

## Modification of the Fixman analytic function in binary liquid mixtures

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### ABSTRACT

The mode-coupling theory of Fixman failed to explain the experimental behavior of the binary liquid mixtures at critical concentration and above critical temperature. The analytic function of Fixman's theory was modified in order to get an agreement with the experimental behavior of the binary liquid mixtures at critical concentration and above the critical temperature. Ultrasonic absorption and velocity of some binary liquid mixtures were used to test the validity of the Modified-Fixman's theory. It is found that the ratio of heat capacities  $\gamma_0 = \frac{c_V}{c_P}$  (at constant volume and pressure) of the binary liquid mixtures is the term which plays the role to modify the Fixman's theory to get a good agreement with the experimental behavior. © 2015 Trade Science Inc. - INDIA

### INTRODUCTION

Binary mixture is a system contains two systems that not have a homogenous composition, and become uniform thermodynamic properties after critical point at which binary system behave same homogenous phase under the same condition of temperature, pressure, specific heat, viscosity, and thermal conductivity<sup>[9]</sup>

The simple fluid systems can be studied by using the ultrasonic pressure amplitude attenuation per wavelength  $\alpha_\lambda(\omega)$  or absorption coefficient and the sound velocity  $u(\omega)$ , mainly when absorption coefficient of ultrasound near critical point is being observed It was found that there is an increase in this absorption and loss of energy from the sound wave to the fluctuations near the critical point<sup>[13,18,8]</sup>.

Several theories studied the critical behavior of binary liquid mixtures. One of these theories is mode coupling theory which was developed by Fixman to describe the absorption and dispersion of sound near criti-

cal point of binary mixture<sup>[6]</sup>. Mode-coupling theory developed by Kawasaki in terms of critical behavior of bulk viscosity<sup>[11]</sup>. Mistura focused on the critical behavior of complex specific heat<sup>[13]</sup>, the second theory by Kroll-Ruhland and Onuki which described the propagation of acoustic wave in the vicinity of critical point using the renormalization group theory to determine the bulk viscosity<sup>[12]</sup>. The third theory by Ferrel-Bhattacharjee which developed the dynamic scaling theory for the critical ultrasonic attenuation in a binary liquid mixture<sup>[4,5]</sup>. Tanaka and Wada showed that the form of critical amplitude of in Kroll-Ruhland is the same as in the case of Ferrel-Bhattacharjee dynamic scaling theory. Hornowski and his group developed the modified version of the mode-coupling theory for the acoustic anomaly based on the critical behavior of a relaxing complex heat capacity<sup>[10]</sup>.

In this paper, the mode-coupling theory of Fixman will be used to explain the behavior of the experimental data. Correction terms may be added to the theory to

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be able to explain the trend of the experimental data

### THEORY

The mode-coupling theories lead to the same general expression for the attenuation per wavelength  $\alpha_\lambda$  at critical concentration<sup>[11,17]</sup> which is:

$$\frac{\alpha_\lambda}{u^2(\omega)} = \pi A(T) I(\omega^*) \quad (1)$$

Where;  $u(\omega)$  is the velocity of sound;  $A(T)$  is the critical amplitude;  $I(\omega^*)$  is the scaling function.

However, the expression for critical amplitude  $A(T)$  is different for each theory. The scaling function is generalized relaxation function, which is given by<sup>[11,17]</sup>:

$$I(\omega^*) = \int \left[ \frac{x^2 dx}{\{1+x^2\}^2} \right] \left[ \frac{\omega^* K(x)}{\{K(x)^2 + \omega^{*2}\}} \right] \quad (2)$$

Where  $\omega^*$  reduced frequency

$$\omega^* = \frac{\omega}{\omega_D}; \omega_D \text{ is the characteristic frequency given by} \quad (3)$$

$$\omega_D = 2D_0 \xi_0^{-2} t^{1.93}$$

Where;  $D_0$  is the diffusion coefficient<sup>[5,13]</sup>;  $\xi_0$  is the correlation length.

Near the critical point mass diffusion coefficient satisfies an Stokes-Einstein expression, hence Eq. (10) can be written in the following form:

$$\omega_D = \frac{k_B T}{3\pi\mu\xi_0^3} = \frac{k_B T}{3\pi\mu_0\xi_0^3} t^{(3+\chi_\mu)\nu} \quad (4)$$

Where the correlation length and shear viscosity are given by formula<sup>[3]</sup>

$$\xi = \xi_0 t^{-\nu} \text{ and } \mu = \mu_0 t^{\chi_\mu}$$

$k_B$  is the boltzmann's constant and  $t = \frac{T-T_c}{T_c}$  is the reduced temperature, which determines distance from the critical point on temperature scale.

The formula (11) can be written in the form:

$$\omega_D = \omega_0 t^{z\nu} \quad (5)$$

Where;  $z = 3 + \chi_\mu$ ,  $\nu$  and  $\chi_\mu$  are critical exponents with ( $z\nu = 1.93$ )

The analytic function  $K(y)$  of Kawasaki, Mistura, and Chaban is given by<sup>[8]</sup>.

$$K(x) = \frac{3}{4} \left[ 1 + x^2 + \left( x^3 - \frac{1}{x} \right) \arctan(x) \right] \quad (6)$$

While the Fixman's analytic function  $K(x)$  is given

by<sup>[13]</sup>

$$K(x) = x^2 [1 + x^2] \quad (7)$$

The expressions for the critical amplitudes  $A(T)$  of the binary mixture in the mode-coupling theories are given as follows:

Fixman's and Kawasaki's critical amplitudes  $A_F(T)$  and  $A_K(T)$  are given by<sup>[8,15]</sup>:

$$A_F(T) = A_K(T) = \left[ \frac{K_B(\gamma_0-1)\nu^2}{\pi\rho u C_{pb} \xi_0^3} \right] t^{-\alpha} \quad (8)$$

Mistura's form of the critical amplitude is given by<sup>[8,16]</sup>.

$$A_M(T) = A_F(T) [\gamma_0 - 1]^{-2} [1 - 0.5\eta] \quad (9)$$

Chaban's form  $A_C(T)$  is given by<sup>[7]</sup>:

$$A_C(T) = A_F(T) \left[ 1 - \left( \frac{\rho C_{pb}}{\alpha_{pb}} \right) \left( \frac{dT_c}{dP} \right) \right] \quad (10)$$

Where;  $\rho$  is the density of the mixture;  $C_{pb}$  is background heat capacity at constant pressure;  $\gamma_0 = \frac{C_p}{C_v}$  is the ratio of heat capacities;  $\alpha_{pb}$  is the background amplitude of the thermal expansion.

$\xi_0$  is the correlation length,  $\frac{dT_c}{dP}$  is the slope of the critical line of consult points as a function of pressure.  $T_c$  is the critical temperature of the binary mixture and  $\eta$ ,  $\nu$ ,  $\alpha$  are critical exponents.

Hornowski's modification is based on the critical behavior of a relaxing complex heat capacity. The general expression for the critical amplitude  $A_H(T)$  has been derived in terms of the dimensionless parameter<sup>[10]</sup>

$$d = \left[ \frac{C_{vb} \rho}{T \alpha_{pb}} \right] \left[ \frac{dT_c}{dP} \right] \quad (11)$$

Where  $C_{vb}$  is the back ground specific heat coefficient at constant volume

The critical Hornowski's amplitude  $A_H(T)$  is given by<sup>[10]</sup>:

$$A_H(T) = A_K(T) [1 - 0.5\eta]^2 f(d) \quad (12)$$

Where the function

$$f(d) = [(\gamma_0 - 1)^2 - 2d \gamma_0 [d - (\gamma_0 - 1)^{-1}]] \quad (13)$$

### RESULTS

Two binary mixtures 3Methylpentane+ Nitroethane and Nitrobenzen-n Hexane use to study Fixman and Modification of Fixman analytic func-

tion at different frequency.

### 3Methylpentane+Nitreothane

Data  $\alpha_\lambda$  of was taken from Garland and Sanchez paper<sup>[8]</sup>, as well as the sound velocity.

Figure (1) show plots of experimental absorption values  $\frac{\alpha_\lambda}{u^2 \pi A(T)}$  vs. reduced frequency  $\omega^*$  of Fixman along with the theoretical scaling integral  $I(\omega^*)$  of binary mixture 3Methylpentane+Nitreothane.

Figure (2) show plots of experimental absorption values  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  vs. reduced frequency  $\omega^*$  of Fixman and Modification of Fixman along with the theoretical scaling integral  $I(\omega^*)$  of binary mixture 3Methylpentane+Nitreothane.

Figure (3) show plots of experimental absorption values  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  vs. reduced frequency  $\omega^*$  of Modification of Fixman along with the theoretical

TABLE 1 : The necessary data which are needed to calculate  $A_F(T)$  of 3methylpentane –nitrothane

Quantity	Value	References
$T_c$	299.6	(Abdelraziq, 2003)
$C_{pc}$ (erg/gK)	$1.94 \times 10^7$	(Greer and Hocken, 1975)
$\xi$ (Å)	2.16	(Abdelraziq, 2003)
$D_n$ (cm <sup>2</sup> /s)	$3.28 \times 10^{-5}$	(Greer and Hocken, 1975)
$\rho$ (g/cm <sup>3</sup> )	0.791	(Abdelraziq, 2003)
$\omega_0$ (Hz)	$1.23 \times 10^{11}$	(Garland, 1983)
$\eta_0$ (cp)	0.35	(Greer and Hocken, 1975)
$\gamma_0$	1.28	(Garland, 1983)

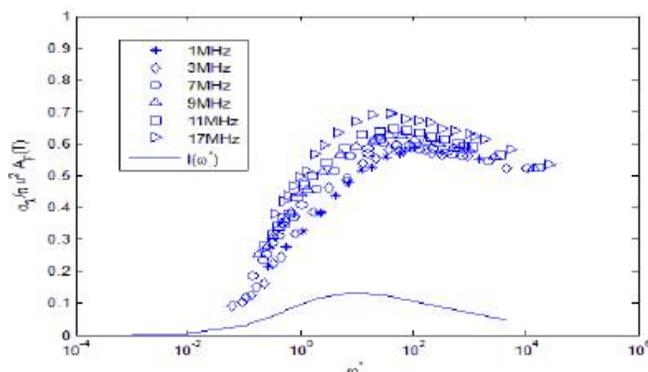


Figure 1 : Experimental absorption values  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for 3methylpentane+nitreothane according to Fixman theory along with the theoretical scaling integral  $I(\omega^*)$

scaling integral  $I(\omega^*)$  of binary mixture 3Methylpentane+Nitreothane.

### Nitrobenzen-n hexane

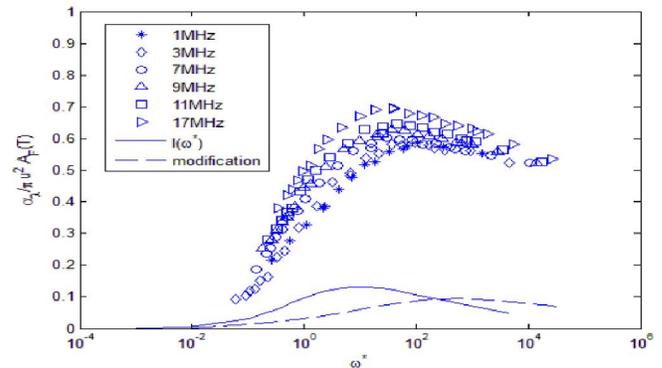


Figure 2 : Experimental absorption values  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for 3methylpentane+nitreothane according to Fixman theory along with the theoretical scaling integral  $I(\omega^*)$  solid line, dashed line represent modification form of Fixman's theory.

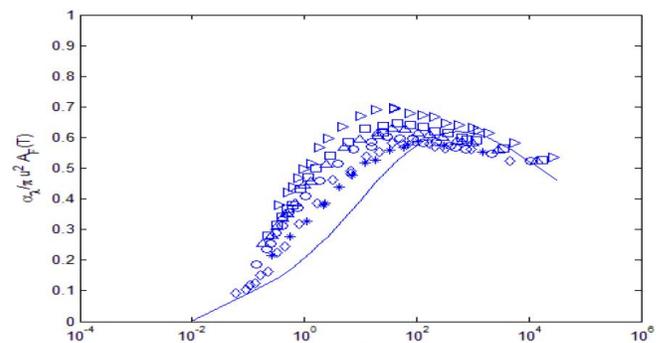


Figure 3 : Experimental absorption values  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for 3methylpentane+nitreothane according to modification Fixman theory along with the theoretical scaling integral  $I(\omega^*)$  in solid line.

Data of was taken from Abdelraziq, as well as the sound velocity.

Figure (4) show plots of experimental absorption values  $\frac{\alpha_\lambda}{u^2 \pi A(T)}$  vs. reduced frequency  $\omega^*$  of Fixman along with the theoretical scaling integral  $I(\omega^*)$  of binary mixture Nitrobenzen-n Hexane

Figure (6) show plots of experimental absorption values  $\frac{\alpha_\lambda}{u^2 \pi A(T)}$  vs. reduced frequency  $\omega^*$  of Fixman along with the theoretical scaling integral  $I(\omega^*)$  of

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TABLE 2 : The necessary data which are needed to calculate  $A_F(T)$  of Nitrobenzen- n Hexane

Quantity	Value	References
$T_c$	293.25	(Abdelraziq, 2003)
$C_{pc}(\text{erg/gK})$	$1.9 \times 10^7$	(Greer and Hocken, 1975)
$\xi_0 (\text{\AA})$	2.03	(Abdelraziq, 2003)
$D_0 \left(\frac{\text{cm}^2}{\text{s}}\right)$	$3.28 \times 10^{-5}$	(Greer and Hocken, 1975)
$\rho (\text{g/cm}^3)$	0.8432	(Abdelraziq, 1989)
$\omega_n (\text{Hz})$	$2 \times 10^{10}$	(Abdelraziq, 1989)
$\eta_0 (\text{cp})$	0.563	(Abdelraziq, 1989)
$\gamma_0$	1.24	(Abdelraziq, 1989)

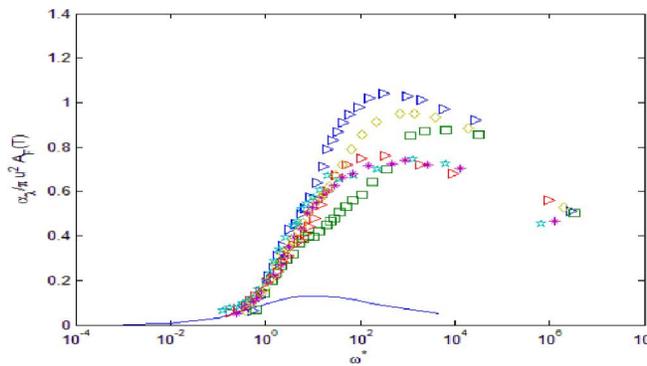


Figure 4 : The experimental value  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for nitrobenzene- n hexane according to Fixman theory along with the theoretical scaling function  $I(\omega^*)$  in solid line.

binary mixture Nitrobenzen-n Hexane

DISCUSSION

Analytic function of Fixman theory is given by the following equation:

$$K(x) = x^2[1 + x^2]$$

Modification for Fixman analytic function is given by:

$$|K(x)| = 2x^2 * (10x^2 + 1 + 6x^4 + 8x^3) \tag{14}$$

Where;  $\gamma_0$ : The ratio of heat capacities at constant pressure and volume,  $\nu$ : critical exponent equal 0.63. and  $x = q\xi$ ,  $\xi$  correlation length,  $q$ : wave number.

Closed to the critical point, the fluctuations in thermodynamic properties increase, then the system acting kind of arrangement after this point, this behavior of binary system after this point is described by analytic func-

tion of mode coupling theories, which is proportional to the correlation length.

The analytic function of Fixman [equation (7)] is poor for describing this behavior of system below or  $\omega^* > 10$  in high reduced frequency (closed to  $T_c$ ), modification form of analytic function of Fixman's analytic function appear in equation (14), this modification shows in Figure (3) and Figure (6), as noticed that new term in old analytic function caused a reduction in the amplitude of the scaling function, because this terms have relationship to the correlation length which describe the range of fluctuations of thermodynamic properties of system after critical point, and this term cause Expansion in the scaling function as shown in Figure 4.

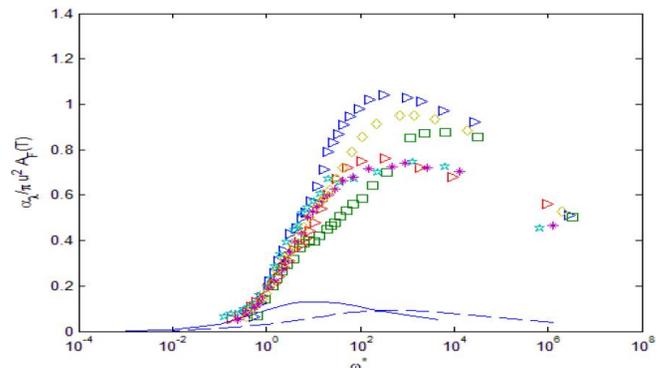


Figure 5 : The experimental value  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for nitrobenzene- n hexane according to Fixman theory along with the theoretical scaling function  $I(\omega^*)$  [solid line], modification Fixman theory along with the theoretical scaling function  $I(\omega^*)$  [dashed line].

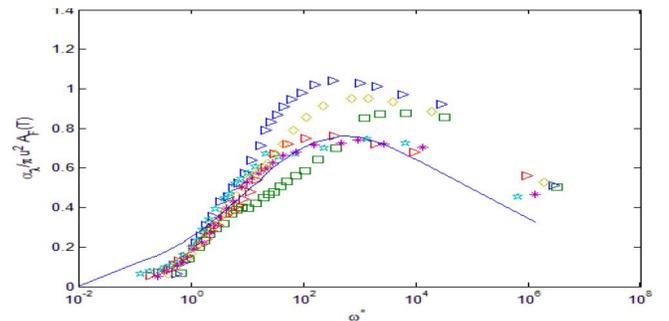


Figure 6 : The experimental value  $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$  Vs. reduced frequency  $\omega^*$  for nitrobenzene- n hexane according to modification Fixman theory along with the theoretical scaling function  $I(\omega^*)$  in solid line with adding new parameter to scaling function.

The new term is not enough to match the theory to the experimental value, then need another term must be added to the scaling function after integration to raise the amplitude, this term depending on the ratio of heat capacities  $\gamma_0$  which is equal  $\frac{\gamma_0}{\gamma_0-1} + 2$ .

The results show a much better agreement in modification of Fixman analytic function than the values obtained using the theories of Fixman, especially at the low reduced frequencies  $\omega^*$ . However, for the large values of reduced frequency  $\omega^* > 10$  the mode-coupling theory of Fixman still exhibits poor agreement with the observed data, but at modification of Fixman analytic function there is a good agreement at high frequency.

### CONCLUSION

Mode-coupling theories used to describe the behavior of critical binary mixture after critical point, it have been disagreement with the experimental value of binary mixture over the range of reduced frequency  $\omega^* > 10$ . The Modified-Fixman's theory was found much better than old Fixman's analytic function when applied it in binary mixtures 3Methylpentane+Nitroethane and Nitrobenzen-n Hexane.

The effective term which plays an important role in this modification depend on the ratio of heat capacities at constant volume and pressure.

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