

Two - Scale - Factor Universality of Binary Liquid Critical Mixtures

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Abstract: The universal quantity R_ξ^+ of some binary liquid mixtures has been calculated, using the results of recent experimental collateral data. The values of X_ξ for the systems are in good agreement with the other experimental and also with the theoretical values. The obtained average value of $R_\xi^+ = 0.2691 \pm 0.0028$ supports the theoretical value of $R_\xi^+ = v[n/4\pi]^{1/d}$, in three dimensions for $n = 1$ and $d = 3$ which indicates that fluid and binary mixtures transitions belong to the same class of universality "two-scale-factor universality".

Key Words: Liquid Mixtures, Scale Factor Universality, Thermal Expansion, Specific Heat

Introduction

The universality of the R_ξ which implies two-scale-factor universality, has been rather well studied in the case of binary fluids. It may be recalled that the modern theories of critical phenomena are able to predict R_ξ with remarkable precision. The basic problem in getting an accurate estimate for X_ξ is the large uncertainty because of the correlation length ξ_0^3 factor involved which multipliers three times any uncertainty in ξ_0 . In addition, the specific heat is not known very accurately for a number of binary liquids.

In early attempts to verify two-scale-factors universality from specific heat results, it could not be shown exactly that X_ξ is the same for a number of binary liquid systems (H. Klein and D. Woermann 1976). A better estimate was available in a subsequent attempt but vagaries of data analysis precluded a decisive conclusion (J. Thoen *et al.*, 1978).

An alternative approach is to try the thermal expansion coefficient α_{pc} . In general the thermal expansion coefficient can be known better than the specific heat coefficient C_{pc} . Using the thermal expansion data one could improve the estimates of X_ξ values for different systems (H. Klein and D. Woermann, 1978). Subsequently a better method of estimating ξ_0 and the use of recent specific heat amplitude values gave encouraging results.

The purpose of the present paper is to calculate values for the quantity X_ξ for some binary liquid mixtures from two-scale-factor using recent values of correlation length ξ_0 , specific heat C_{pc} and thermal expansion α_{pc} .

Theory: The hypothesis of universality has played a central role in the study of phase transition. It arises from the fact that the characteristics lengths near a critical point are much larger than the microscopic interaction scale. An extension of these hypothesis, namely, the two-scale-factor universality hypothesis, states that the critical amplitudes do not depend on three different scales of parameter (length, temperature, external field), but only on two (C. Bervillier and C. Godreche, 1980). Most of the observed quantities depend only on the dimensionalities of the space (d) and of the order parameter (n) (G. Zalczer *et al.*, 1983). The fluid and binary mixtures transitions belong to the same class of universality $d = 3, n = 1$.

The universality concept of critical phenomena generalizes the law of corresponding states and asserts that the equation of state and the correlation function near critical points contain together only two material dependent scale factor. Since all binary liquid mixtures with critical mixing points belong to the same universality class the universality concept offers the

possibility to relate the critical amplitudes of different properties of these systems. The exponents are universal and related by the so-called scaling laws. The amplitudes of the correlation length, thermal expansion and specific heat can be deduced using the universal amplitude combinations (G. Zalczer *et al.*, 1983; E. A. Clerke *et al.*, 1983; H. Tanaka and Y. Wada, 1983; D. T. Jacobs, 1986; R. B. Kopelman and R. W. Gammon, 1984; E. Bloemen *et al.*, 1980; Y. Shiwa and K. Kawasaki, 1981; Y. Shiwa and K. Kawasaki, 1981).

The critical amplitude of correlation length ξ_0 of local concentration fluctuations in the one-phase region which can be determined by light-scattering experiments is defined by:

$$\xi = \xi_0^+ (t)^{-\nu} \quad (t) > 0, \quad (1)$$

$$\xi = \xi_0^- (-t)^{-\nu} \quad (t) < 0, \quad (2)$$

where $\nu = 0.63$ is the critical exponent, $t = (T - T_c)/T_c$ and T_c is the critical temperature.

The specific heat at constant pressure C_p in zero field is singular and is given by:

$$C_p = C_{pc}^+ (t)^{-\alpha} + C_{pb}^+ \quad (t) > 0 \quad (3)$$

$$C_p = C_{pc}^- (-t)^{-\alpha} + C_{pb}^- \quad (t) < 0, \quad (4)$$

where C_{pc} and C_{pb} are the critical and background amplitudes of the specific heat and $\alpha = 0.11$ is the critical exponent.

The asymptotic behaviour of the thermal expansion α_p can be represented by power law of the form,

$$\alpha_p = \alpha_{pc}^+ (t)^{-\alpha} + \alpha_{pb}^+ \quad (t) > 0 \quad (5)$$

$$\alpha_p = \alpha_{pc}^- (-t)^{-\alpha} + \alpha_{pb}^- \quad (t) < 0 \quad (6)$$

where α_{pc} and α_{pb} are the critical and the background amplitudes of the thermal expansion. The limitation of the reduced temperature $t > 0$ and $t < 0$ is typically given in the range $10^{-4} < |t^*| < 10^{-3}$.

With these three amplitudes ξ_0^+ , C_{pc}^+ , and α_{pc}^+ , it is possible to construct a quantity, denoted R_ξ^+ , which is universal in the same sense as critical indices are universal. This quantity is defined as:

$$R_\xi^+ = \xi_0 [\alpha_{pc} C_{pc} / k_B]^{1/d} = \xi_0 [\alpha_{pc} T_c \alpha_{pc} / (k_B T_c)]^{1/d}, \quad (7)$$

where $d = 3$ is the dimension of the space, k_B designates Boltzmann's constant, ρ_c is the density of the critical mixture at critical temperature T_c and concentration and $T_c' = dT_c/dP$ is the pressure derivative of the critical temperature along the critical line.

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In several theoretical papers, X_{ξ}^+ is represented by R_{ξ}^+ , where

$$R_{\xi}^+ = X_{\xi}^{1/3} \quad (8)$$

The theoretical value of R_{ξ}^+ in three dimensions is will approximated by the phenomenological formula (C. Bervillier and C. Godreche, 1980):

$$R_{\xi}^+ = v[n/4\pi]^{1/d} \quad (9)$$

which yields: $n = 1$, $R_{\xi}^+ = 0.2710 \pm 0.0004$; $n = 2$, $R_{\xi}^+ = 0.3627 \pm 0.0005$; $n = 3$, $R_{\xi}^+ = 0.4372 \pm 0.0013$. The critical exponent $v = 0.63$ (C. Bervillier and C. Godreche, 1980). The mode-coupling theory can predict the amplitude of the critical anomaly of specific heat C_p from a more fundamental quantity, the correlation length ξ_0 . The amplitude of the critical anomaly of specific heat is given by:

$$C_{pc} = (k_B v^2 / 4\pi\rho_c \xi_0^3) t^{-\alpha} \quad (10)$$

The expression of C_{pc} up to four-diffusion-mode coupling is

$$C_{pc} = (k_B v^2 / \pi\rho_c \xi_0^3) [J^{(0)} + J^{(1)}], \quad (11)$$

where $J^{(0)}$ and $J^{(1)}$ are, respectively, the limiting values of $J^{(0)}(\omega^*)$ and $J^{(1)}(\omega^*)$ at $\omega^* = \infty$ the $J^{(0)}(\omega^*)$ and $J^{(1)}(\omega^*)$ are the scaling functions given by Shiwa and Kawasaki, (Y. Shiwa and K. Kawasaki, 1981; Y. Shiwa and K. Kawasaki, 1981; H. Tanaka and Y. Wada, 1985; S. J. Fast and S. S. Yun, 1987; S. J. Fast and S. S. Yun, 1988; C. W. Garland and G. Sanchez, 1983) $\omega^* = (\omega/\omega_D)$ is the reduced frequency.

ω_D is a characteristic temperature-dependent relaxation rate that can be approximated by the Stokes-Einstein expression, $\omega_D = (k_B T_c / 3\pi\eta\xi^3) = (k_B T_c / 3\pi\eta_0\xi_0^3) t^{z\nu}$, where the expressions $\xi = \xi_0 t^{-\nu}$ for the correlation length and $\eta = \eta_0 t^{x\nu}$ for the shear viscosity have been used. η_0 is the shear viscosity coefficient and x, ν are critical exponents, $x, \nu = 0.04$ and $z\nu = 1.93$. (E. A. Clerke *et al.*, 1983)

Results and Discussion

The data to calculate X_{ξ} and R_{ξ}^+ are given in Table 1. The correlation length ξ_0 was calculated using the recent values of $\omega_0 = (k_B T_c / 3\pi\eta_0\xi_0^3)$ which were determined from the measurements of the ultrasonic absorption and the measured shear viscosity coefficient of several binary liquid mixtures. In addition, either the thermal expansion coefficient α_{pc} or the specific heat coefficient C_{pc} is needed to calculate the value of X_{ξ} .

Table 1: Results of Analysis of Binary Liquid Critical Mixtures

System	T_c (K)	η_0 (cp)	ξ_0 (Å)	C_{pc}	α_{pc} (K ⁻¹)	$X \cdot 10^2$	R_{ξ}
Nitrobenzene + n-hexane	293.05 ^b	0.550 ^a	3.54 ^c	6.6x10 ⁵ ^a erg/gK	3.12x10 ⁻⁵ ^a	1.9679 ^a 1.95 ^z	0.26998 ^a
Nitroethane + isooctane	304.66 ^d	0.483 ^a	2.42 ^e	2.14x10 ⁶ ^a erg/gK	1.48x10 ⁻⁵ ^a	1.9683 ^a 1.66 ^z	0.27000 ^a
Carbontetrachloride + perfluoromethylcyclohexane	301.62 ^f	0.737 ^g	2.28 ^h	1.28x10 ⁶ ^g erg/gK	2.68x10 ⁻⁴ ^g	1.9747 ^a 1.85 ^z	0.27029 ^a
Cyclohexane + aniline	303.36 ⁱ	1.01 ^a	2.25 ^j	2.7x10 ⁶ ^k erg/gK	5.2x10 ⁻⁵ ^a	1.9708 ^a 1.85 ^z	0.27011 ^a
Methanol + n-heptane	323.88 ^l		2.80 ^a	1.46x10 ⁵ ^a erg/gK		1.8452 ^a 1.48 ^z	0.26425 ^a
Isobutyric + acid-water	299.43 ^l		3.7 ^a	4.53x10 ⁵ ^a erg/gK	7.8x10 ⁻⁵ ^a	1.8169 ^a 1.71 ^z	0.26289 ^a
Triethylamine + water	291.6 ^m		1.0 ^m	2.58x10 ⁷ ^m erg/gK	1.66x10 ⁻³ ^a	1.90579 ^a 1.91 ^z	0.26711 ^a
Triethylamine + heavy water	287.8 ⁿ		1.08 ⁿ	1.96x10 ⁷ ⁿ erg/gK	1.38x10 ⁻³ ^a	1.96259 ^a 1.96 ^z	0.2697 ^a
Methanol + carbondisulfide	310 ^o		1.52 ^a	7.89x10 ⁵ ^o erg/cm ³ K	3.8x10 ⁻⁵ ^o	2.00784 ^a 1.9682 ^a	0.27179 ^a
Methanol + cyclohexane	319.05 ^p	0.41 ^a	3.24 ^q	9.54x10 ⁵ ^r erg/gK	7.0x10 ⁻⁵ ^a	1.95201 ^a 1.95 ^z	0.26925 ^a
3 methylpentane + nitrothane	299.6 ^s	0.35 ^a	2.16 ^t	3.24x10 ⁶ ^u erg/gK	3.1x10 ⁻⁵ ^a	2.05934 ^a 2.06 ^z	0.27410 ^a
Nitrobenzene + n-heptane	292.56 ^v	0.68 ^a	3.8 ^a	4.95x10 ⁴ ^a erg/cm ³ K		1.9682 ^a 1.9682 ^a	0.26999 ^a
Hexane + β,β' dichloroethyl ether	285.86 ^w	0.44 ^a	2.6 ^a	1.55x10 ⁵ ^a erg/cm ³ K		1.97997 ^a 1.97997 ^a	0.27053 ^a
2,6-Iutidine + water	306.73 ^x	1.64 ^a	2.1 ^a	3.43x10 ⁵ ^a erg/cm ³ K		1.98998 ^a 1.98998 ^a	0.27099 ^a
Polystyrene + cyclohexane	285.73 ^y		5.8 ^y	1.46x10 ⁵ ^a erg/gK	1.3x10 ⁻⁷ ^y	1.8639 ^a 1.8639 ^a	0.26514 ^a

^aThis work.

^bG. Zalczer *et al.*, 1983.

^cS. H. Chen *et al.*, 1983.

^dH. Tanaka and Y. Wada, 1983.

^eY. Garabos *et al.*, 1982.

^fM. Pelger *et al.*, 1977.

^gI. R. Abderlaziq, 2000.

^hP. Calmetters, 1977.

ⁱH. Tanaka *et al.*, 1982.

^jI. R. Abderlaziq, 2001.

^kI. R. Abderlaziq, 1996.

^lH. Klein and D. Woermann, 1975.

^mG. P. Furrow and S. C. Greer, 1983; I. R. Abderlaziq *et al.*, 1992.

ⁿE. Bloemen *et al.*, 1980.

^oH. Klein and D. Woermann, 1978.

^pS. J. Fast and S. S. Yun, 1988.

^qD. T. Jacobs, 1986.

^r R. B. Kopelman, R. W. Gammon, and M. R. Moldover, 1984.
^s E. A. Clerke *et al.*, 1983.
^t R. F. Change *et al.*, 1979.
^u E. A. Clerke *et al.*, 1983; G. Sanchez *et al.*, 1983.
^v A. Dega-Dalkowska, 1984.
^w E. M. Bains and M. A. Breazeale, 1974.
^x V. P. Gutschick and C. J. Pings, 1971.
^y S. C. Greer, and D. T. Jacobs, 1980; D. T. Jacobs and S. C. Greer, 1981.
^z S. J. Fast and S. S. Yun, 1985; S. J. Fast and S. S. Yun, 1987.

The determination of the critical amplitudes of the specific heat are generally about 2 - 4 Å. However, in both systems triethylamine - water and triethylamine - heavy water value of approximately 1 Å is observed. This may explain why one observes in these two systems a much larger anomaly in C_{pc} compared to other systems.

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Conclusion

The value of X_c appears to be material independent for the binary liquid mixtures, supporting the idea that X_c is constant for all systems. The values of X_c for the systems $(1.949 \pm 0.062) \times 10^{-2}$ are in good agreement with the other experimental values and also with the theoretical values. The analysis shows that the evidence is accumulating in support of the two-scale-factor universality of binary liquid mixtures. If the theoretical value of X_c is accepted to be material independent for the binary liquid mixtures, one can confirm that the value of critical amplitude of the specific heat is accepted. The obtained average value of $R_c = 0.2691 \pm 0.0028$ supports the theoretical value of $R_c^+ = \sqrt{[n/4\pi]^{1/3}}$, in three dimensions for $n = 1$, which indicates that the fluid and binary mixtures transitions belong to the same class of universality. In general, the relationship called "two-scale-factor universality" was initially difficult to confirm because of lack of experimental precision but recent work seems

to confirm the expected relationship for binary liquid mixtures.

References

Abdelraziq, I. R., S. S. Yun and F. B. Stumpf, 1992. J. Acoust. Soc. Am., 91: 844.
 Abdelraziq, I. R., 1996. J. Islamic Univ., 4: 90.
 Abdelraziq, I. R., 2001. An-Najah Univ. J. Res., 15: 11-20.
 Abdelraziq, I. R., 2000. J. Acoust. Soc. Am. 107: 788.
 Bloemen, E., J. Thoen and W. Van Dael, 1980. J. Chem. Phys. 73: 4628.
 Bains, E. M. and M. A. Breazeale, 1974. J. Chem. Phys., 61: 1238
 Bervillier, C. and C. Godreche, 1980. Phys. Rev. B 21: 5427.
 Clerke, E. A., J. V. Sengers; R. A. Ferrell and J. K. Bhattacharjee, 1983. Phys. Rev. A 27: 2140-2151.
 Change, R. F., H. Burstyn and J. V. Sengers, 1979. Phys. Rev. A19: 866.
 Chen, S. H., C. C. Lai; J. Rouch and P. Tartaglia, 1983. Phys. Rev. A27: 1086.
 Calmetters, P., 1977. Phys. Rev. Lett. 39: 1151.
 Dega-Dalkowska, A., 1984. Chem. Phys. Lett., 107: 575-578.
 Fast, S. J. and S. S. Yun, 1985. J. Chem. Phys. 83: 5888, S. J. Fast and S. S. Yun, 1987, J. Chem. Phys. 86: 497.
 Fast, S. J. and S. S. Yun, 1988. J. Acoust. Soc. Am. 83: 1384.
 Fast, S. J. and S. S. Yun, 1987. J. Acoust. Soc. Am. 81: 1418.
 Furrow, G. P. and S. C. Greer, 1983. J. Chem. Phys., 79: 3474-3481.
 Gutschick, V. P. and C. J. Pings, 1971. J. Chem. Phys., 55: 3845.
 Garabos, Y., G. Zalczer and D. Beysens, 1982. Phys. Rev. A 25: 1147.
 Garland, C. W. and G. Sanchez, 1983. J. Chem. Phys. 79: 3090-3099.
 Greer, S. C. and D. T. Jacobs, 1980. J. Phys. Chem., 84: 2888-2890.
 Hohenberg, P. C., A. Aharony; B. I. Halperin and E. D. Siggia, 1976. Phys. Rev. B 13: 2986-2996.
 Jacobs, D. T., 1986, Phys. Rev. A 33: 2605-2611.
 Jacobs, D. T. and S. C. Greer, 1981. Phys. Rev. A24: 2075-2083.
 Klein, H. and D. Woermann, 1975. Berichte der Bunsen-Gesellschaft 79: 1180-1186.
 Klein, H. and D. Woermann, 1978. Ber. Bunsenges, Phys. Chem. 82: 1084-1086.
 Klein, H. and D. Woermann, 1976. J. Chem. Phys., 64: 5316-5317.
 Kopelman, R. B., and R. W. Gammon, 1984. Phys. Rev. A 29: 2048-2053.
 Kopelman, R. B., R. W. Gammon and M. R. Moldover, 1984. Phys. Rev. A29: 2048.
 Pelger, M., H. Klein and D. Woermann, 1977. J. Chem. Phys. 67: 5362.
 Shiwa, Y. and K. Kawasaki, 1981. Prog, Theor. Phys. 66: 406.
 Shiwa, Y. and K. Kawasaki, 1981. Prog. Theor. Phys. 66: 118.
 Stauffer, D., M. Ferer and M. Wortis, 1972. Phys. Rev. Lett. 29: 345
 Sanchez, G., M. Meichle and C. W. Garland, 1983. Phys. Rev. A28: 1647.
 Tanaka, H. and Y. Wada, 1983. Chem. Phys. 78: 143.
 Tanaka, H. and Y. Wada, 1985. Phys. Rev. A 32: 512.
 Tanaka, H., Y. Wada and H. Nakajima, 1982. Chem. Phys., 68: 223. Thoen, J., E. Bloemen and W. Van Dael, 1978. J. Chem. Phys. 68: 735-749.
 Thoen, J., E. Bloemen and W. Van Dael, 1978. J. Chem. Phys. 68: 735-749.
 Zalczer, G., A. Bourgou and D. Beysens, 1983. Phys. Rev. A, 28: 440.