$

Within the framework of the suggested model, we integrate Eq. (1) to find

$$P = nT + \frac{n^2 \tilde{v}(0)}{2} - \frac{T}{4} \left[\frac{2 + n\beta \tilde{v}(0)}{\sqrt{1 + n\beta \tilde{v}(0)}} - 2 \right]. \quad (4)$$

One can use the equation of state (4) to obtain a detailed description of the subcritical region, similar to the description obtained using the van der Waals equation. Traditional conditions defining the critical state are provided by the set of equations

$$\left(\frac{\partial P}{\partial n} \right)_T = T + n\tilde{v}(0) - \frac{a\tilde{v}(0)}{8} \frac{n\beta \tilde{v}(0)}{(1 + n\beta \tilde{v}(0))^{3/2}} = 0, \quad (5)$$

$$\left(\frac{\partial^2 P}{\partial n^2} \right)_T = \tilde{v}(0) - \frac{a\beta \tilde{v}^2(0)}{16} \frac{(2 - n\beta \tilde{v}(0))}{(1 + n\beta \tilde{v}(0))^{5/2}} = 0,$$

whose solution is easy and permits an exact representation of the critical parameters,

$$n_c = \frac{a}{30(5/3)^{3/2}}, \quad \beta_c = \frac{20(5/3)^{3/2}}{a\tilde{v}(0)}, \quad (6)$$

$$P_c = n_c T_c \left(15 \left(\frac{5}{3} \right)^{3/2} - 32 \right).$$

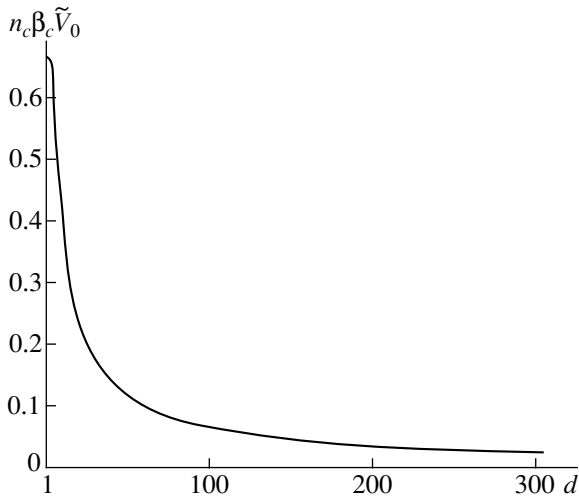


Fig. 1. Dependence of the quantity $n_c \beta_c \tilde{v}_0$ on the parameter d .

These parameters make it possible to reduce the equation of state (4) to the dimensionless form

$$\pi(\tau, \varphi) = \frac{1}{Z_c} \left(\frac{\tau}{\varphi} + \frac{1}{2\varphi^2} - 5 \left(\frac{5}{3} \right)^{3/2} \tau \left[\frac{3 + 1/\tau\varphi}{\sqrt{1 + 2/3\tau\varphi}} - 3 \right] \right). \quad (7)$$

Here, $\tau = \beta_c/\beta$ and $\varphi = n_c/n$ denote the reduced temperature and volume, and $Z_c \approx 0.275$ is the compressibility factor. The form of Eq. (7) is convenient for the construction of isotherms which have a characteristic S -like shape indicative of the first-order PT. By following the procedure described in [6], one can find in the neighborhood of the critical point (CP) the expressions for the density of coexisting phases and for the density in metastable states in the form of expansions in powers of the dimensionless temperature.

We will treat a less trivial one-dimensional model, for which the pair potential

$$v(r) = \frac{\exp(-ar)}{2} \left(\frac{A}{a} - Br \right) \quad (8)$$

has features of "real" properties (presence of the potential well, repulsion at small distances, and attraction at large distances); however, it is limited at zero, $v(0) = A/2a$. The simple analytical form of the model potential makes it possible to determine its minimum and find a Fourier transform,

$$\tilde{v}(k) = \frac{(A-B)a^2 + (A+B)k^2}{(k^2 + a^2)^2}, \quad (9)$$

which is nonnegative if the inequality $A \geq B$ is valid. This is the condition of validity of approximation (1) at

any temperature, because, in this case, the integrand in (1) has no singular points.

To find the equation of state for a system with potential (8), we integrate (1) with due regard for the Fourier transform (9). As a result, we derive

$$P = nT + \frac{n^2 \tilde{v}_0}{2} - \frac{Ta}{4} \left[\sqrt{dn\beta \tilde{v}_0 + 2(1+q)} + \frac{(1+q)^2}{q\sqrt{dn\beta \tilde{v}_0 + 2(1+q)}} - 4 \right], \quad (10)$$

where $\tilde{v}_0 = \tilde{v}(0) = (A-B)/a^2$, $d = (A+B)/(A-B)$, and $q = \sqrt{1 + n\beta \tilde{v}_0}$. One can demonstrate that, in the limit $B \rightarrow 0$, equation of state (10) assumes the form of (4), and potential (8) transforms to (2). A set of equations that is similar to (5) but more cumbersome (here it is represented in a compact form) defines the critical state of model (8),

$$\left(\frac{\partial P}{\partial n} \right)_T = q^2 + \frac{an}{2} \frac{\partial^2}{\partial n^2} Q = 0, \quad (11)$$

$$\left(\frac{\partial^2 P}{\partial n^2} \right)_T = \beta \tilde{v}_0 - \frac{1}{2} \left(\frac{\partial^2}{\partial n^2} Q + n \frac{\partial^3}{\partial n^3} Q \right) = 0,$$

$$Q = \sqrt{dn\beta \tilde{v}_0 + 2(q+1)}.$$

An exact solution of such a system appears to be rather complicated and has not yet been obtained. Nevertheless, at least two approaches exist to the construction of its solution. The first approach is based on the representation of solutions based on the perturbation theory in the form of series in powers of small parameter: the attractive part of potential (8) is approximated by the second term, which may be treated as a small perturbation. The second approach implies the use of numerical methods of solution for any values of B that satisfy the inequality $A \geq B$. Obviously, both approaches must reflect the dependence of the critical parameters on the characteristics of the interatomic potential. However, the second approach is preferred, because it enables one to draw more complete qualitative and quantitative conclusions. To realize this latter approach, it is convenient to reduce the set of equations for determining the CP to a single nonlinear equation relative to the dimensionless quantity $n_c \beta_c \tilde{v}_0$ by way of dividing the first equation of the set by the second one,

$$\begin{aligned} & 2(2 + d(q-1))[(1+q)(2 + d(q-1)) + q(1+dq)^2] \\ & = 3(q-1)[q(1+q)(1+dq)(2 + d(q-1)) \\ & + (1+q)^2(2 + d(q-1))^2 + q^2(1+dq)^3], \end{aligned} \quad (12)$$

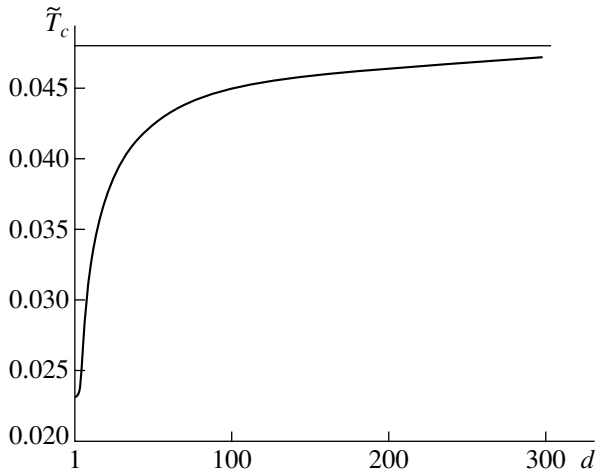


Fig. 2. Dependence of \tilde{T}_c on the parameter d defining the potential well depth.

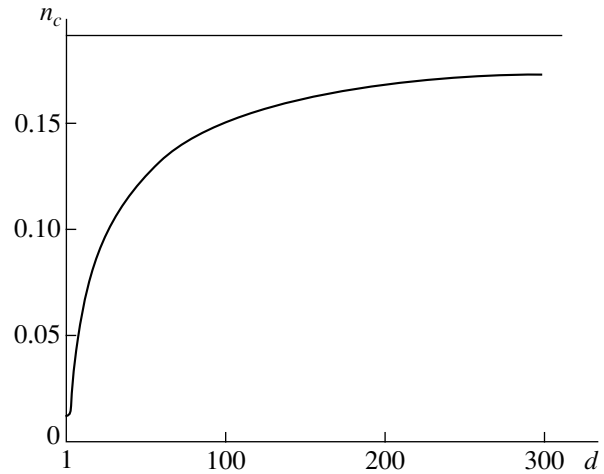


Fig. 3. Dependence of \tilde{n}_c on the parameter d .

$$q = \sqrt{1 + n_c \beta_c \tilde{v}_0}.$$

Equation (12) may have several roots. By the meaning of the problem, only one positive root, namely, $n_c \beta_c \tilde{v}_0 = 2/3$ at $d = 1$ ($B = 0$), is of interest as the initial one. Note that the point $d = 1$ is not a branching point for the roots of Eq. (12), which is solved using the Newton method. Figure 1 gives the dependence of $n_c \beta_c \tilde{v}_0$ on the parameter d related to the potential well depth, which was plotted using 43 points. The range of variation of the parameter d from unity to 300 corresponds to the variation of the potential well depth from zero to 99 percent of its maximum value. For the sake of simplicity of further analysis of the results, we will register the potential parameters a and A . In this case, the depth of the potential well is controlled by the quantity B . The function

$$v_m(d) = -\frac{A}{2ae} \left(\frac{d-1}{d+1} \right) \exp\left(-\frac{d+1}{d-1} \right),$$

which defines the minimum of potential (8), is monotonic and assumes the minimum value equal to $v_m = -A/2ae^2$ at $B = A$ ($d \rightarrow \infty$).

The critical temperature T_c was calculated by the equation $(\partial P / \partial n)_T = 0$, from which follows

$$T_c = \left(\frac{A}{a} \right) \frac{q(1+dq)^2 + Q^2}{4(1+d)q^5 Q^3} (q^2 - 1) = \left(\frac{A}{a} \right) \tilde{T}_c. \quad (13)$$

The values of $n_c \beta_c \tilde{v}_0$ required for this purpose and the respective values of d obtained during the solution

of Eq. (12) are also used to determine the critical density, whose value was calculated by the formula

$$n_c = a \left(\frac{q(1+dq)^2 + Q^2}{8q^5 Q^3} \right) (q^2 - 1)^2 = a \tilde{n}_c. \quad (14)$$

Figures 2 and 3 give the results of calculation of \tilde{T}_c and \tilde{n}_c . One can see that the critical temperature and density increase with the potential well depth. One can expect that T_c and n_c will approach their asymptotic values with a further increase in the well depth. If this is the case, the set of equations for determining the CP must have a solution in the limit $d \rightarrow \infty$. Indeed, in this case, Eq. (11) takes the form

$$\left(\frac{\partial P}{\partial n} \right)_T = 1 - \frac{aw}{2} \beta \frac{n\beta w}{(2n\beta w + 4)^{3/2}} = 0,$$

$$\left(\frac{\partial^2 P}{\partial n^2} \right)_T = -\frac{a}{2} (\beta w)^2 \frac{4 - n\beta w}{(2n\beta w + 4)^{5/2}} = 0,$$

and its solution is provided by the following values:

$$\beta_c = \frac{12\sqrt{3}}{aw}, \quad n_c = \frac{a}{3\sqrt{3}},$$

where $w = A/a^2$. The respective horizontal asymptotes are shown in Figs. 2 and 3. The obtained results may be used for the estimation of the thermodynamic properties of simple liquids in thin cylindrical pores.

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