

thermal conduction, diffusion, and thermal diffusion), but at present the lack of the necessary data does not give a quantitative description when one considers irreversibility in the Heaviside approach.

Following Planck, we may formulate two topics whose elucidation would improve substantially our concepts on irreversibility (in Planck's or Heaviside's approaches).

1. Whether the simplicity in a gaseous system (homogeneous mixtures filling all the available volume) is the result of interaction between equilibrium thermal radiation and matter, i.e., whether the gas molecule motion and distribution is Brownian motion, whose cause arises from interaction with radiation (localized) in matter and equilibrium between the localized radiation and that entering from outside?

2. Whether the energy spectrum for a blackbody (Planck's radiation law) is a χ^2 distribution for the unobservable elementary interactions (of radiation and matter), which are subject to a Gaussian distribution, which appears attractive in view of the resonant form of interaction between matter and radiation.

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NEW CONSEQUENCES OF THE LINEAR MODEL OF THE PARAMETRIC EQUATION OF STATE

Yu. E. Sheludyak and V. A. Rabinovich

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New possibilities of applying the linear model of the parametric equation of state are shown; in reduced coordinates, this model is associated with a single determining similarity parameter b depending on the compressibility coefficient of the individual materials at the critical point Z_{cr} .

Analysis of the theoretical models and experimental data permits the hypothesis that the series of critical-amplitude complexes

$$A\Gamma/B^2, D\Gamma B^{\delta-1}, \Gamma/\Gamma', A'/A, A_2/A \quad (1)$$

is universal [1], but only the universality of the complex

$$A_1\Gamma'/B^2 = \beta^2 \quad (2)$$

has been rigorously proven [2]. As well as the conventional notation for critical amplitudes [3], A_1 denotes the jump in isochoric specific heat at the boundary curve and A_2 is the corresponding quantity for the specific heat C_V at the boundary curve from the side of the single-phase region.

A linear model of the parametric equation of state is widely used to describe the thermodynamic properties of the individual materials in the critical region [4]

$$\begin{aligned} \Delta\mu &= ar^{\beta\delta}\theta(1-\theta^2); \\ \Delta\rho &= kr^{\beta}\theta; \\ t &= r(1-b^2\theta^2), \end{aligned} \quad (3)$$

where $\Delta\mu = (\mu - \mu_{cr})/(\rho_{cr}v_{cr})$; μ_{cr} is an analytical function of the temperature; $\Delta\rho = \omega - 1 = \rho/\rho_{cr} - 1$, $t = \tau - 1 = T/T_{cr} - 1$. On the basis of the isolated curves, the variable θ has

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fixed values: $\theta = 0$ at the critical isochore; $\theta = \pm 1/b$ at the critical isotherm; $\theta = \pm 1$ at the boundary curve.

The critical indices of the individual materials are universal constants [5]; therefore, the equation of state in Eq. (3) only includes three fitting parameters: a , k , b .

In most of the published works, it was assumed that a and k are individual constants of the material, and b has the universal value

$$b^2 = \frac{\gamma - 2\beta}{\gamma(1 - 2\beta)}. \quad (4)$$

In this particular case, the expressions obtained from Eq. (2) for the various thermodynamic functions are simplified. For example, the equations for the derivative $(\partial\mu/\partial\rho)_T$ and the singular part of the specific heat C_V take the form

$$\left(\frac{\partial\mu}{\partial\rho}\right)_T \frac{\rho_{cr}^2}{p_{cr}} = \frac{a}{k} r^\gamma \left\{ 1 + \theta^2 \left[\frac{2(\gamma-1)}{1-2\beta} - 1 \right] \right\}; \quad (5)$$

$$\frac{C_V^{sing}}{RZ_{cr}^\tau} = ak r^{-\alpha} \frac{\gamma^2(\gamma-1)(1-2\beta)}{2\alpha(\gamma-2\beta)}. \quad (6)$$

In [6, 7], in writing the equation of state of water in the critical region, all three coefficients of a , k , b of the linear model in Eq. (3) were fitting parameters. In this general case, the expressions for the thermodynamic functions become more complex. The equations for the derivative $(\partial\mu/\partial\rho)_T$ and the singular part of the specific heat C_V take the form

$$\left(\frac{\partial\mu}{\partial\rho}\right)_T \frac{\rho_{cr}^2}{p_{cr}} = \frac{a}{k} r^\gamma \frac{1 + \theta^2 [b^2(2\beta\delta - 1) - 3] + \theta^4 b^2(3 - 2\beta\delta)}{1 - \theta^2 b^2(1 - 2\beta)}; \quad (7)$$

$$\frac{C_V^{sing}}{RZ_{cr}^\tau} = ak r^{-\alpha} \frac{c_0 + \theta^2 c_2 + \theta^4 c_4 + \theta^6 c_6}{[1 - \theta^2 b^2(1 - 2\beta)]^3}, \quad (8)$$

where

$$c_0 = -(2 - \alpha)(1 - \alpha) f_0; \quad (9)$$

$$c_2 = f_0 b^2 (1 - 2\beta)(2 - \alpha)(1 - \alpha + 2\beta) - f_2 \gamma (\gamma - 1); \quad (10)$$

$$c_4 = f_2 b^2 \gamma (1 - 2\beta)(1 - \alpha) + f_4 (\gamma - 2\beta)(\alpha + 4\beta - 1); \quad (11)$$

$$c_6 = f_4 b^2 (\gamma - 1)(\gamma - 2\beta)(1 - 2\beta); \quad (12)$$

$$f_0 = \frac{b^2 \alpha \gamma + 2\beta - \gamma}{2b^4 \alpha (1 - \alpha)(2 - \alpha)}; \quad (13)$$

$$f_2 = \frac{\gamma - 2\beta}{2b^2 \alpha (1 - \alpha)} - \frac{1 - 2\beta}{2(1 - \alpha)}; \quad (14)$$

$$f_4 = -\frac{1 - 2\beta}{2\alpha}. \quad (15)$$

Expressions for the critical amplitudes are obtained from eqs. (3), (7), and (8)

$$A = akc_0 = ak \left(\frac{\gamma - 2\beta}{2b^4 \alpha} - \frac{\gamma}{2b^2} \right); \quad (16)$$

$$B = \frac{k}{(b^2 - 1)^\beta}; \quad (17)$$

$$\Gamma = \frac{k}{a}; \quad (18)$$

$$D = \frac{a}{k^\delta} (b^2 - 1) b^{\delta-3}. \quad (19)$$

Equations (16)-(19) depend on the critical indices and all three coefficients a , k , b . Combining the critical amplitudes in the form of the complexes in Eq. (1), expressions which do not contain a and k are obtained

$$\frac{A\Gamma}{B^2} = (b^2 - 1)^{2\beta} \frac{\gamma - 2\beta - b^2\alpha\gamma}{2b^2\alpha}; \quad (20)$$

$$D\Gamma B^{\delta-1} = \frac{b^{\delta-3}}{(b^2 - 1)^{\gamma-1}}; \quad (21)$$

$$\frac{\Gamma}{\Gamma'} = \frac{2}{(b^2 - 1)^{\gamma-1} [1 - b^2(1 - 2\beta)]}; \quad (22)$$

$$\frac{A'}{A} = \frac{f_0 + f_2 + f_4}{f_0(b^2 - 1)^{2-\alpha}}; \quad (23)$$

$$\frac{A_2}{A} = \frac{(c_0 + c_2 + c_4 + c_6)(b^2 - 1)^\alpha}{c_0[1 - b^2(1 - 2\beta)]^3}. \quad (24)$$

Thus, the complexes of the critical amplitudes in Eq. (1) are a function of b , and take universal values only in the case where b is universal. Note that, with the classical indices $\beta = 1/2$ and $\gamma = 1$, Eqs. (21) and (22) do not depend on b , and take the values $D\Gamma B^{\delta-1} = 1$, $\Gamma/\Gamma' = 2$ coinciding with the predictions of the Van der Waals equation [1], i.e., in the general case, transition in the limit from the linear model to the predictions of classical theory is seen.

Differentiating Eqs. (20)-(24) with respect to b , it may be established that they have a maximum or minimum at the values of b^2 determined by Eq. (4). In Fig. 1, the dependence of the critical-amplitude complexes Q on b^2 referred to the value of the complex at the extremal point is shown. These curves are calculated for the theoretical indices $\beta = 0.324$ and $\gamma = 1.24$. With $\pm 10\%$ deviation of b^2 from Eq. (4), the values of the various critical-amplitude complexes vary by 1-4%, and with $\pm 20\%$ deviation of b^2 from the extremal point, by 5-30%.

The values of b^2 obtained in [6, 7] are higher than for Eq. (4) by 6.6% [6] and 1.1% [7]; these values of the critical-amplitude complexes practically coincide with their values at the extremal point. Thus, variation of all three coefficients a , k , b of the linear model of the parametric equation of state is not proven, and the universality of the complexes in Eq. (1) has not been refuted.

At the same time, analysis of the general expressions for the critical amplitudes in Eqs. (16)-(19) and their complexes in Eqs. (20)-(24) reveals new possibilities of this equation of state, if it is assumed that the coefficients a and k have universal features, while b is an individual constant of the material uniquely related to the compressibility coefficient at the critical point Z_{cr} .

In this case, the relative critical amplitudes

$$A^* = A/(ak), \quad B^* = B/k, \quad \Gamma^* = \Gamma \frac{a}{k}, \quad D^* = D \frac{k^\delta}{a}$$

depend only on b . The curves of the relative critical amplitudes E^* on b according to Eqs. (16), (17), and (19) are shown in Fig. 2. The dependences of A^* , B^* , D^* , on b^2 are of the same form as the dependences of A , B , D on the compressibility coefficient at the critical point Z_{cr} [1]: the critical amplitudes A and A^* , B and B^* are decreasing functions, while D and D^* are increasing functions. According to the predictions of the theoretical models, the critical amplitude Γ is a weakly increasing function of Z_{cr} , while the variation in Γ is comparable with the error in its experimental determination [1]; in the linear model of the parametric equation of state, $\Gamma^* = 1$.

In the region $b^2 = 1.1-1.4$, B^* is close to the value of B in the region $Z_{cr} = 0.22-0.29$ [8]. This permits the assumption that $k = 1$ or is close to unity.

Knowing the dependence $B(Z_{cr})$, a relation between the coefficient b^2 and the compressibility coefficient at the critical point Z_{cr} may be established from Eq. (17). The dependence $b^2(Z_{cr})$ calculated from the data of [1] with $k = 1$ and $\beta = 0.324$ is shown in Fig. 3, where the dashed curves correspond to the limits of variation in b^2 with $\pm 5\%$ deviation in critical amplitude B from the value of [1]. The value $b^2 = 1.356$ determined by Eq. (4) when $\beta = 0.324$ and $\gamma = 1.240$ corresponds to $Z_{cr} \sim 0.29$ characteristic of gases with spherically symmetric molecules.

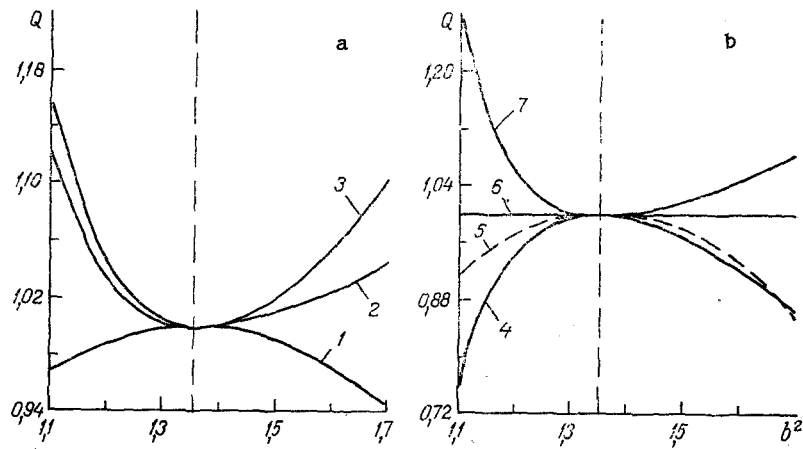


Fig. 1. Dependence of the critical-amplitude complexes Q referred to the value at the extremal point on b^2 : 1) $D\Gamma'B^{\delta-1}$; 2) $D\Gamma B^{\delta-1}$; 3) Γ/Γ' ; 4) $A\Gamma/B^2$; 5) A_2/A ; 6) $A_1\Gamma'/B^2$; 7) A'/A .

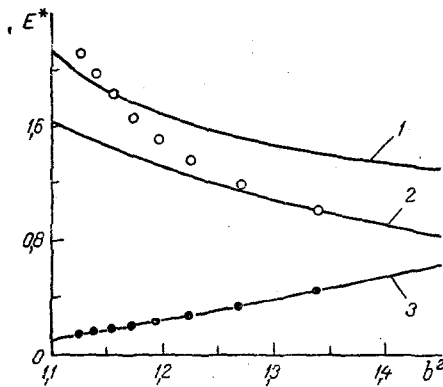


Fig. 2

Fig. 2. Dependence of the relative critical amplitudes on b^2 : 1) $1 - B^*$; 2) A^* ; 3) D^* .

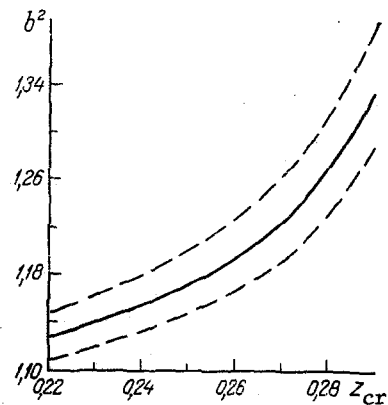


Fig. 3

Fig. 3. Dependence $b^2(Z_{cr})$ calculated from data [1] on the critical amplitude B when $k = 1$ and $\beta = 0.324$.

As follows from Eq. (18), α is determined by the critical amplitude of the isothermal compressibility: $\alpha = k\Gamma = 17.12$ when $\Gamma = 0.0584$ [9].

The open and filled points in Fig. 2 correspond to the dependence of A^* and D^* , respectively on b^2 according to the data of [1] with $k = 1$ and $\alpha = 17.12$. The values of D^* are in good agreement with those calculated from Eq. (19), while A^* is basically higher than the values calculated from Eq. (16). The deviation increases with decrease in Z_{cr} and reaches 37% when $Z_{cr} = 0.22$. The reason for these deviations may be the method of estimating the critical amplitude adopted in [1]: A was determined from B and Γ in the complex $A\Gamma/B^2$ with a "universal" value of the coefficient b^2 in Eq. (4). However, direct experimental estimates of A at small Z_{cr} are closer to those calculated from Eq. (16) than to the result of [1] and the value $A = 33.5$ obtained in [7] for water. Data on the velocity of sound in water ($Z_{cr} = 0.229$) give $A = 26.7$ [10] when $\alpha = 0.11$. Calculation from Eq. (16) with $k = 1$, $\alpha = 17.12$, and $\alpha = 0.112$ gives $A = 25.6$; with identical α , the difference between the critical amplitudes A is even smaller.

Thus, as well as the two methods of describing the critical region of the individual materials employed within the framework of the linear model of the parametric equation of state, one more may be used: that in which the coefficients α and k are universal constants of the equation, and b characterizes the individual properties of the material. In this approach, the linear model of the parametric equation of state is an equation of state in reduced variables, with one determining similarity criterion. The critical amplitudes and their complexes in this equation are universal functions of the similarity parameter b .

NOTATION

$\alpha, \beta, \gamma, \delta$, critical indices; $A, A', A_1, A_2, B, \Gamma, \Gamma', D$, critical amplitudes; a, k, b , coefficients of the linear model of the parametric equation of state; r, θ , parametric variables determining the distance to the critical point and the path by which it is approached; μ , chemical potential; ρ , density; T , temperature; p , pressure; $Z_{cr} = p_{cr}v_{cr}/RT_{cr}$, compressibility coefficient at the critical point; R , universal gas constant.

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MEASUREMENT OF THE THERMAL DIFFUSIVITY IN CONDITIONS OF SUBSONIC HEATING.

CALCULATION OF DYNAMIC CORRECTION

V. I. Gorbатов, S. A. Il'inykh,
S. G. Taluts, and V. E. Zinov'ev

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Corrections associated with the rate of change in mean temperature are calculated for the dynamic method of plane temperature waves. It is shown that the correction is only significant close to the points of phase transition and at heating rates above 1000 K/sec.

The dynamic method of plane temperature waves was proposed in [1] for the investigation of the thermophysical characteristics of materials. A sample in the form of a thin plane-parallel plate is heated at a rate of up to 1000 K/sec with a modulation period of the temperature wave of no more than 10 msec, which allows the thermal diffusivity to be measured over a broad temperature range in a time of less than 1 sec. The creation of this method permits a reduction by two or three orders of magnitude in the time to measure the temperature dependence of the thermal diffusivity and allows information to be obtained in the temperature range where the sample cannot retain its form and state for a long time, i.e., close to phase and structural transformations. However, the possibility of using the information obtained for determining the temperature dependence of the thermophysical characteristics in this temperature range requires separate theoretical investigation. The point is that all the traditional nonsteady methods are based on solving linear or linearized heat-conduction equation and therefore the working region of the temperature intervals is always limited. Expansion of the region of application of nonsteady methods requires the solution of complex nonlinear heat-conduction equations, taking account of all the factors responsible for this nonlinearity. Analytical methods of solving problems of this type have not yet been adequately developed. At the same time, computer solution of such problems by numerical methods does not present any difficulties.

All the results of the present work are obtained using a "machine" experiment: essentially, the physical process used to measure the thermophysical coefficients is replaced by

V. V. Vakhrushev Sverdlovsk Mining Institute. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 55, No. 3, pp. 485-490, September, 1988. Original article submitted April 23, 1987.