Ultrasonic absorption in critical binary mixture of perfluoromethylcyclohexane and carbon tetrachloride

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The results of ultrasonic absorption and velocity measurements for the system perfluoromethylcyclohexane-carbon tetrachloride are presented. In addition, viscosity measurements were made. Ultrasonic absorption at 5, 7, 10, 15, 21, and 25 MHz, above critical temperature T_c, is analyzed using the dynamic scaling theory of Ferrell and Bhattacharjee. The values of α/f^2 vs $f^{-1.06}$ show a good agreement with the theory. The experimental values of α/α_c for the binary mixture are compared to the scaling function $F(\omega^*)$. © *2000 Acoustical Society of America.* [S0001-4966(99)02409-1]

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INTRODUCTION

There are several theories available to analyze ultrasonic absorption measurements.[1–3] However, in this article, the dynamic scaling theory of Ferrell and Bhattacharjee[4] is applied to analyze the absorption and velocity data for the critical binary mixture of perfluoromethylcyclohexane and carbon tetrachloride. This binary mixture has an upper critical temperature T_c of 301.622 K and a critical composition of 0.5527 volume fraction carbon tetrachloride.[5]

In the literature, the available ultrasonic absorption data are not enough to evaluate measurements using the dynamic scaling theory. The ultrasonic absorption was measured by Kruus[6] for the frequencies 3.5, 10.0, and 16.6 MHz at the critical temperature and two other temperatures. Accordingly, in the present work further absorption data are measured for an extended temperature range 301.62–333.16 K and frequency range of 5–25 MHz to support FB theory which enables us to measure and calculate some thermodynamic quantities. The experimental results of absorption are compared to the prediction of the dynamic scaling theory.[4] The theory indicates that α/α_c in Eq. (10) should be a function of the reduced frequency ω^*, and should scale with the scaling function $F(\omega^*)$.

The shear viscosity of the perfluoromethylcyclohexane and carbon tetrachloride as a function of temperature at critical concentration has also been studied in order to determine the value of ω_0 in Eq. (2). The critical amplitudes of the shear viscosity, mutual diffusion coefficient, thermal expansion, and specific heat of the mixture have been obtained. The adiabatic coupling constant g and the change in critical temperature with respect to pressure (dT_c/dp) are calculated. In addition, values of adiabatic and isothermal compressibilities are calculated

I. THEORETICAL CONSIDERATIONS

In the dynamic scaling theory the total absorption coefficient at the critical temperature and concentration can be simply expressed as[7]

$$\alpha(\mathrm{crit},T_c)/f^2 = Sf^{-1.06} + b, \tag{1}$$

where b represents the contribution of the frequency-independent background absorption. The S value is given by[4]

$$S = [\{\pi C_{pc} g^2 \nu_c \text{œ}\}/\{2z\gamma T_c C_p^2(t_f)\}][a\omega_0/2\pi]^{\text{œ}/z\gamma}. \tag{2}$$

Here $\text{œ}=0.11$ and $z\gamma = 1.9$ are the critical exponents,[8] C_{pc} is the critical amplitude in the following expression for the specific heat at constant pressure of a mixture of critical composition:[9]

$$C_p = C_{pc} t^{-\text{œ}} + C_{pb}. \tag{3}$$

C_{pb} is the background specific heat, $a=(\omega/\omega_0)^{t_f - z\gamma}$ is a dimensionless scaling factor of order unity,[10] ω_0 is a characteristic temperature-dependent relaxation rate, g is the adiabatic coupling constant, v_c is the adiabatic sound velocity at T_c, and $C_p(t_f)$ is the specific heat at a characteristic reduced temperature t_f, which can be approximated by $t=(T-T_c)/T_c$ value at which $\alpha(\mathrm{crit},T_c)/f^2$ for a given frequency is one-half its value at T_c.[7]

The adiabatic coupling constant g was introduced by Ferrell and Bhattacharjee and is given by[4]

$$g = \rho_c C_p[(dT_c/dP) - (T\alpha_p/\rho C_p)]$$
$$\cong (C_{pc}\alpha_{pc}T_c/C_{pc}) - \alpha_{pb}T, \tag{4}$$

where ρ_c is the density at critical temperature and concentration, α_p is the isobaric thermal expansion coefficient which can be represented by a power law of the form[11]

$$\alpha_p = \alpha_{pc} t^{-\text{œ}} + \alpha_{pb}. \tag{5}$$

Note that α_{pc} and α_{pb} being the critical and background parts of the thermal expansion coefficients.

The absorption coefficient $\alpha(\mathrm{crit},\omega,T)$ can also be expressed as a function of the dimensionless reduced frequency ω^*,

$$\omega^* = \omega/\omega_D = 2\pi f/\omega_0 t^{z\gamma}, \tag{6}$$

where ω_D is given by[7]

$$\omega_D = k_B T/3\pi\,\eta\xi^3 = (k_B T_c/3\pi\,\eta_0\xi_0^3)t^{z\gamma} = \omega_0 t^{z\gamma}. \tag{7}$$

Here k_B designates Boltzmann's constant, and the correlation length ξ and the shear viscosity η are given by

$$\xi = \xi_0 t^{-\gamma} \tag{8}$$

and

$$\eta = \eta_0 t^{-x_\eta \gamma}, \tag{9}$$

where $x_\eta = 0.06$ is the critical exponent.

The expression for the critical term of the absorption as a function of reduced frequency ω^* is[4]

$$\alpha(\text{crit}, \omega, T)/\alpha(\text{crit}, \omega, T_c) = \alpha/\alpha_c = F(\omega^*) = (1+\omega^{*-0.5})^{-2}, \tag{10}$$

where $\alpha(\text{crit}, \omega, T)$ is the critical term at critical concentration and temperature T, and $\alpha(\text{crit}, \omega, T_c)$ is the critical term at critical concentration and critical temperature T_c.

The isothermal β_T and adiabatic β_s compressibilities and specific heat at constant volume C_v can be represented under the assumptions that all the quantities are expressed as power laws of the form[11]

$$\beta_T = \beta_{Tc} t^{-\alpha} + \beta_{Tb}, \tag{11}$$

$$\beta_s = \beta_{sc} t^{-\alpha} + \beta_{sb}, \tag{12}$$

$$C_v = C_{vc} t^{-\alpha} + C_{vb}, \tag{13}$$

where β_{Tc}, β_{sc}, C_{vc} and β_{Tb}, β_{sb}, C_{vb} are critical and background parts of the mentioned quantities, respectively.

II. EXPERIMENT

The purified carbon tetrachloride CCl_4 and perfluoromethylcyclohexane C_7F_{14} were obtained from Fisher Scientific. The chemicals were used without any further purification. The absorption and velocity measurements were made with a Matec pulse-echo system. The shear viscosity was measured using a Brookfield digital viscometer. Setup and operational procedures are discussed in our previous papers.[12–17]

III. RESULTS AND ANALYSIS

The binary mixture C_7F_{14}–CCl_4 has an upper critical temperature of 301.622 K and a critical composition of 0.5527 volume fraction carbon tetrachloride.[5] The thermostatic control error was $\pm 0.01\,^\circ$C. The absorption measurements were made for the frequencies 5, 7, 10, 15, 21, and 25 MHz in one region starting at 60 °C toward critical temperature $T_c = 28.47\,^\circ$C.

In Fig. 1 the temperature dependence of the absorption α/f^2 for the critical binary mixture of C_7F_{14}–CCl_4 at six different frequencies are shown. The error in the absorption measurements was less than 3%.

Figure 2 shows a plot of absorption α_c/f^2 at critical mixture and temperature T_c vs $f^{-1.06}$. A least-square fit yields an experimental slope S of $0.99\times10^{-7}\pm0.08\times10^{-7}\,\text{cm}^{-1}\,\text{s}^{0.94}$ and an intercept of $529.25\times10^{-17}\,\text{cm}^{-1}\,\text{s}^2$ which represents the frequency-independent background term of α_c/f^2. The data form a straight line as predicted by FB theory. The calculated value of S using Eq. (2) and the calculated value of $g = 0.158\pm0.009$ is $S = 0.74\times10^{-7}\pm0.08\times10^{-7}\,\text{cm}^{-1}\,\text{s}^{0.94}$. Using our calculated values of (dT_c/dP) and $(\partial T/\partial P)_s$, the adiabatic coupling constant g is 0.222 ± 0.008, so the corresponding value of S is $1.28\times10^{-7}\pm0.09\times10^{-7}\,\text{cm}^{-1}\,\text{s}^{0.94}$. Kruus[6] has measured the absorption coefficient for C_7F_{14}–CCl_4 binary mixture for the frequencies 3.5, 10.0, and 16.6 MHz at critical temperature and two other temperatures. His data were evaluated using the Fixman's theory and α_c/f^2 is plotted versus $f^{-1.06}$ along

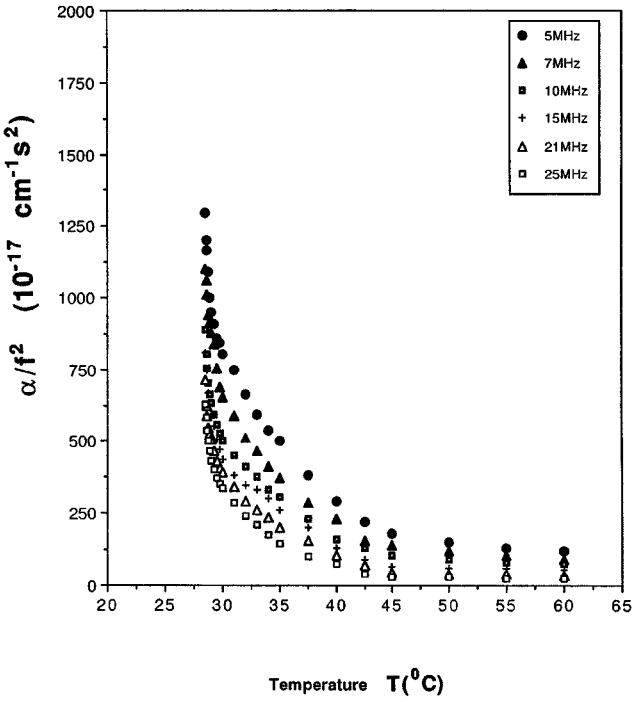

FIG. 1. Temperature dependence of α/f^2 for the critical binary mixture of perfluoromethylecyclohexane and carbon tetrachloride.

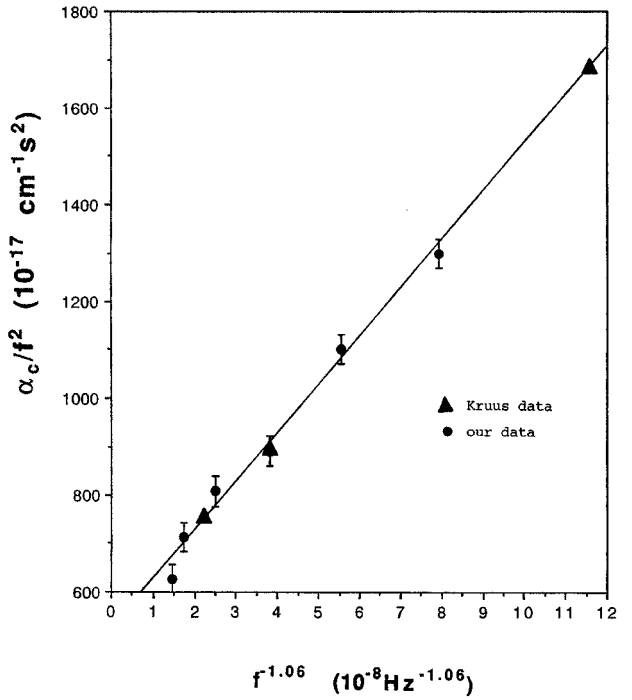

FIG. 2. α_c/f^2 values versus $f^{-1.06}$ at T_c of Kruus (Ref. 6) data along with our data for the critical mixture of perfluoromethylecyclohexane and carbon tetrachloride.

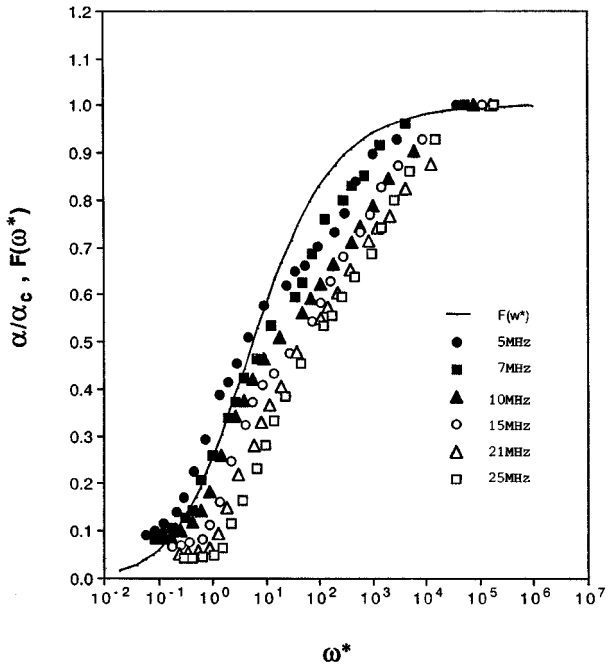

FIG. 3. Plot of α/α_c versus the reduced frequency ω^*. The smooth curve is the scaling function $F(\omega^*)$ given by Eq. (10).

with our data as shown in Fig. 2. From a least-square fit of his data, the slope is $S=1.01\times10^{-7}\,\mathrm{cm}^{-1}\,\mathrm{s}^{0.94}$ and the intercept is $516\times10^{-17}\,\mathrm{cm}^{-1}\,\mathrm{s}^2$. Our values (absorption, slope, and intercept) show good agreement with Kruus's data. For example, at frequency 10 MHz and $T=28.37\,^\circ\mathrm{C}$ his measurement of absorption is $\approx900\times10^{-17}\,\mathrm{cm}^{-1}\,\mathrm{s}^2$, and our measurement at the same frequency and temperature $T=28.50\,^\circ\mathrm{C}$ is $891\times10^{-17}\,\mathrm{cm}^{-1}\,\mathrm{s}^2$.

The experimental values of α/α_c at different frequencies are plotted versus the reduced frequency ω^* along with the theoretical curve $F(\omega^*)$ as shown in Fig. 3. The value of ω_0 was calculated using the measured shear viscosity $\eta_0=0.737\pm0.012$ centipoise shown in Fig. 4.

The velocity versus temperature and frequency at critical concentration are shown in Figs. 5 and 6. A least-square fit

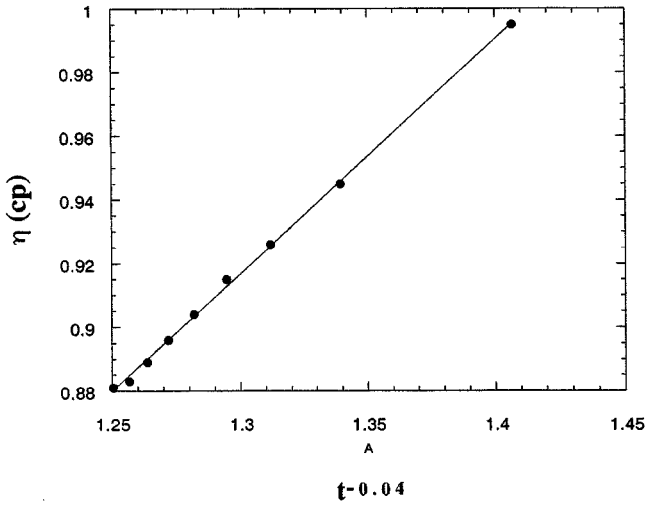

FIG. 4. The measured values of the shear viscosity $\eta(cp)$ vs $t^{-0.04}$ for the critical mixture of perfluoromethylecyclohexane and carbon tetrachloride.

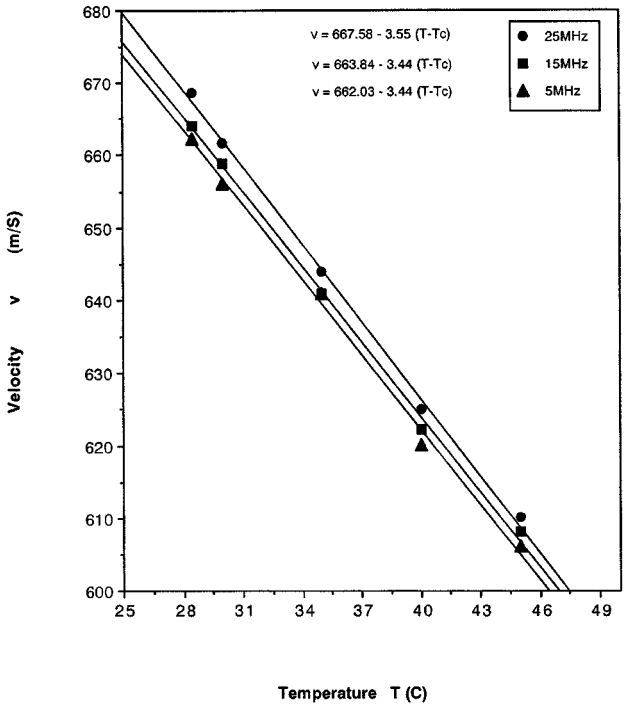

FIG. 5. The velocity versus temperature at critical concentration at three different frequencies.

of 5, 15, and 25 MHz yields the values of critical velocities and slopes at different temperatures. The sound velocity as a function of temperature at a critical concentration can be expressed by

$$v=662.03-3.44(T-T_c)\ \text{in m/s}\quad \text{for 5 MHz},$$

$$v=663.84-3.44(T-T_c)\ \text{in m/s}\quad \text{for 15 MHz},$$

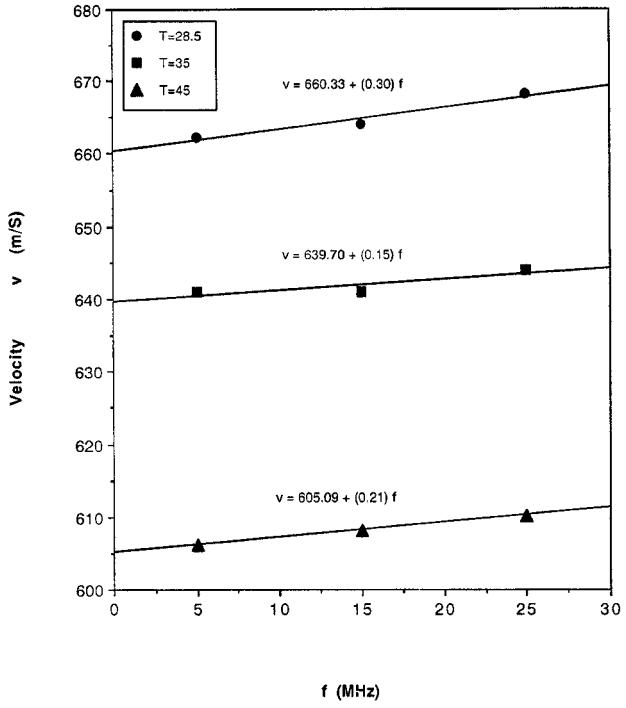

FIG. 6. The velocity versus frequency at critical concentration at three different temperatures.

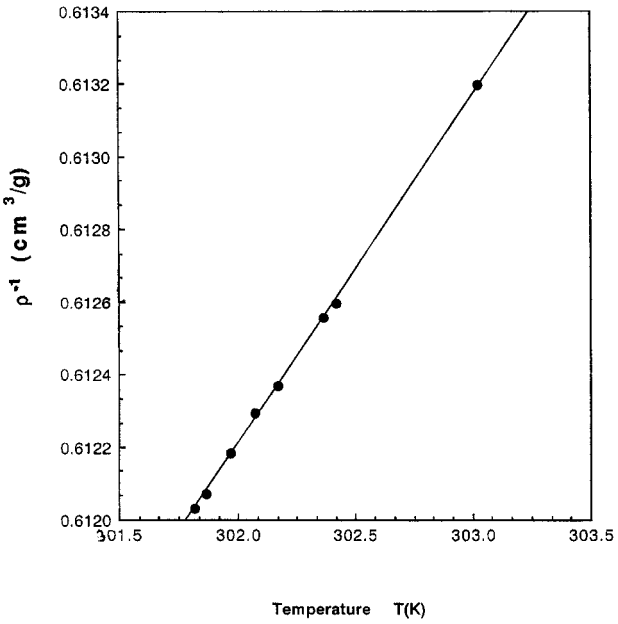

FIG. 7. The reciprocal density ρ^{-1} versus the temperature for the critical mixture of perfluoromethylecyclohexane and carbon tetrachloride. Points represents the data obtained by Darrell *et al.* (Ref. 18).

$$v = 667.58 - 3.55(T - T_c) \text{ in m/s for 25 MHz.}$$

The error in the velocity measurements was less than 0.2%. No anomaly was observed near the critical temperature.

The regular part (background) of the specific heat at constant pressure has been given by[5]

$$C_{pb} = 0.818 \times 10^7 \text{ erg/g K.}$$

Using this value and the two-scale factor universality,[4] α_{pc} and C_{pc} can be calculated, where

$$\xi_0[\text{œ}\rho_c C_{pc}/k_B]^{1/3} = \xi_0[\text{œ}T_c\alpha_{pc}/k_B T_c']^{1/3} = 0.270.$$

The density data for the critical mixture of C_7F_{14}–CCl_4 as a function of temperature has been reported by Darrell *et al.*[18] From their density data, Fig. 7, the slope $(\partial\rho^{-1}/\partial T)_p$ has been estimated from the linear fit of ρ^{-1} at various temperatures, where $(\partial\rho^{-1}/\partial T)_p = 9.58 \times 10^{-4}$ cm^3/g K. Using the thermal expansion coefficient $\alpha_p \equiv \rho(\partial\rho^{-1}/\partial T)_p$ and the power law of α_p, Eq. (5), yields a value of α_{pb}. The values of the thermal expansion and specific heat are then calculated to be

$$\alpha_p = 2.683 \times 10^{-4} t^{-0.11} + 9.795 \times 10^{-4} \text{ K}^{-1},$$

$$C_p = 0.128 \times 10^7 t^{-0.11} + 0.818 \times 10^7 \text{ erg/g K.}$$

The thermodynamic quantities, C_{pc}, C_{pb}, α_{pc}, α_{pb}, T_c, and $(dT_c/dP) = T_c'$ enable us to determine the adiabatic coupling constant g and the thermodynamic quantities mentioned in Eqs. (11), (12), and (13). Some measured and calculated quantities are given in Table I.[19]

IV. CONCLUSION

It can be seen from Fig. 1 that the absorption coefficient for the critical concentration increases as the critical temperature is approached from the high-temperature region for all frequencies. The velocity for the critical mixture increases with increasing frequency. This indicates the dispersion in the sound velocity as expected for binary liquid mixtures. The experimental values of ω^* for the critical binary mixture at different frequencies show good agreement with the theo-

TABLE I. Some measured and calculated values.

Quantity	Measured	Calculated	From references
T_c (K)			301.622[a]
ξ_0 (Å)			2.28[b]
η_0 (cp)	0.737		
ω_0 (Hz)		4.73×10^{10}	
D_0 (cm^2/s)		1.31×10^{-5}	
ρ_c (g/cm^3)			1.633[c]
v_c (cm/s)	66 220		
α_{pc} (K^{-1})		2.683×10^{-4}	
α_{pb} (K^{-1})		9.795×10^{-4}	
C_{pc} (erg/g K)		0.128×10^7	
C_{pb} (erg/g K)			0.818×10^{7}[a]
(dT_c/dP) (cm^2 K/dyne)		3.879×10^{-8}	
$(\partial T/\partial P)_s$ (cm^2 K/dyne)		2.636×10^{-8}	
S (cm^{-1} s$^{0.94}$)	0.99×10^{-7}	1.28×10^{-7}	1.01×10^{-7}[d]
		0.74×10^{-7}	
g		0.158	
β_{Tc} (cm^2/dyne)		1.04×10^{-11}	
β_{Tb} (cm^2/dyne)		50.63×10^{-11}	
β_{sc} (cm^2/dyne)		0.12×10^{-11}	
β_{sb} (cm^2/dyne)		48.46×10^{-11}	
C_{vc} (erg/g K)		0.108×10^7	
C_{vb} (erg/g K)		0.783×10^7	

[a]Reference 5.
[b]Reference 19.
[c]Reference 18.
[d]Reference 6.

retical function $F(\omega^*)$ at the low ($\omega^*<10$) and high ($\omega^*>10^3$) reduced frequencies ω^*. The measured absorption of the α_c/f^2 vs $f^{-1.06}$ yields a straight line as predicted by the FB theory. The coupling constant g is positive which indicates that the phase separation near the critical point is induced by a sudden increase of the pressure.

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