BRIEF
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Determination of the Critical Parameters of a Classical One-Component System with Model Interaction Potential

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It is well known that the knowledge of free energy enables one to investigate all thermodynamic properties of a system. This paper deals with the investigation of phase transitions in classical one-component systems with two-particle central interaction potentials $v(|\mathbf{r}|)$ using the factorization method suggested previously in [1] to calculate the configuration integral. The present communication is based on the expression for the free energy of a system located in a volume V, whose N particles interact by means of a two-particle potential admitting the Fourier expansion [2]

$$F = -T\ln Z = F_{id} + \frac{N}{2}(n\tilde{v}_0 - v_0)$$

$$-\frac{TV}{2}\int_{\Omega^+}\frac{d^D\mathbf{k}}{(2\pi)^D}\ln(g_+(\mathbf{k})\sqrt{\pi N}\exp(X_+^2)\mathrm{erfc}(X_+)) \quad (1)$$

$$-\frac{TV}{2}\int_{\Omega^-}\frac{d^D\mathbf{k}'}{(2\pi)^D}\ln(g_-(\mathbf{k}')\sqrt{\pi N}\exp(X_-^2)\mathrm{erfc}(X_-)),$$

where F_{id} is the free energy of ideal gas, $n = N/V$ is the density, $\beta = 1/T$, T is the temperature in energy units, $X_\pm = \sqrt{N}(g_\pm(\mathbf{k}) \pm 1)$, $g_\pm(\mathbf{k}) = 1/n\beta v^\pm(\mathbf{k})$, $\Omega^\pm$ is a set of wave vectors $\mathbf{k}$, the Fourier transform

$$\begin{cases} v^+(\mathbf{k}) = \tilde{v}(\mathbf{k}), & \mathbf{k} \in \Omega^+ \\ v^-(\mathbf{k}) = -\tilde{v}(\mathbf{k}), & \mathbf{k} \in \Omega^- \end{cases}$$

of the two-particle central potential depends on the module of the vector $\mathbf{k}$, and v_0 and $\tilde{v}_0$ respectively denote the values of the potential and its Fourier transform at $r = 0$ and $k = 0$.

We will treat a model in which the interaction potential $v(|\mathbf{r}|)$ has a nonnegative Fourier transform (the set Ω^- is empty), which corresponds to repulsion in the k-space. We will demonstrate below that the potential $v(|\mathbf{r}|)$ with $v(k) > 0$ is not necessarily repulsive in the coordinate space and may possess characteristic features of real potentials. The quantity $g_+(k)$ is positive by definition; therefore, at $N \sim 10^{23}$, the parameter $X_+ \gg 1$.

Then, we use the asymptotics of the probability integral to find the expression for free energy,

$$F = F_{id} + \frac{N}{2}(n\tilde{v}_0 - v_0)$$

$$-\frac{TV}{2}\int_{\Omega^+}\frac{d^D\mathbf{k}}{(2\pi)^D}\ln(1 + n\beta v^+(k)). \quad (2)$$

Note that the result (2) may be derived both by the method of collective variables [3] and by the saddle-point method [4].

Equation (2) yields the equation of state[1]

$$P = P_{id} + \frac{n^2 v_0^+}{2}$$

$$-\frac{T}{2}\int_{\Omega^+}\frac{d^D\mathbf{k}}{(2\pi)^D}\left[\ln(1 + n\beta v^+(k)) - \frac{n\beta v^+(k)}{1 + n\beta v^+(k)}\right], \quad (3)$$

which, together with the set of equations

$$\left(\frac{\partial P}{\partial n}\right)_T = T + n v_0^+ - \frac{T}{2}\int_{\Omega^+}\frac{d^D k}{(2\pi)^D}\frac{n(\beta v^+(k))^2}{(1 + n\beta v^+(k))^2} = 0,$$

$$\left(\frac{\partial^2 P}{\partial n^2}\right)_T = v_0^+ - \frac{T}{2}\int_{\Omega^+}\frac{d^D k}{(2\pi)^D}\frac{(\beta v^+(k))^2(1 - n\beta v^+(k))}{(1 + n\beta v^+(k))^3} = 0 \quad (4)$$

(which is one of the options of preassignment of the critical state), defines the critical pressure, temperature, and density.

The search for an analytical solution of the set of equations (4) in the general case of arbitrary potential is difficult; however, one can formulate the necessary condition of its solvability [5]

$$\lim_{|\mathbf{k}| \to \infty} [(v^+(k))^2 |\mathbf{k}|^D] = 0,$$

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[1] The integrand $\varphi(x) = \ln(1 + x) - x/(1 + x)$ is nonnegative for any values of x; therefore, the last term in equation (3) leads to a decrease of pressure.

which provides for the convergence of the integrals in [4]. The objective of this study (solution of (4)) may be accomplished in some special cases.

Let us assume that, in the three-dimensional case, the interaction between particles proceeds with the aid of the Yukawa potential with the Fourier transform

$$\tilde{v}(k) = v^+(k) = A/(k^2 + a^2), \quad (5)$$

where $A > 0$ and $a > 0$ are parameters of the potential.

The integration for k yields the equation of state

$$P = nT + \frac{n^2 \tilde{v}_0}{2} - \frac{Ta^3}{12\pi}\left[1 - \sqrt{1 + n\beta\tilde{v}_0}\left(1 - \frac{n\beta\tilde{v}_0}{2}\right)\right]. \quad (6)$$

We substitute equation (6) into the set of equations (4)

$$\left(\frac{\partial P}{\partial n}\right)_T$$

$$= T\left[1 + n\beta\tilde{v}_0 - \frac{a^3}{16\pi}n(\beta\tilde{v}_0)^2(1 + n\beta\tilde{v}_0)^{-1/2}\right] = 0,$$

$$\left(\frac{\partial^2 P}{\partial n^2}\right)_T$$

$$= \beta\tilde{v}_0\left[1 - \frac{a^3}{32\pi}\beta\tilde{v}_0(2 + n\beta\tilde{v}_0)(1 + n\beta\tilde{v}_0)^{-3/2}\right] = 0$$

and solve this set to find the critical parameters

$$n_0 = \frac{a^3}{12\pi\sqrt{3}}, \quad \beta_0 = \frac{1}{T_0} = \frac{24\pi\sqrt{3}}{a^3\tilde{v}_0}, \quad (7)$$

$$P_0 = (2 - \sqrt{3})n_0 T_0.$$

Dijkstra and Van Roij [6] used the central-field theory and the Monte Carlo method and managed to demonstrate the presence of a first-order phase transition in a system with a repulsive Yukawa potential. The parameters (7) enable one to calculate the compressibility factor $Z_c = 2 - \sqrt{3} = 0.268$ (for the investigated materials, $Z_c < 0.375$ [7]) and reduce the equation of state (6) to a dimensionless form,

$$\pi(\tau, \varphi)$$

$$= \frac{1}{Z_c}\left(\frac{\tau}{\varphi} + \frac{1}{\varphi^2} - \sqrt{3}\left[1 - \sqrt{1 + \frac{2}{\tau\varphi}\left(1 - \frac{1}{\tau\varphi}\right)}\right]\right). \quad (8)$$

Here, $\tau = T/T_0$, $\varphi = V/V_0$, and $\pi = P/P_c$ are the reduced temperature, volume, and pressure, respectively. The isotherms constructed using equation (8) are continuous curves exhibiting, at $0 < \tau < 1$, "van der Waals" loops and vertical asymptote $\varphi = 0$, as must be in the case of a potential without a hard core ("van der Waals" isotherms have a vertical asymptote $\varphi = 1/3$).

The spinodal equation corresponding to equation of state (8) has the form

$$\left(\frac{\partial\pi}{\partial\omega}\right)_\tau = \frac{\tau}{Z_c}\left(1 + \frac{2\omega}{\tau} - \frac{3\sqrt{3}\omega}{\tau^3\sqrt{1 + 2\omega/\tau}}\right) = 0, \quad (9)$$

where $\omega = n/n_0 = 1/\varphi$, and admits an exact solution. At the critical point with $\tau = 1$ and $\varphi = \omega = 1$, the equality $(\partial\pi/\partial\omega) = 0$ is valid (i.e., the isothermal compressibility is infinite), and a region of absolutely unstable states exists for all subcritical isotherms, in which $(\partial\pi/\partial\omega) < 0$, this being indicative of a first-order phase transition.

The presence of an exact solution to the set of equations (4) defining the critical point for the model interatomic potential makes possible the search for approximate solutions for "real" interactions by the methods of perturbation theory in which the solution of (7) serves as the function of zero approximation.

The interatomic potential

$$v(r) = \frac{\exp(-ar)}{4\pi}\left(\frac{A}{r} - \frac{B}{2a}\right), \quad (10)$$

as well as, for example, a linear combination of Yukawa potentials [8], appears "realistic." With a certain selection of coefficients, potential (10) has a potential well and is repulsive in the case of small distances and attractive in the case of large distances. The validity of the condition

$$(B/A) < a^2 \quad (11)$$

provides for the above-identified properties of the potential and for the positiveness of its Fourier transform, which has the following form in the space of dimension $D = 3$:

$$\tilde{v}(k) = \frac{A}{k^2 + a^2} - \frac{B}{(k^2 + a^2)^2}. \quad (12)$$

As distinct from [8], the suggested model attracts particular interest because it enables one to analytically find the minimum of potential (10),

$$v(r_m) = \frac{A}{4\pi}\left(\frac{1}{r_m} - \frac{a\varepsilon}{2}\right)\exp[-ar_m], \quad (13)$$

where $r_m = (1 + \sqrt{1 + 2\varepsilon})/\varepsilon a$ and $\varepsilon = B/Aa^2$. This fact may enable one to find the dependence of the critical parameters n_c and β_c of the system on the potential well depth $v(r_m)$. The integration of (3) with Fourier transform (12) leads to the equation of state

$$P = nT + \frac{n^2\tilde{v}_0}{2} - \frac{Ta^3}{12\pi}\left[2 + \left(\frac{n\beta w}{2} - 1\right)Q\right.$$

$$\left. - \frac{2n\beta w + n\beta w\sqrt{1 + n\beta\tilde{v}_0} - n\beta\tilde{v}_0}{2Q}\right], \quad (14)$$

where $\tilde{v}_0 = A/a^2 - B/a^4$, $w = A/a^2$, and $Q =$
$$\sqrt{2 + n\beta w + 2\sqrt{1 + n\beta\tilde{v}_0}}.$$

Note that, in the case of $B \longrightarrow 0$, r_m tends to infinity, and $v(r_m) \longrightarrow 0$, which brings about the disappearance of the potential well; i.e., potential (10) changes to the Yukawa potential, and the equation of state (14) goes, as it must, to the equation of state (6) for a system with a potential of the Yukawa type.

The solution to the set of equations (4) with equation (14) involves serious difficulties. The emerging equations reduce to algebraic equations of high degrees; therefore, no exact analytical expressions of critical parameters for model (10) have been found. Nevertheless, condition (11) provides a natural possibility ($\varepsilon < 1$) of carrying out the search for critical parameters using perturbation theory. We will first perform the expansion of (14) in powers of small parameter accurate within first-order terms,

$$P(n, T) = P_0(n, T) + \varepsilon P_1(n, T) + \ldots,$$

where $P_0(n, T)$ is the equation of state (6),

$$P_1(n, T)$$
$$= -\frac{n^2 w}{2a^2} + \frac{Ta^3}{16\pi}\left[\frac{(n\beta w)^2}{\sqrt{1 + n\beta w}(1 + \sqrt{1 + n\beta w})^2}\right].$$

We will seek the solution to the set of equations (4) in the form

$$n_c = n_0 + \varepsilon n_1 + \ldots, \quad \beta_c = \beta_0 + \varepsilon\beta_1 + \ldots,$$

where n_0 and β_0 are critical parameters in (7). We will now linearize the set of equations (4),

$$\frac{\partial P_0}{\partial n}(\varepsilon n_1, \varepsilon\beta_1) = -\varepsilon\frac{\partial P_1}{\partial n}(n_0, \beta_0),$$

$$\frac{\partial^2 P_0}{\partial n^2}(\varepsilon n_1, \varepsilon\beta_1) = -\varepsilon\frac{\partial^2 P_1}{\partial n^2}(n_0, \beta_0).$$

We solve this set with respect to n_1 and β_1 to find the critical parameters n_c and β_c,

$$n_c = n_0(1 - 1.647\varepsilon + \ldots),$$
$$\beta_c = \beta_0(1 - 3.915\varepsilon + \ldots). \tag{15}$$

The critical temperature is related to a minimum on the interaction potential curve. By the order of magnitude, this minimum for all substances is equal to T_c [9]. An analysis of expressions (13) and (15) reveals that an increase in ε causes an increase in the potential well depth; in this case, in the first order of the perturbation theory, the critical density decreases and the critical temperature increases. Therefore, the parametric dependence of $\beta_c(\varepsilon)$ on $v(r_m(\varepsilon))$ in a first approximation leads to a physically reasonable result which is in qualitative agreement with the data given in [10]. Note that, within the suggested model (10) and approximation (2), one can demonstrate that, with $\tilde{v}_0 = 0$, no phase transition is present in the system.

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