Russian Physics Journal, Vol. 40, No. 9, 1997

CLASSICAL MODEL CONTAINING A PHASE TRANSITION

A. Yu. Zakharov and I. K. Loktionov

UDC 536.7

A relationship has been established between interatomic-potential characteristics and thermodynamic functions for one-component pair-interaction classical systems. A sufficient condition for a phase transition is deduced from first principles. There is a region around the critical point in which scale laws are violated; in particular, the isochoric specific heat is large but finite at the critical point.

The following questions have to be answered to obtain a description of the origin of phase transitions: 1) which interaction potentials lead to phase transitions and which do not? 2) What is the relationship between the interaction-potential parameters and the phase-transition characteristics? Existing theories are in essence phenomenological and do not answer these questions.

The thermodynamic potentials of a system enable one to establish whether it does or does not have a phase transition. The purpose of the present paper is to present an asymptotically exact calculation in the thermodynamic limit and to analyze some thermodynamic functions for one-component classical systems and establish a sufficient condition for a phase transition.

A previous paper [1] demonstrates that the following is the statistical sum Z for a one-component classical system containing N identical particles in a volume V:

$$\ln Z = \ln Z_{id} + (V/2)\left\{\int\limits_{(\Omega^+)} \frac{d^D\kappa}{(2\pi)^D} \ln\left[\frac{V}{2\beta v^+(\kappa)} \int\limits_0^\infty J_0^N(\rho) \times \right.\right.$$
$$\times \exp\left(-\frac{V\rho^2}{4\beta v^+(\kappa)}\right)\rho d\rho\Big] + \int\limits_{(\Omega^-)} \frac{d^D\kappa'}{(2\pi)^D} \ln\left[\frac{V}{2\beta v^-(\kappa')} \int\limits_0^\infty I_0^N(\rho) \times \right. \tag{1}$$
$$\left.\left. \times \exp\left(-\frac{V\rho^2}{4\beta v^-(\kappa')}\right)\rho d\rho\Big]\right\} + \frac{N\beta}{2}(v(0) - n\tilde{v}(0)),$$

in which β is reciprocal temperature, $\Omega^+(\Omega^-)$ the sets of all wave vectors for which the Fourier transform $\tilde{v}(\kappa)$ of the interatomic central potential v(r) is positive (negative), and the positive functions $v^\pm(\kappa)$ are defined as

$$v^\pm(\kappa) = \pm\tilde{v}(\kappa),\ \kappa \in \Omega^\pm, \tag{2}$$

in which $J_0(\rho)$ and $I_0(\rho)$ are Bessel functions and D are the dimensions of the space.

We first calculate the integrals on the right in (1) in the thermodynamic limit (N, V $\to \infty$; N/V = n = const). The integral with respect to Ω^+ contains $J_0(\rho)$ and is calculated at once because $\max\limits_{\{\rho\}} J_0(\rho) = J_0(0) = 1$, and $\rho \neq 0$ $|J_0(\rho)| < 1$, for all $\rho \neq 0$. The function is $J_0(\rho) \simeq 1 - (\rho^2/4)$ in the region of a point $\rho_0 = 0$, so

$$\int\limits_0^\infty J_0^N(\rho) \exp\left(-\frac{N\rho^2}{4n\beta v^+(\kappa)}\right)\rho d\rho \simeq (2/N)\frac{n\beta v^+(\kappa)}{1 + n\beta v^+(\kappa)} \tag{3}$$

Donetsk State Technical University. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 9, pp. 92-95, September, 1997. Original article submitted March 6, 1996; revision submitted February 11, 1997.

1064-8887/97/4009-0911$18.00

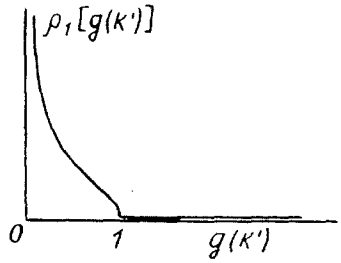

Fig. 1. Dependence of the position of the minimum point $F(\rho)$ on the parameter $g(\kappa')$.

and the contribution from the repulsion in κ space in (1) is

$$(-V/2)\int\limits_{(\Omega\tau)}\frac{d^D\kappa}{(2\pi)^D}\ln(1+n\beta v^+(\kappa)). \tag{4}$$

The situation is somewhat more complicated with the integral

$$\Phi=\int\limits_0^\infty \exp\left(N\ln I_0(\rho)-\frac{N\rho^2}{4n\beta v^-(\kappa')}\right)\rho d\rho. \tag{5}$$

The main contribution to the integral for $N\to\infty$ comes from the region of the point of minimum value ρ_0 in the function

$$F(\rho)=(\rho^2/n\beta v^-(\kappa'))-4\ln I_0(\rho). \tag{6}$$

The position of the ρ_0 point is substantially dependent on the parameter $g(\kappa')=1/n\beta v^-(\kappa')$: if $g(\kappa')\geq 1$, then $\rho_0\equiv 0$; while if $0<g(\kappa')<1$, the point $\rho_0=0$ becomes a point of maximum in $F(\rho)$ (an analog of the Higgs phenomenon), and the minimum is determined by the nonzero root of

$$(g(\kappa')-2I_0'(\rho)/\rho I_0(\rho))\rho=0. \tag{7}$$

Figure 1 shows schematically the dependence of the position of the minimum point in $F(\rho)$ on the parameter $g(\kappa')$.

Then if the set Ω^- is not empty, there exists a singular point on the temperature axis

$$T_c=\max_{\kappa'\in\Omega^-}\{nv^-(\kappa')\}=nv^-(\kappa_0), \tag{8}$$

having the property that the ρ_0 point represents a minimum in (6) for $T>T_c$ for all κ', and then the integral in (5) for all κ' is

$$\Phi=(2/N)\frac{n\beta v^-(\kappa')}{1-n\beta v^-(\kappa')}. \tag{9}$$

The (9) representation does not apply for $T\leq T_c$ at least for some of the wave vectors from Ω^-.

Consider the case $T\geq T_c$. We expand $F(\rho)$ near $\rho_0=0$ up to terms of the fourth order to get

$$\Phi=2\sqrt{\pi N}\exp\left[N\left(\frac{1-n\beta v^-(\kappa')}{n\beta v^-(\kappa')}\right)^2\right]\operatorname{erfc}\left[\sqrt{N}\left(\frac{1-n\beta v^-(\kappa')}{n\beta v^-(\kappa')}\right)\right] \tag{10}$$

(erfc(x) is the error function). This means that passing to the limit $N \to \infty$ in (5) gives (9) only for $1 - n\beta v^-(\kappa') \neq 0$, and otherwise it is simply zero. Therefore, the two limiting transitions (thermodynamic and $T \to T_c$) do not commutate. Also, one naturally distinguishes several parts in the temperature dependence of the thermodynamic functions for $T \geq T_c$:

1. The high-temperature region $\max_{\{\kappa\}} |n\beta\tilde{v}(\kappa)| << 1$, when the substance is close to an ideal gas.

2. The region of intermediate temperatures $\max_{\{\kappa\}} |n\beta\tilde{v}(\kappa)| \simeq 1$, in which there is an appreciable contribution from the interactions.

3. The precritical region

$$N^{-1/2} \ll (1 - \max_{\{\kappa'\}} (n\beta v^-(\kappa'))) \ll 1, \tag{11}$$

in which the (5) integral is represented asymptotically accurately by (9) and

$$\ln Z = -(V/2)\left\{\int_{(\Omega^+)} \frac{d^D\kappa}{(2\pi)^D} \ln(1 + n\beta v^+(\kappa)) + \int_{(\Omega^-)} \frac{d^D\kappa'}{(2\pi)^D} \ln(1 - n\beta v^-(\kappa'))\right\} + \\ + N\beta(v(0) - n\tilde{v}(0))/2 + \ln Z_{id}. \tag{12}$$

In this region one gets singular behavior in the thermodynamic functions on account of the spurious (apparent) pole on the right in (9). The collective-variable method has been used [2] to obtain an expression for the Helmholz free energy that is similar to (12).

4. The critical region

$$0 \leq (1 - \max_{\{\kappa'\}} (n\beta v^-(\kappa'))) \leq N^{-1/2}, \tag{13}$$

in which (9) and (12) are unsuitable. Therefore, to calculate the integral Φ in that case, one should use the (10) approximation, from which one readily gets (9) for $\max_{\{\kappa\}}(n\beta v^-(\kappa')) << 1$. Here we do not consider the region below T_c.

We derive the pressure P, internal energy U, and isochoric specific heat C_v outside the critical region, i.e., for $T - T_c >> N^{-1/2}$:

$$P = P_{id} - (T/2)\int_{\Omega^\pm} \frac{d^D\kappa}{(2\pi)^D}\left\{\ln(1 + n\beta\tilde{v}(\kappa)) - \frac{n\beta\tilde{v}(\kappa)}{1 + n\beta\tilde{v}(\kappa)}\right\}; \tag{14}$$

$$U = U_{id} - (V/2)\int_{\Omega^\pm} \frac{d^D\kappa}{(2\pi)^D} \frac{\beta(n\tilde{v}(\kappa))^2}{1 + n\beta\tilde{v}(\kappa)}; \tag{15}$$

$$C_V = C_V^{id} + (V/2)\int_{\Omega^\pm} \frac{d^D\kappa}{(2\pi)^D}\left[\frac{n\beta\tilde{v}(\kappa)}{1 + n\beta\tilde{v}(\kappa)}\right]^2. \tag{16}$$

All the integrand functions on the right in (14)-(16) are nonnegative outside the critical region, so switching in the atomic interactions increases the isochoric specific heat and reduces the internal energy and pressure (we note that the isotherms for real gases in the (P, V) plane always lie below the corresponding isotherms for an ideal gas).

Formulas (14)-(16) are not applicable in the critical region ($0 \leq T - T_c \leq N^{-1/2}$). The main interest attaches to the behavior of C_v in the region of T_c. We use (10) with the approximation

$$\exp(x^2)\operatorname{erfc}(x) \approx 1/(x\sqrt{\pi} + 1) \quad (x \geqslant 0), \tag{17}$$

to derive the most singular part of the specific heat, which is due to the contribution from Ω^-:

$$C_{v,\text{sing}} \approx (V/2)\int_{(\Omega^-)} \frac{d^D\kappa}{(2\pi)^D}\left[\frac{1 - w(\kappa)}{w(\kappa) + \Theta + (1 - w(\kappa))/\sqrt{\pi N}}\right]^2, \tag{18}$$

in which $w(\kappa) = 1 - v^{-1}(\kappa)/v^{-}(\kappa_0)$, with κ_0 defined in (8), and $\theta = (T - T_c)/T_c$. This integral contains two small parameters: θ and $(\pi N)^{-1/2}$. The singular behavior of the specific heat is due to the infrared divergence as those parameters tend to zero. If for $|\kappa| \to \kappa_0$ we have that $w(\kappa) \propto (|\kappa| - \kappa_0)^m$, then

$$C_{v,\text{sing}} \propto (\theta + (\pi N)^{-1/2})^{-\alpha}, \alpha = \begin{cases} 2 - D/m, \kappa_0 = 0, \\ 2 - 1/m, \kappa_0 \neq 0. \end{cases}$$

If $(\pi N)^{-1/2}$ is absent, this formula gives typical scaling behavior for the specific heat; in particular, free Euclidian field theory results [3] are obtained with $m = 2$. The size of the temperature region in which the scaling laws are violated is dependent on the dimensions of the system.

We are indebted to Ya. I. Granovskii for stimulating discussions on these topics.

REFERENCES

1. A. Yu. Zakharov, Phys. Lett. A, **147**, No. 8/9, 442-444 (1990).
2. D. N. Zubarev, Dokl. Akad. Nauk SSSR, **35**, No. 4, 757-760 (1954).
3. D. J. Amit, Field Theory, the Renormalization Group, and Critical Phenomena. XVI, McGraw-Hill, New York (1978).