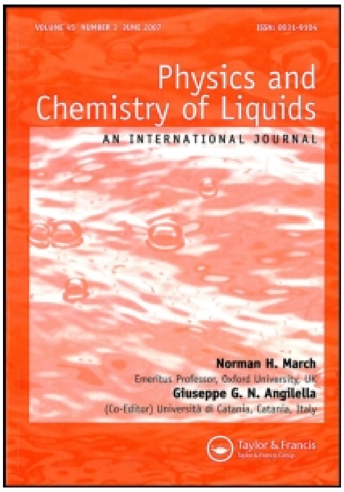

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ISOCHORIC HEAT CAPACITY IN THE CRITICAL REGION

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We study the isochoric heat capacity in the critical region. We have modified the results of Kiselev and Friend, and Chen, Albright and Sengers (CAS). Crossover parameters are chosen so that the isochoric heat capacity curve at $T = 648.0\,\mathrm{K}$ fits the experimental data accurately. We demonstrate that the experimental data is consistent with the modified CAS theory.

Keywords: Equation of state; Water; Critical point

1. INTRODUCTION

It was known before 1900 that things were not right with criticality according to the Van der Waals equation [3]. At that time people usually calculated the thermodynamic quantities from $T = 0$. And we are familiar with the results near $T = 0$. Although H_2O has been the topic of considerable research since the beginning of the century, the peculiar physical properties are still not well understood [9]. In the 1970s, criticality has been widely studied by many scientists [8]. A crossover theory [1] was developed recently by Kiselev and Friend using renormalization group theory, which was consistent with experimental data [2]. In 1999, a global crossover equation of state was put forward by Wyczalkowska *et al.* [7], which incorporated the classical Van der Waals behavior (including the ideal-gas limit and the

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high-density hard-sphere limit) far away from the critical point and the singular behavior near critical point. But just as we point out in the beginning of introduction, things were not right with criticality according to the Van der Waals equation. We here study further the thermodynamic quantities from the critical point with the help of crossover theory. We modify somewhat the results of Kiselev and Friend, and of Chen, Albright and Sengers (CAS) and find that the results can be extrapolated to a wider range than that considered by Kiselev and Friend.

2. THEORIES

(i) Crossover Theory of Chen, Albright and Sengers (CAS) and of Kiselev and Friend

Firstly we review briefly the crossover theory proposed by CAS, which was successful in explaining the experimental data. The procedure is based on an approximation to the solution of the renormalization – group theory of critical phenomena, modified to include the effect from a cutoff wave number for the crossover to the classical limit. Just after the publication of [2], the six-term Landau form crossover theory [3] was published with the same approximations. In 1999, Kiselev and Friend put forward another more complicated crossover theory. Wyczalkowska *et al.*, gave another crossover theory which used the Van der Waals equation [7].

(ii) Modification of CAS Theory

We take as starting point here the CAS theory rather than the theory of Kiselev and Friend because of the simpler representation of Helmholtz free energy and the simpler physical basis of the theory.

Consider one kind of fluid, water, for example, with volume V, mass density ρ and mass m so that

$$m = \rho V \tag{1}$$

From thermodynamics [5], the isochoric heat capacity can be expressed in terms of Helmholtz free energy A as

$$C_v = -T\left(\frac{\partial^2}{\partial T^2}A\right)_v \tag{2}$$

With the help of the critical mass density P_c, critical pressure P_c and critical temperature T_c, we can construct a dimensionless heat capacity as

$$\tilde{C}_v = \frac{C_v T_c}{V P_c} = -\tilde{T}^2 \left(\frac{\partial^2}{\partial \tilde{T}^2} \tilde{A} \right)_{\Delta\tilde{\rho}} \tag{3}$$

where $\tilde{A}$ represents a dimensionless Helmholtz free energy with

$$\tilde{A} = \frac{A T_c}{V T P_c} \tag{4}$$

$$\tilde{T} = -\frac{T_c}{T}, \quad \Delta\tilde{T} = \tilde{T} + 1 \tag{5}$$

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \quad \tilde{\rho} = \frac{\rho}{\rho_c} \tag{6}$$

Then we can write dimensionless heat capacity as [2]

$$\frac{\tilde{C}_v}{\tilde{T}^2} = -\frac{d^2}{d\tilde{T}^2}\tilde{A}_0(\tilde{T}) - \tilde{\rho}\frac{d^2}{d\tilde{T}^2}\tilde{\mu}_0(\tilde{T}) - \left(\frac{\partial^2}{\partial \tilde{T}^2} \Delta\tilde{A} \right)_{\Delta\tilde{\rho}} \tag{7}$$

The expression $\left((\partial^2/\partial\tilde{T}^2)\Delta\tilde{A}\right)_{\Delta\tilde{\rho}}$ can be readily calculated, where $\Delta\tilde{A}$ satisfies the relation used by CAS, namely

$$\tilde{A} = \rho\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) + \Delta\tilde{A} \tag{8}$$

$$\left(\frac{\partial^2}{\partial \Delta\tilde{T}^2} \Delta\tilde{A} \right)_{\Delta\tilde{\rho}} = \left(\frac{\partial^2 \Delta\tilde{A}}{\partial \Delta\tilde{T}^2} \right)_{\Delta\rho} - 2d1 \frac{\partial^2 \Delta\tilde{A}}{\partial\Delta\rho\partial\Delta\tilde{T}} + d1 \left(\frac{\partial^2 \Delta\tilde{A}}{\partial\Delta\rho^2} \right)_{\Delta\tilde{T}} \tag{9}$$

$$\left(\frac{\partial^2 \Delta\tilde{A}}{\partial \Delta\tilde{T}^2} \right)_{\Delta\tilde{\rho}} = c_t^2 \left(\frac{\partial^2}{\partial t^2} \Delta\tilde{A}_s \right)_M G^{-1} \tag{10}$$

$$\frac{\partial^2 \Delta\tilde{A}}{\partial\Delta\tilde{T}\partial\Delta\tilde{\rho}} = c_t c_\rho \left\{ \frac{\partial^2 \Delta\tilde{A}_s}{\partial t \partial M} - c\left[\frac{\partial^2 \Delta\tilde{A}_s}{\partial t \partial M} \right]^2 + c\left(\frac{\partial^2 \Delta\tilde{A}_s}{\partial t^2} \right)_M \left(\frac{\partial^2 \Delta\tilde{A}_s}{\partial M^2} \right)_t \right\} G^{-1} \tag{11}$$

$$\left(\frac{\partial^2 \Delta\tilde{A}_s}{\partial\Delta\rho^2} \right)_{\Delta\tilde{T}} = c_\rho^2 \left(\frac{\partial^2 \Delta A_s}{\partial M^2} \right)_t G^{-1} \tag{12}$$

with

$$\Delta\rho = \Delta\tilde{\rho} - d1\Delta\tilde{T} \tag{13}$$

$$G = \left(1 - c\frac{\partial^2\Delta\tilde{A}_s}{\partial t\partial M}\right)^2 - c^2\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial t^2}\right)_M\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial M^2}\right)_t \tag{14}$$

where Eq. (13) represents a global asymmetry with the coefficient $d1$.

Using the expression proposed by CAS, the order parameters t and M have the respective forms

$$t = c_t\Delta\tilde{T} + c\left[\frac{\partial}{\partial M}\Delta\tilde{A}_s\right]_t \tag{15}$$

$$M = c_\rho\Delta\rho + c\left[\frac{\partial}{\partial t}\Delta\tilde{A}_s\right]_M \tag{16}$$

where $\tilde{u}_0$ and $\tilde{u}_1$ which emerged from the truncated Taylor expansion $\tilde{\mu}_0(\tilde{T})$, can be determined by zero-point values of energy and entropy and are not considered here [2], and $\tilde{A}_1$ emerged from the truncated Taylor expansion. $\tilde{A}_0(\tilde{T})$ also is not considered here. One finds then

$$\Delta\tilde{A}_s = \frac{1}{2}tW(t,M)M^2D(t,M) + \frac{u1v1}{4!}U(t,M)M^4D(t,M)^2 - \frac{1}{2}t^2R(t,M) \tag{17}$$

It takes the two-term Landau form which just is the function of order parameters t and M with the transforms $t \to tW(t,M)\times U(t,M)^{-1/2}$ and $M \to MD(t,M)^{1/2}U(t,M)^{1/4}$ in comparison with the mean-field Landau form [4].

We have used the forms of $W(t,M)$, $D(t,M)$, $U(t,M)$, and $R(t,M)$ as proposed by CAS [2]. Then we can obtain the system-dependent coefficients recorded in Table I.

TABLE I The system-dependent coefficients

P_c	22.064	c_ρ	2.0499656
T_c	647.096	c	−0.126525
ρ_c	322.0	c_t	2.975956
$\tilde{u}_2$	−20.5667	$D1$	−0.3345628
$\tilde{u}_3$	14.8446	$\tilde{A}_2$	−6.85525
$\tilde{u}_4$	10.806	$\tilde{A}_3$	5.28876
$v1$	2.4806	$\tilde{A}_4$	1.089334

3. RESULTS AND DISCUSSION

From the above results, we have constructed Fig. 1–6 using Table I together with the universal coefficients employed by CAS [2]. From the figures, we can see that if we only choose the Helmholtz free

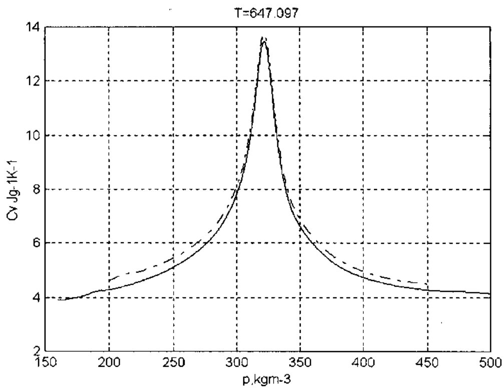

FIGURE 1 Isochoric heat capacity of H_2O versus the mass density ρ at $T = 647.097$ K. The dash not curve represents the value predicted by CAS [1], and solid curve is the result of the modified CAS theory.

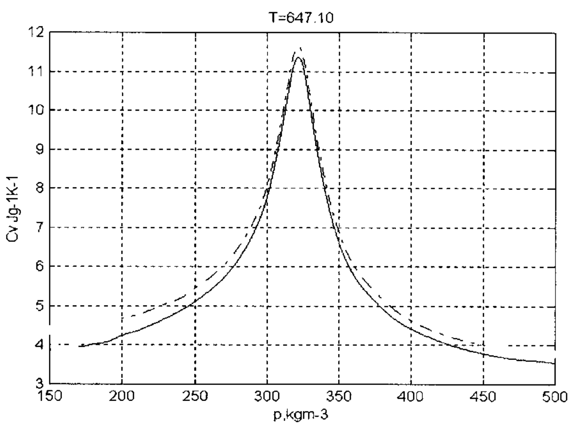

FIGURE 2 Isochoric heat capacity of H_2O versus the mass density ρ at $T = 647.1$ K. The dash dot curve represents the value predicted by CAS [1], and solid curve is the result of the modified CAS theory.

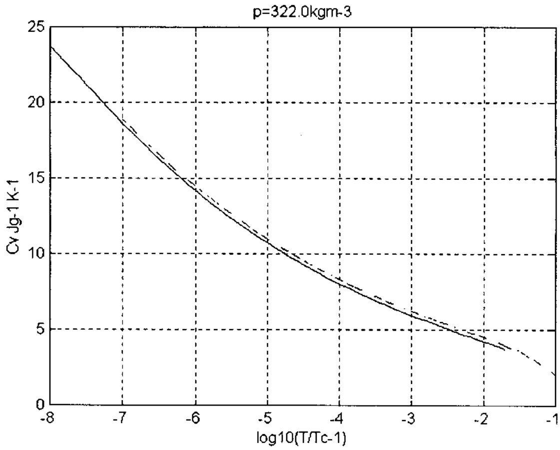

FIGURE 3 Isochoric heat capacity of H_2O versus $\log_{10}(T/T_c - 1)$ in the range -1 to -8, the dash dot curve represents the value predicted by CAS [1], and solid curve is the result of the modified CAS theory.

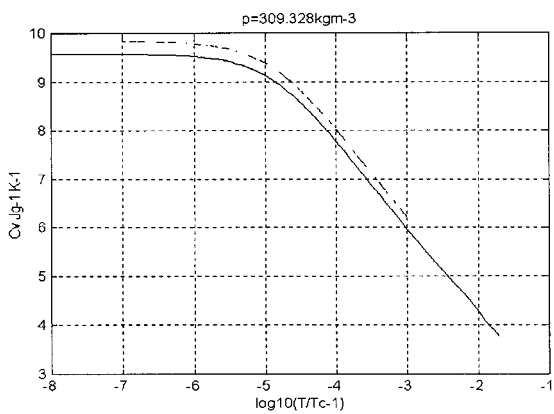

FIGURE 4 Isochoric heat capacity of H_2O versus $\log_{10}(T_c/T - 1)$ at $\rho = 309.328\,\text{kg}\,\text{m}^{-3}$ in the range -1.8 to -8. The dash dot curve represents the value predicted by CAS [1], and solid curve is the result of the modified CAS theory.

energy as in the two-term Landau model, and choose more accurate data, we can obtain good results over a wide range of ρ and T. The 3D Fig. 5 displays the variation of C_v with T and ρ. The range of $\log_{10}(T/T_c{-}1)$ has been extrapolated to -8 in Figs. 3 and 4, and the

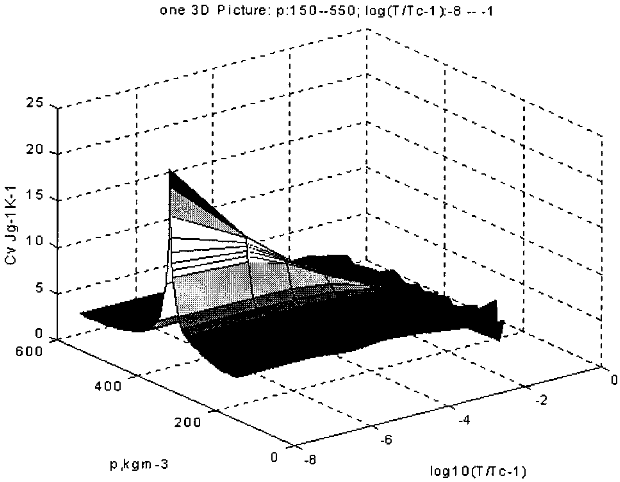

FIGURE 5 The 3D represents isochoric heat capacity of H_2O versus ρ and $\log_{10}(T_c/T-1)$.

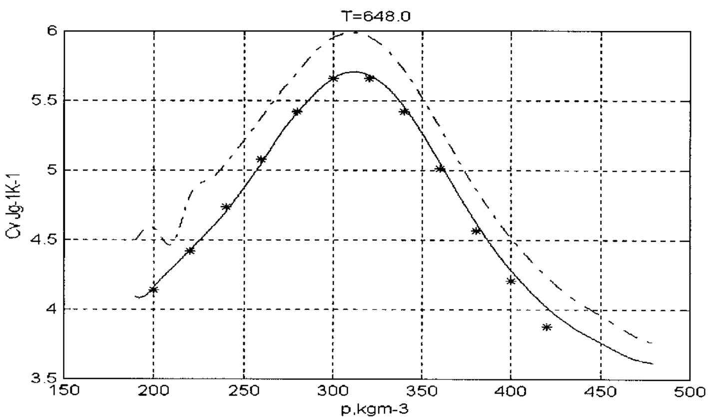

FIGURE 6 Isochoric heat capacity of H_2O versus ρ at the temperature 648 K. The dash dot curve represents the value predicted by CAS [1], and solid curve is the result of the modified CAS theory, and * means the experimental data [6].

range of ρ in Figs. 1 and 2 has been extrapolated to $180\,\mathrm{kg\,m^{-3}}$ and $500\,\mathrm{kg\,m^{-3}}$. From Figs. 4 and 6, we find that the value of C_v very close to the critical point is in reasonable accord with that of Kiselev and Friend.

4. CONCLUSION

We have proposed here a somewhat modified CAS theory. Defined parameters are then proposed to fit the experimental data [6]. We emphasize that it is quite difficult for experimental scientists to determine the heat capacity very close to the critical region because a small temperature divergence will result in a large heat capacity divergence according to the modified CAS theory [see Figs. 1 and 2].

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