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Universal Crossover Behavior of Fluids and Fluid Mixtures in the Critical Region

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A new universal scaled equation of state for one-component fluids, binary mixtures, and ionic solutions, which represents the thermodynamic behavior of fluids in a wide range of temperatures and densities including the critical region, is proposed. Near the critical point this equation reduces to a theoretically based scaled equation including the leading nonasymptotic (Wegner) correction and a correction accounting for the asymmetry of fluids with respect to the critical isochore. Far away from the critical point the new equation goes over into the classical Landau expansion (van der Waals equation). The new equation is applied to represent experimental P–V–T data for H_2O and CO_2, as well as to represent $C_{v,x}$ data for dilute aqueous solutions of NaCl. A crossover from fluctuation to mean-field behavior is observed at increased concentrations of NaCl. A universal crossover function for the heat capacity $C_{v,x}$ of one-component fluids and binary mixtures is presented.

KEY WORDS: critical phenomena; crossover equation of state; specific heat; aqueous ionic solutions.

1. INTRODUCTION

In accordance with the modern concept of critical phenomena [1, 2], the behavior of the thermodynamic properties in the critical region is determined by a distance to the critical point r and the value of the dimensionless Ginzburg number $Gi \equiv (l/\xi_0)^{\sigma}$, where l is the average distance between particles, and ξ_0 is the amplitude of the asymptotic critical power law of the correlation length ξ). At the critical isochore (at $T > T_c$) and along the coexistence curve (at $T < T_c$), the "distance" $r = \tau$, where $\tau = T/T_c - 1$ is the dimensionless temperature deviation from the critical

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temperature T_c. In the fluctuation regime ($\tau \ll Gi$) the density of the free energy per unit volume $\hat{A} = A/V$ can be represented in the form of the Wegner expansion [3]:

$$\hat{A} = \hat{A} + |u_\tau|^{2-\alpha} \, [\hat{f}_0(u_h/u_\tau|^{\beta\delta}) + \hat{c}_i \, |u_\tau|^{\Delta_i} \hat{f}_i(u_h/|u_\tau|^{\beta\delta}) + \cdots] \qquad (1)$$

where $\hat{A}_0$, u_τ, and $\hat{c}_i$ are analytical functions of τ, while u_h is a function of the deviation of the chemical potential from its value on the critical isochore $\Delta\mu = (\rho_c/P_c)[\mu(\rho, T) - \mu(\rho_c, T)]$. To make the chemical potential dimensionless, the critical pressure P_c ad critical density ρ_c are used. All simple fluids and their mixtures belong to the same universality class with universal critical exponents α, β, and δ, universal correction-to-scaling exponents Δ_i, as well as universal scaling functions $\hat{f}_i(z)$ [4]. The case $Gi \ll \tau \ll 1$ corresponds to the mean-field region in the Landau theory [5], where the free energy can be represented by an expansion in powers of an order parameter $\Delta\eta$:

$$\hat{A} = \hat{A}_0 + \tfrac{1}{2} u_2 \tau \, \Delta\eta^2 + \tfrac{1}{4} u_4 \, \Delta\eta^4 \qquad (2)$$

Here u_2 and u_4 are system-dependent constants. The order parameter $\Delta\eta$ is related to the reduced temperature difference τ and the reduced density difference $\Delta\rho = \rho/\rho_c - 1$ by $\Delta\eta = \Delta\rho + B_3\tau$, where B_3 is another system-dependent coefficient related to a rectilinear diameter of the coexistence curve. The range $\tau \simeq Gi$ corresponds to a certain intermediate region where a crossover from fluctuation behavior at $\tau \ll Gi$ to the mean-field behavior at $Gi \ll \tau \ll 1$ takes place. In this region simple power laws are no longer valid. Existing estimates for the Ginzburg number [4] show that for nonconducting fluids the entire experimentally attainable range of temperatures is related to the crossover behavior.

The thermodynamic behavior of simple binary mixtures in the vicinity of the vapor–liquid critical line has also a universal character and can be described on the basis of fluctuation scaling theory and the isomorphism hypothesis [1, 4, 6, 7]. In accordance with this theory all simple liquids and their mixtures belong to the same universality class. This means that in terms of the appropriately chosen isomorphic variables, they obey the same universal scaling laws with the same universal critical exponents. It is essential that in solutions the heat capacity $C_{v,\mu}$ at constant chemical potential is the value isomorphous to the heat capacity C_v of a single-component liquid, rather than the heat capacity $C_{v,x}$ at constant molar concentration x. The heat capacity $C_{v,x}$ remains finite everywhere except at the critical points of the pure components. On approaching the critical line of a solution the so-called Fisher renormalization of the critical heat capacity exponent α to $-\alpha/(1-\alpha)$ takes place, i.e., there exists an intermediate range of temperatures in which the effective index $\alpha_{\mathrm{eff}} \simeq 0$. Nevertheless, in this case the free energy remains singular due to long-range critical fluctuations. It is this fluctuation part that determines the peculiar behavior of the heat capacity $C_{v,x}$ in the critical region. This conclusion has been confirmed by the progress achieved in recent years in describing the isochoric heat capacity $C_{v,x}$ of binary mixtures on the basis of universal scaled equations of state [8, 9]. A quite different situation occurs in electrolytic solutions where the intermolecular potential itself is long range. As a consequence the mean-field Landau theory remains valid for $Gi \ll \tau \ll 1$ [5] with $\alpha_{\mathrm{L}} = 0$ and the coexistence-curve exponent $\beta_{\mathrm{L}} = 1/2$. In the case that Gi is small ($Gi \simeq 10^{-8}$–10^{-10}) the singular part of the free energy is negligible in the entire experimentally attainable range. The heat capacity of such a system is then an analytical function of temperature and density. Values of $Gi \simeq 10^{-2}$–10^{-3} correspond to a pretransitional region where a crossover occurs from fluctuation behavior of the system ($\alpha_{\mathrm{eff}} = 0.11$, $\tau \ll Gi$) to mean-field behavior with suppressed long-wavelength fluctuations ($\alpha_{\mathrm{eff}} = 0$, $\tau \gg Gi$). Dilute solutions of NaCl in water can be classified as such a system. As noted elsewhere [10, 11], even at concentrations $x > 0.01\,\%$ of NaCl mol fractions, the exponent β tends to its mean-field value $\beta \simeq 1/2$, and we shall find that the experimental P–ρ–T–x data are well described by an analytic classical equation of state.

In this paper, a new crossover equation of state for single- and two-component fluids is presented. This equation is developed on the basis of an asymmetric equation of state presented previously for one-component fluids [12–14] and for binary mixtures [15, 16]. Comparisons with experimental P–V–T data for steam [17–19] and carbon dioxide [20, 21] as well as with specific heat data for dilute solutions of NaCl in water [22] are given.

2. CROSSOVER EQUATION FOR ONE-COMPONENT FLUIDS

The crossover equation of state proposed by Albright, Sengers, and co-workers [23, 24] is the best justified theoretically. The range of validity of this two-term crossover model is substantially larger than that of the so-called fundamental equation of state [25] and, on the other hand, coincides practically with that of the asymmetric scaled equation of state (ASEQ) [12–14]. To represent the thermodynamic properties of fluids over a large range of temperatures and densities around the critical point, a six-term crossover model was proposed [26].

The ASEQ yields a representation of the thermodynamic properties in the density range $0.65 < \rho/\rho_{\mathrm{c}} < 1.4$ along the critical isotherm and in the temperature range $0.98 < T/T_{\mathrm{c}} < 1.2$ along the critical isohore and coexistence curve including metastable states. Moreover, ASEQ represents such sophisticated effects as the behavior of the line of the isobaric heat-capacity maxima in the one-phase region. It allows us to choose the ASEQ as a zero approximation rather than the Landau expansion. The ASEQ includes the first nonasymptotic term to the Wegner expansion (1) and a term accounting for asymmetry with respect to the critical isochore. The renormalization-group (RG) theory indicates that the free energy can be represented in the form [27]

$$\begin{aligned}\hat{A}(\tau, \Delta\eta) &= \hat{A}(\Omega\tau, Z\,\Delta\eta)\\ &= \hat{A}_0 + (u_2/2)\,\tau\Omega Z\,\Delta\eta^2 + (u_4/4)\,UZ^2\,\Delta\eta^4 - (u_0/2)\,\tau^2 K \qquad (3)\end{aligned}$$

where u_2 and u_4 are as before constants in the Landau expansion (2), while u_0 is a new system-dependent constant related to a so-called kernel term in the singular part of the free energy.

The rescaling functions Ω, Z, U, and K can be expressed in terms of a crossover function Y,

$$\Omega = Y^{\kappa_1}, \qquad Z = Y^{\kappa_2}, \qquad U = Y^{\kappa_3}, \qquad K = Y^{\kappa_4} - 1 \qquad (4)$$

and the exponents κ_1, κ_2, κ_3, and κ_4 are expressed in terms of the known critical exponents $\kappa_1 = (2\nu - 1)/\Delta$, $\kappa_2 = -\eta\nu/\Delta$, $\kappa_3 = \nu/\Delta$, and $\kappa_4 = -\alpha/\Delta$, where ν is the critical exponent of the correlation length ξ, the exponent η defines the long-distance behavior of the correlation function, and $\Delta = \Delta_1$ in Eq. (1). The crossover function Y is chosen so that in the regular region the right-hand side of the relation (3) coincides fully with the Landau expansion ($Y = 1$ in Refs. 23 and 24), while at $\tau \ll 1$ the functions Ω, U, and Z reproduce the Wegner expansion. Introducing the fundamental results (3) and (4) into the ASEQ [12–14], we obtain a new equation which incorporates the crossover from the critical behavior to classical behavior [28]:

$$\begin{aligned}\hat{A} = P_c\{&R^{\kappa_a}(q)\, r^{2-\alpha} ak\Psi_a(\theta^2) + R^{\kappa_{na}}(q)\, r^{2-\alpha+\Delta} ck\Psi_c(\theta^2)\\ &+ R^{\kappa_{as}}(q)\, r^{2-\alpha+\Delta_a} k[d\Psi_d(\theta) + f\Psi_f(\theta)]\} + \hat{A}_0(T, \rho) \qquad (5)\end{aligned}$$

with

$$\hat{A}_0(T, \rho) = \left\{(\rho/\rho_c)\, m_0 - 1 + \sum\, [(\rho/\rho_c)\, m_i + f_i]\, \tau^i\right\} P_c \qquad (5a)$$

$$\tau = r(1 - b^2\theta^2) \qquad (6)$$

$$\Delta\eta = \Delta\rho + B_3\tau = kR^{\kappa_b}(q)\, r^\beta\theta \qquad (7)$$

Here a, k, c, d, f, f_0, m_0, m_i, and f_i are system-dependent coefficients, Δ is the exponent of the first nonasymptotic term in the Wegner expansion [$i=1$ in the expansion (1)], and $\Delta_a=\gamma+\beta-1$ is the critical exponent of the asymmetric term. The universal scaling functions $\Psi_a(\theta^2)$, $\Psi_c(\theta^2)$, $\Psi_d(\theta)$, and $\Psi_f(\theta)$ coincide fully with the corresponding functions in the ASEQ [12–14] and are given in the Appendix. The asymmetric term in Eq. (5) deals with the "mixing" of the thermodynamic variables in fluids and is not related to the incorporation of the term $\sim\Delta\eta^5$ into the Landau–Ginzburg–Wilson Hamiltonian [29]. The value of the asymmetric critical exponent $\Delta_a\simeq 0.565$ slightly differs from the theoretical value $\Delta_5=0.69$, which is calculated up to the order ε^2 ($\varepsilon=4-d$; d is dimensionality) [29]. This exponent was also calculated up to the order ε^3 [30, 31]. It was found that the convergence of the expansion is poor and that Δ_5 could be anywhere between 0.5 and 1.5.

The argument of the crossover function $R(q)$ can be rewritten in the form

$$q=rg\simeq rGi^{-1} \tag{8}$$

Here g is a new system-depended constant connected with the Ginzburg number Gi. Since in the parametric representation the distance from the critical point is determined by the polar coordinate r, the choice of $g\simeq Gi^{-1}$ is the most natural and can be considered to be the definition of the Ginzburg parameter in this approach. More rigorous calculations show that $g\simeq Gi^{-1/2\alpha}$. This means that at $\alpha=1/2$ in accordance with the Ornstein–Zernike's approximation, the relation given by Eq. (8) becomes valid. Then using the concept of an effective critical exponent for the heat capacity,

$$\alpha_{\text{eff}}(\tau)=\partial\ln C_v(\tau,\Delta\eta=0)/\partial\ln\tau \tag{9}$$

and an effective critical exponent of the isothermal compressibility K_T

$$\gamma_{\text{eff}}(\tau)=\partial\ln K_T(\tau,\Delta\eta=0)/\partial\ln\tau \tag{10}$$

as well as obvious asymptotics for the crossover function $R(q)$:

$$\lim_{q\to 0} R(q)=1, \qquad \lim_{q\to\infty} R(q)=q \tag{11}$$

we obtain

$$\kappa_a=\alpha, \qquad \kappa_{na}=\alpha-\Delta, \qquad \kappa_b=\tfrac{1}{2}-\beta, \qquad \kappa_{as}=2\alpha+\beta-\tfrac{1}{2} \tag{12}$$

We note that such choice of the exponent κ_{as} provides for the transformation of the asymmetric term in Eq. (5) to the asymmetric terms in the

Landau expansion $\simeq\tau^2\Delta\eta$, $\simeq\tau\Delta\eta^3$, and $\simeq\Delta\eta^5$ at the limit of $q\gg 1$ (see Appendix B). Whence it follows that the crossover function R can be represented in the form

$$R(q)=1+q^2/(b_0+q) \tag{13}$$

where b_0 is a nonuniversal constant of order unity. (In Ref. 28 the parameter b_0 was assumed to be equal to unity.) Equations (5)–(7) in combination with Eqs. (12) and (13) determine the universal crossover equation of state for one-component fluids. This crossover function, Eq. (13), and its first and second derivatives are analytic monotonous functions, the asymptotic behavior of which at $q\gg 5$ coincides practically with the asymptotic behavior at $q\to\infty$ (see Fig. 1). Thus at $q\to 0$ ($q\ll 10^{-2}$) Eqs. (5)–(7) and ASEQ are fully identical, and at $q\gg 1$ they yield the Landau expansion given by Eqs. (2) including asymmetric terms ($\simeq\tau^2\Delta\eta$, $\simeq\tau\Delta\eta^3$, $\simeq\Delta\eta^5$). This is best illustrated by the dependence of the effective critical exponents α_{eff} and γ_{eff}, the isochoric heat capacity C_v, and the inverse of the isothermal compressibility K_T^{-1} on the parameter q. Differentiating Eq. (5) twice with respect to τ and $\Delta\rho$, we obtain the following expressions for C_v and K_T^{-1} along the isochore in the approximation $c=d=f=B_3=0$

$$(\rho_c T_c^2 C_v)/(P_c T)=A^+ r^{-\alpha}\hat{\Phi}_c(q)-(\rho_c/P_c)(d^2\hat{A}_0/d\tau^2) \tag{14}$$

$$\bar{K}_T^{-1}=K_T^{-1}/P_c=(a/kg^{\gamma})\,\hat{\Gamma}_c(q) \tag{15}$$

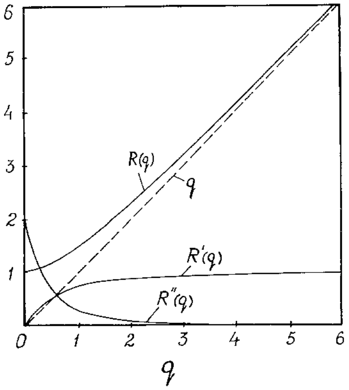

Fig. 1. Crossover function $R(q)$ and its first and second derivatives $R'(q)$ and $R''(q)$ ($b_0=1$) as a function of q.

Here A^+ is the dimensionless amplitude of the asymptotic power law for the isochoric heat capacity, and the functions $\hat{\Phi}_c(q)$ and $\hat{\Gamma}_c(q)$ are given by

$$\hat{\Phi}_c(q) = q^{-\alpha}\Phi_c(q) = q^{-\alpha}R^{\alpha}(q)\,R_2(q) \tag{16}$$

$$\hat{\Gamma}_c(q) = q^{\gamma}\Gamma_c(q) = q^{\gamma}R^{1-\gamma}(q)\{1 - [\gamma(\gamma-1)/(1-\alpha)(2-\alpha)]\,qR'/R\} \tag{17}$$

with

$$R_2(q) = 1 + (2\alpha/(1-\alpha))(qR'/R) + (\alpha q^2/(1-\alpha)(2-\alpha))\cdot[R''/R - (R'/R)^2\,(1-\alpha)] \tag{18}$$

Effective critical exponents $\alpha_{\text{eff}}(q)$ and $\gamma_{\text{eff}}(q)$ can be derived by differentiating Eqs. (14) and (15) with respect to temperature [see Eqs. (9) and (10)]:

$$\alpha_{\text{eff}}(q) = \alpha - q\Phi'_c(q)/\Phi_c(q) \tag{19}$$

$$\gamma_{\text{eff}}(q) = \gamma + q\Gamma'_c(q)/\Gamma_c(q) \tag{20}$$

The effective exponents calculated from Eqs. (19) and (20) are shown in Fig. 2. One can see from the curves that when the parameter q increases,

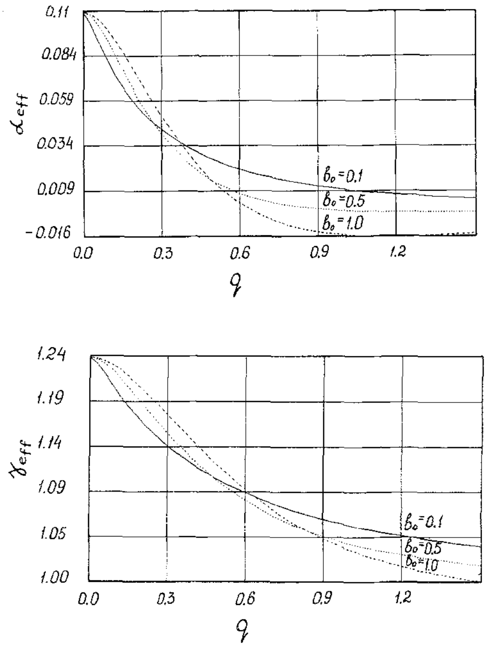

Fig. 2. Effective exponents α_{eff} and γ_{eff} as a function of q.

the effective critical exponents α_{eff} and γ_{eff} tend monotonously to their mean-field values $\alpha = 0$ and $\gamma = 1$.

However, the character of this crossover depends on the parameter b_0. For $b_0 \geqslant 0.4$, the functions $\alpha_{\text{eff}}(q)$ and $\gamma_{\text{eff}}(q)$ intersect the abscissa when the parameter q increases and the critical exponents change their sign at certain values of q (different for α_{eff} and γ_{eff}). For $b_0 \leqslant 0.4$, $\alpha_{\text{eff}}(q)$ and $\gamma_{\text{eff}}(q)$ are smooth monotonous functions of the parameter q. The meaning of the parameter b_0 in the crossover function $R(q)$ becomes clear from the behavior of inverse susceptibility K_T^{-1} along the critical isochore ($\rho = \rho_c$, $\vartheta = 0$, $q = \tau g$). At large values of the parameter q (see Fig. 3) K_T^{-1} is a linear function of $T(K_T^{-1} \sim q \sim \tau')$. However, the dimensionless temperature τ' is not equal to the dimensionless temperature τ in the critical region

$$\tau' = (T - T'_c)/T'_c = \tau - \delta\tau' \simeq (T - T_c)/T_c - \delta T'_c/T'_c \tag{21}$$

because the temperature T'_c differs from the true critical temperature T_c,

$$T'_c = T_c + \delta T'_c \tag{22}$$

The function Ω takes into account the critical temperature shift in the crosover equatios (3) and (4),

$$\tau' = \tau\Omega \tag{23}$$

This is easy to derive in our approach, where $Y = [q/R(q)]^{\Delta}$ and

$$\Omega(q) = Y^{(2\nu - 1)/\Delta}(q) = [q/R(q)]^{2\nu - 1} \tag{24}$$

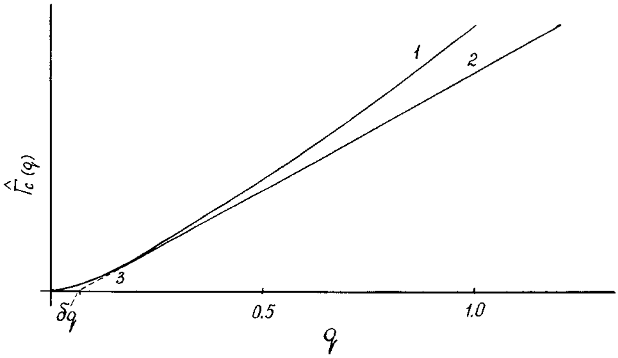

Fig. 3. Crossover function for the inverse susceptibility $\hat{\Gamma}_c(q) = K_T^{-1} k g^{\gamma}/a$ along the critical isochore as a function of q: 1—asymptotic law $\hat{\Gamma}_c(q) = q^{\gamma}$; 2—values of $\hat{\Gamma}_c(q)$ predicted by Eq. (17); 3—asymptotic law $\hat{\Gamma}_c(q') = q'$, $q' = q - \delta q'$ ($\delta q' = g\,\delta T'/T_c$).

Expanding $\Omega(q)$ into power of q^{-1} and retaining the first term in the expansion for large q, we obtain from Eqs. (13) and (24),

$$\tau' = \tau - (1 - b_0)(2\nu - 1)/g \tag{25}$$

The expression for δT_c follows from a comparison of Eq. (25) with the Eqs. (21) and (22):

$$\delta T'_c = (1 - b_0)(2\nu - 1)\, T_c/g \tag{26}$$

That is, the transfer from the fluctuation region to a regular one results not only in changes of the effective exponents but in the renormalization of the critical temperature, Eq. (21). At $b_0 < 1$, $\delta T_c > 0$, and the true critical temperature $T_c < T'_c$ is consistent with that resulting from the RG theory [32].

In this work, Eqs. (5)–(7) have been used to represent experimental P–V–T data of steam and carbon dioxide in a broad range around the critical point. The critical parameters of steam and carbon dioxide as well as the values of the adjustable constants are listed in Table I. The critical exponents have been fixed at the values $\alpha = 0.11$, $\beta = 0.325$, and $\Delta = 0.5$ in agreement with the theoretical predictions. Comparisons of experimental pressure data for steam [17–19] and carbon dioxide [20, 21] with the values calculated from the crossover equation of state and van der Waals equation are presented in Figs. 4 and 5. To obtain the parameters of the van der Waals equation the experimental values of the critical temperature,

Table I. Parameter Values in the Crossover Equations (5)–(7) for Steam and Carbon Dioxide

	H_2O	CO_2
f_1	−7.769	−6.967
f_2	20.09	20.13
f_3	29.09	−0.408
f_4	−70.37	6.276
a	21.4	20.01
c	−1.342	−2.32
d	11.59	12.52
f	−19.83	−16.57
k	1.417	1.198
B_3	−0.6	−0.65
g	1	0.5
b_0	0.3	0.3
P_c	22.05 MPa	7.375 MPa
ρ_c	322.778 $kg \cdot m^{-3}$	466.5 $kg \cdot m^{-3}$
T_c	647.067 K	304.126 K

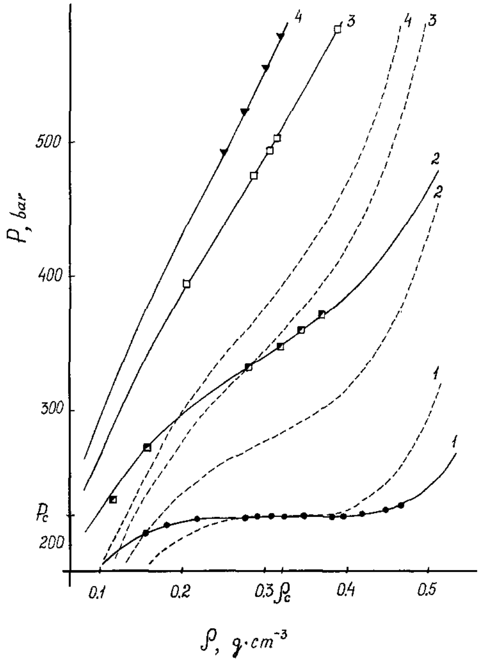

Fig. 4. Isotherms of H_2O in the critical region: 1, $T/T_c = 1.000$; 2, 1.071; 3, 1.156; 4, 1.195. The solid curves generated by Eq. (5); the dashed curves, by van der Waals equation. The symbols represent the experimental data [17–19].

critical density, and critical pressure of steam and carbon dioxide were used. It is seen that the crossover model proposed in this paper represents P–V–T data over a larger temperature range than scaled equations formulated before [12–14, 23–25]. For example, the experimental P–V–T date for CO_2 at the critical isochore are reproduced within a temperature range up to $1.3\,T_c$. With regard to the density range it was found to be $0.6 \leqslant \rho/\rho_c \leqslant 1.4$ at $T = T_c$, and therefore it coincides with the range for the ASEQ [12, 14].

3. CROSSOVER IN BINARY MIXTURES

The approach developed in the previous section may be extended to binary mixtures. For this purpose additional universal scaled functions $\Phi(\phi)$ and $\Phi_1(\phi_1)$ must be introduced into Eqs. (5)–(7) [28], so that

$$\begin{aligned}\hat{A}(T,\rho,x)=P_c\Big\{&akr^{2-\alpha}R^{\alpha}(q)\,\Phi(\phi)\,\Psi_a(\theta^2)+ckr^{2-\alpha+\Delta}R^{\alpha-\Delta}(q)\,\Psi_c(\theta^2)\\&+kr^{3-\beta+2\alpha}R^{2\alpha+\beta-1/2}(q)[d\Psi_d(\theta)+f\Psi_f(\theta)]\\&+(\rho/\rho_c)\,m_0-1+\sum\,[(\rho/\rho_c)\,m_i+f_i]\,\tau^i\Big\}\end{aligned}\tag{27}$$

Here the polar coordinates r and θ are related to the dimensionless density $\Delta\rho(x)=\rho/\rho_c(x)-1$ and temperature $\tau(x)=T/T_c(x)-1$

$$\Delta\rho(x)=kr^{\beta}R^{1/2-\beta}(q)\,\Phi_1(\phi_1)\theta,\qquad \tau(x)=r(1-b^2\theta^2)\tag{28}$$

The universal scaling functions $\Psi_a(\theta^2)$, $\Psi_c(\theta^2)$, $\Psi_d(\theta)$, and $\Psi_f(\theta)$ coincide with the corresponding functions for a single-component fluid given in the Appendix. The crossover functions $\Phi(\phi)$ and $\Phi_1(\phi_1)$ are also given in the Appendix and take into account the Fisher renormalization in solutions and agree with the corresponding functions in earlier papers [9, 15]. The

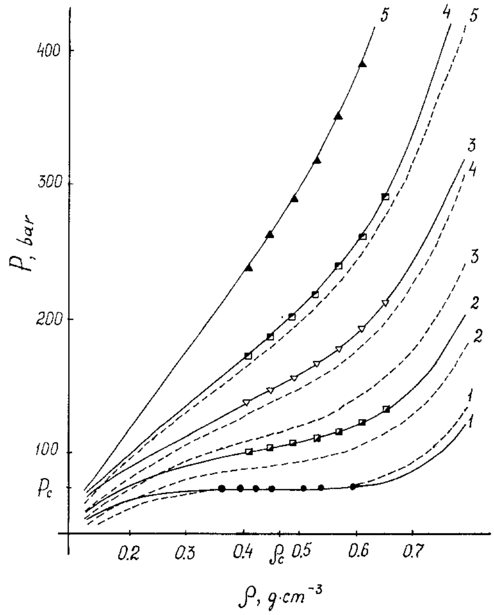

Fig. 5. Isotherms of CO_2 in the critical region: 1, $T/T_c=1.000$; 2, 1.061; 3, 1.145; 4, 1.226; 5, 1.375. The solid curves generated by Eq. (5); the dashed curves, by van der Waals equation. The symbols represent the experimental data [20, 21].

parameter $\phi = r\zeta^{1/\alpha}$ determines the renormalization of the heat-capacity critical exponent α, while the parameter $\phi_1 = r\zeta_1^{1/\gamma}$ determines the renormalization of the compressibility critical exponent γ. The parameter ζ_1 is given by

$$\zeta_1 = (\rho_c T_c P_c R)(a/kx(1-x))[(dP_c/dx) - (dT_c/dx)(\partial P/\partial T)_{x_c,\rho_c}]^{-2} \tag{29}$$

where R is the universal gas constant. For $r \to 0$ and $\phi \gg 1$, the function $\Phi(\phi) \simeq 1$ and the heat capacity $C_{v,x} = -T(\partial^2 \hat{A}/\partial T^2)_{\rho,x}$ behaves as that of a pure substance:

$$C_{v,x} \simeq ak\gamma(\gamma-1)/(2\alpha b^2)\, r^{-\alpha} - 2(m_2 + f_2) \tag{30}$$

At $\phi \ll 1$ the renormalization $\alpha \to -\alpha/(1-\alpha)$ takes place, and for $r \to 0$ the singular part of the heat capacity tends to a finite value

$$[C_{v,x}]_{\text{sing}} \simeq 2ak\zeta - ak\zeta^{(2-\alpha)/(1-\alpha)} r^{\alpha/(1-\alpha)} \simeq 2ak\zeta \tag{31}$$

which at $\zeta \to 0$ also tends to zero. For $Gi \ll r \ll 1$ (i.e., in the case of small of the Ginzburg number), a crossover from the fluctuation behavior to the mean-field behavior with suppressed long-wavelength fluctuations of the order parameter is to be found. The function $R(q)$ takes into account this crossover, where $b_0(x)$ is a nonuniversal constant and $g(x) \simeq Gi(x)$. At $q \ll 1$ $(g < 1)$ the function $R(q) \to 1$ and for $r \to 0$ the heat capacity tends to infinity in accordance with Eq. (30). At $q \gg 1$ $(g \gg 1)$ the function $R(q) \simeq g$, the effective exponent α_{eff} tends to zero and the heat capacity $C_{v,x}$ remains finite. These two types of renormalization are possible depending on the values of the parameters ζ and g. In the case of $\zeta^{1/\alpha} \gg 1$ and $g \ll 1$ the Fisher renormalization takes place $\alpha \to -\alpha/(1-\alpha)$. The parameters a and k remain finite, and in first approximation they can be calculated from their quantities for the pure components:

$$k = k_0(1-x) + k_1 x, \qquad a = a_0(1-x) + a_1 x \tag{32}$$

In the case of $\zeta^{1/\alpha} \gg 1$ and $g \gg 1$ the crossover from scaling to mean-field behavior occurs and $\alpha_{\text{eff}} \to 0$.

4. APPLICATION TO IONIC AQUEOUS SOLUTIONS

In order to understand this type of renormalization the analysis of the experimental heat capacity $C_{v,x}$ data [22] for NaCl aqueous solutions has been performed in two stages.

First, the parameters a, c, d, f, f_3, f_4, m_2, and m_3 of Eq. (26) have been found for each concentration by the method of least-square. We assumed the parameter g to be equal to zero $[R(q)=1]$ and the parameter ζ_1 to be equal to infinity ($\zeta_1 \to \infty$, $\phi_1 \to \infty$, $\Phi_1 \simeq 1$). Initially the parameter ζ was estimated from [16]

$$\zeta = (RT_c\rho_c/P_c)[2\alpha(1-\alpha)\,b^2T_c^2/ak\gamma(\gamma-1)\,x(1-x)](dT_c/dx)^{-2} \quad (33)$$

Here the values of the parameters a and k have been found from Eq. (32) and we have used experimental data [22] to evauate the derivative (dT_c/dx) (see Fig. 6). The values of the parameter ζ, thus determined for the aqueous solution of NaCl, are presented in Table II.

Then the value of the parameter ζ was refined by trial and error from the condition of the best description of the whole experimental data set. The critical exponents were again fixed at the theoretical values $\alpha=0.11$, $\beta=0.325$, and $\Delta=0.5$. It can be seen in Fig. 7 that a sharp decrease in the value of the parameter a is observed when the concentration increases. And at $x>0.247$ % mol fractions NaCl it becomes practically equal to zero. The analysis shows that the qualitative dependence of the parameter a on concentration does not change for magnitudes of the parameter ζ in the interval $1 \leqslant \zeta \leqslant 10$. This means that the Fisher renormalization is lacking and a crossover of the isochoric heat capacity from fluctuation behavior to mean-field behavior takes place. For the description of the crossover behavior in

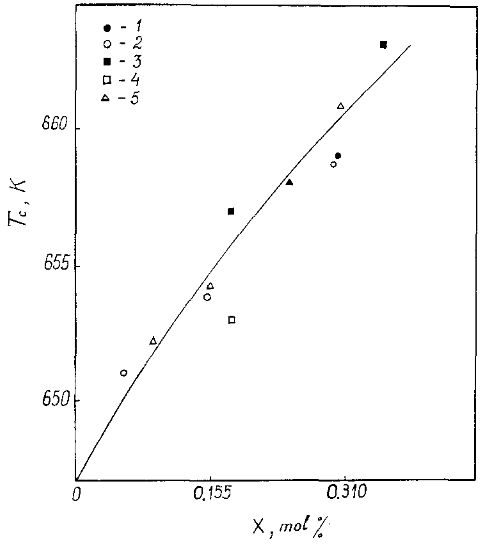

Fig. 6. The critical temperature of NaCl aqueous solutions versus concentration of NaCl: 1, Ref. 36; 2, Ref. 37; 3, Ref. 38; 4, Ref. 39; 5, Ref. 33.

Table II. Parameter Values in the Crossover Equation (27) for the NaCl–H_2O System

Parameter	x, mol% NaCl			
	0.0925	0.154	0.247	0.310
T_c, K	652.4	654.44	658.12	661.09
ρ_c, $kg \cdot m^{-3}$	341.6	354.6	361.7	367.4
a [a]	20.3	1.3	0.2	0.005
c [a]	−24.0	6.8	3.8	34.8
d [a]	−29.4	18.2	7.4	−24.0
f [a]	68.1	−36.1	−8.5	−132.7
f_2 [a]	0.2	9.0	−0.2	−22.5
f_3 [a]	87.3	71.9	67.9	−54.7
f_4 [a]	436.0	−366.0	−258.0	−3.3
m_2 [a]	62.8	−58.9	−54.2	25.8
m_3 [a]	−396.9	317.5	191.8	52.5
(dT_c/dx) (33)	3700	3200	2900	2700
ζ (33)	5.8	4.5	3.5	3.4

[a] To make these parameters dimensionless, the critical pressure $P_c = 22.05$ MPa of H_2O is used.

the second stage of calculation, we assumed $c = d = f = 0$. The parameters ζ and ζ_1 were fixed at values as calculated above, the parameters a, f_2, f_3, m_2, and m_3 were determined by a least-squares fit, while the parameter g was found by trial and error. In this case a sharp increase in the parameter g is observed alongside with a certain insignificant decrease in the

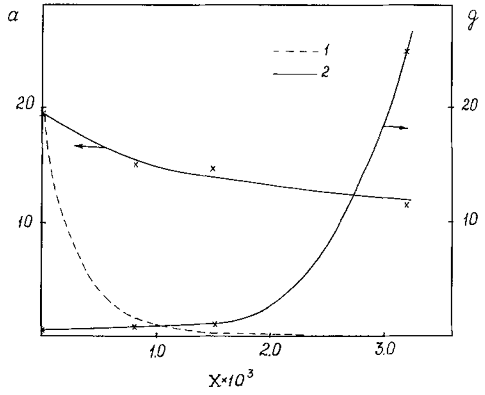

Fig. 7. The parameters a and g as function of the concentration: 1—$g = 0$, ζ is varied in the interval $1 \leqslant \zeta \leqslant 10$; 2 and 3—$\zeta$ is calculated by Eq. (33), g is varied.

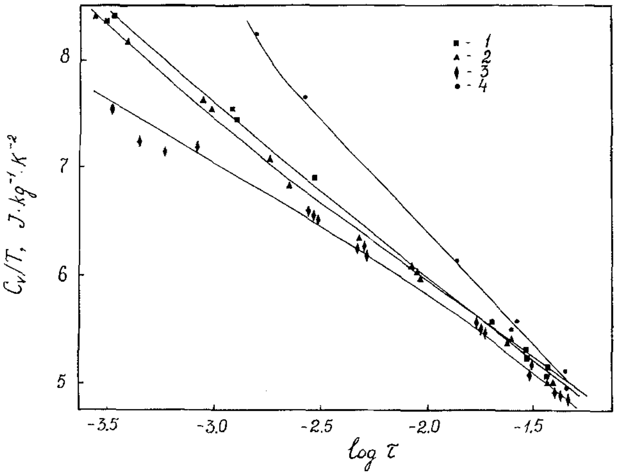

Fig. 8. The specific heat C_v along critical isochores: 1, $x = 0.0925$; 2, 0.154; 3, 0.310% of NaCl mol fractions; 4, pure H_2O. The data points are experimental values and the solid curves represent calculated C_v values.

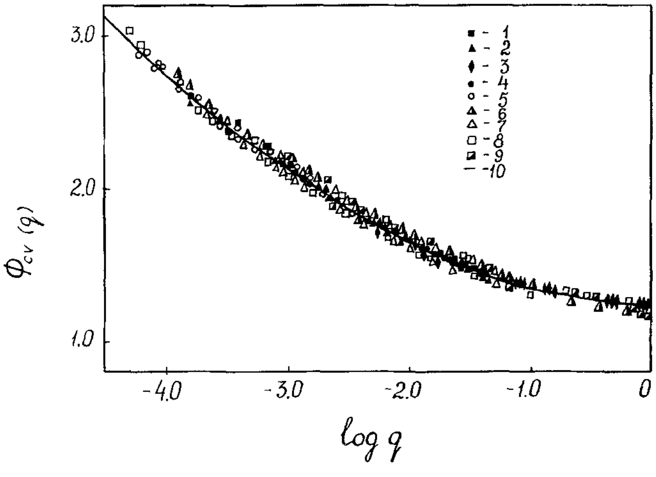

Fig. 9. The universal crossover function for the specific heat $\Phi_{cv}(q)$ along the critical isochore as a function of the parameter q at $b_0 = 0.3$: 1, 2, and 3—aqueous solutions of NaCl at $X = 0.0925$, 0.154, and 0.310 mol fractions; 5—Ar; 6—CH_4; 7—C_2H_6; 8—CO_2; 9—O_2; 10—corresponds to values calculated by Eq. (34).

parameter a (see Fig. 7). It confirms the fact that with increasing concentration, a crossover from scaling behavior to mean-field behavior occurs. Best of all it can be illustrated by the universal crossover function of the heat capacity $C_{v,x}$ on the critical isochore. Since $\phi \gg 1$ in our case, one can assume $\Phi(\phi) = 1$. Then double differentiation of Eq. (26) with respect to temperature in the approximation $c = d = f = 0$ gives

$$\rho_c C_v T_c^2/T = P_c\{ak\gamma(\gamma-1)/(2\alpha b^2)\,\Phi_{cv}(q) - 2(m_2+f_2) - 6(m_3+f_3)\tau - 12 f_4 \tau^2\} \qquad (34)$$

where the function $\Phi_{cv}(q)$ is represented by Eq. (16). A comparison of the values calculated from Eq. (34) and with the experimental data is presented in Figs. 8 and 9. It is seen from Fig. 9, then, at $q > 1$ the function Φ_{cv} tends to finite value, which corresponds to the kernel term of Eq. (3).

5. CONCLUSION

In this paper the character of the behavior of pure substances and dilute aqueous solutions of NaCl in the critical region is analyzed on the basis of a new universal crossover equation of state. The investigation shows that the Ginzburg parameter ($Gi = g^{-1}$) is of the order of unity for pure substances and there is no region of applicability of the Landau (mean-field) theory in this case. The entire range of temperatures under investigation ($0 \leqslant \tau \leqslant 0.3$) corresponds either to the fluctuation regime ($\tau \leqslant 10^{-2}$) or to the crossover regime ($10^{-2} \leqslant \tau \leqslant 0.3$). On the other hand, in dilute aqueous solutions of NaCl the character of behavior of the isochoric heat capacity $C_{v,x}$ at the near-critical isochores varies qualitatively with increasing salt concentration. In the NaCl–H_2O system a crossover occurs from fluctuation behavior at $0 \leqslant x \leqslant 0.247$ to mean-field behavior at $x \geqslant 0.247$ mol fraction NaCl with suppression of long-wave fluctuations of the order parameter ($\alpha_{\text{eff}} = 0$).

It should be noted that this conclusion has not found an unequivocal corroboration in the results of the latest investigations of the coexistence curve for the NaCl–H_2O system in the critical region [34, 35]. Thus the problem of the character of the critical behavior of dilute arouse solutions of NaCl remains open. The final resolution on this problem can be drawn after constructing a global crossover equation of state and applying it to a consistent representation of both P–V–T data and caloric-property data of NaCl–H_2O in the critical region. In this connection accurate experimental P–ρ–T–x data in a broad region around the liquid–vapor critical line need to be obtained.

APPENDIX A

$$\Psi_a(\theta^2) = -(1/2b^4)[2\beta(b^2-1)/(2-\alpha) + 2\beta(2\gamma-1)(1-b^2\theta^2)/\gamma(1-\alpha) + (2\beta-1)(1-b^2\theta^2)^2/\alpha] \tag{A1}$$

$$\Psi_c(\theta^2) = [1/(2b^2)(1-\alpha+\Delta)] \cdot [(\gamma+\Delta)/(2-\alpha+\Delta) - (1-2\beta)\, b^2\theta^2] \tag{A2}$$

$$\Psi_d(\theta) = \vartheta - (2/3)(e-\beta)\, b^2\theta^3 + (1-2\beta)/(5-2e)\, e_1 b^4\theta^5 \tag{A3}$$

$$\Psi_f(\theta) = (1/3)\, b^2\theta^3 + (1-2\beta)/(5-2e)\, e_2 b^4\theta^5 \tag{A4}$$

$$\Phi = f_s^{\alpha}\{2 - f_s^{[\alpha/(1-\alpha)]}\} \tag{A5}$$

where $f_s(\phi) = \phi/(1+\phi)$ and $\phi = r(x)\,\zeta^{1/\alpha}$.

$$\Phi_1(\phi_1) = [\phi_1/(1+\phi_1)]^{\gamma/2} \tag{A6}$$

with $\phi_1 = r(x)\,\zeta_1^{1/\gamma}$.

APPENDIX B

Let us introduce a new function,

$$G(q) = q^{-1}R(q) \tag{B1}$$

and replace the function $R(q)$ in Eq. (7) by Eq. (B1). Then from Eqs. (6) and (7) it follows that

$$\theta^2 = (\Delta\eta^2/k^2 r g^{1-2\beta})\, G^{2\beta-1}(q) \tag{B2}$$

$$r = \tau + (b^2\,\Delta\eta^2/k^2 g^{1-2\beta})\, G^{2\beta-1}(q) \tag{B3}$$

Substitution of Eq. (B2) into Eq. (5) with account of the correlations (A1)–(A4) for the function Ψ_a, Ψ_c, Ψ_d, and Ψ_f yields

$$\begin{aligned}\hat{A} = \hat{A}_0 &+ (1/2)\, a_2\tau\,\Delta\eta^2\, G^{\alpha+2\beta-1}(q) + (1/4)\, a_4\,\Delta\eta^4\, G^{\alpha+4\beta-2}(q) \\ &- (a_0/2)\,\tau^2[G^{\alpha}(q)-1] - (a_0/2)\,\tau^2 + d_1\tau^2\,\Delta\eta\, G^{2\beta+2\alpha-1}(q) \\ &+ d_3\tau\,\Delta\eta^3\, G^{2\alpha+4\beta-2}(q) + d_5\,\Delta\eta^5\, G^{2\alpha+6\beta-3}(q)\end{aligned} \tag{B4}$$

with

$$\begin{aligned}a_0 = [akg^{\alpha}\gamma(\gamma-1)/\alpha b^2(1-\alpha)(2-\alpha)]\{1 &- (c/ag^{\Delta})\, G^{-\Delta}(q) \\ &\times [\alpha(\gamma+\Delta)(1-\alpha)(2-\alpha)]/\gamma(\gamma-1) \\ &\times (1-\alpha+\Delta)(2-\alpha+\Delta)\}\end{aligned} \tag{B5}$$

$$\begin{aligned} a_2 = {} & (2a\beta/kb^2g^{1-2\beta-\alpha})\{[2(b^2-1)/(2-\alpha)+(2\gamma-1)/\gamma(1-\alpha)] \\ & +[cb^2/2ag^{\Delta}(1-\alpha+\Delta)] \\ & \times[2(\gamma+\Delta)/(2-\alpha+\Delta)+(1-2\beta)]\,G^{-\Delta}(q)\} \end{aligned} \tag{B6}$$

$$\begin{aligned} a_4 = {} & [4a\beta(b^2-1)/k^3g^{2-4\beta-\alpha}(2-\alpha)] \\ & \times\{1+[cb^2(2-\alpha)/2ag^{\Delta}\beta(b^2-1)\cdot(1-\alpha+\Delta)] \\ & \times[(\gamma+\Delta)/(2-\alpha+\Delta)+(1-2\beta)]\,G^{-\Delta}(q)\} \end{aligned} \tag{B7}$$

$$d_1 = dg^{2\beta+2\alpha-1} \tag{B8}$$

$$d_3 = (db^2/3k^2g^{2-4\beta-2\alpha})[6+2\beta-2e+(f/d)] \tag{B9}$$

$$\begin{aligned} d_5 = {} & (db^2/k^4g^{3-6\beta-2\alpha})[1-(2/3)(e-\beta)+(1-2\beta)\,e_1/(5-2e) \\ & +(f/d)(1/3)+(1-2\beta)\,e_2/(5-2e)] \end{aligned} \tag{B10}$$

From (B4) and (B5)–(B10) for $q \gg 1$ $[G(q)=1]$, Eq. (B4) is now given by

$$\begin{aligned} \hat{A} = {} & \hat{A}_0-(1/2)\,\tilde{a}_0\tau^2+1/2\tilde{a}_2\tau\,\Delta\eta^2+1/4\tilde{a}_4\,\Delta\eta^4 \\ & +d_1\tau^2\,\Delta\eta+d_3\tau\,\Delta\eta^3+d_5\,\Delta\eta^5 \end{aligned} \tag{B11}$$

where the coefficients $\tilde{a}_0$, $\tilde{a}_2$, and $\tilde{a}_4$ are determined by (B5)–(B7) with $G(q) \equiv 1$.

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