Crossover criticality in complex fluids

Crossover criticality in complex fluids

Mikhail A Anisimov

Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD 20742, USA

Abstract.   If the structure of a complex fluid is characterized by a nanoscopic or mesoscopic length scale comparable with the correlation length of critical fluctuations, a specific sharp crossover from classical mean-field behaviour to Ising asymptotic behaviour is observed. In the region far away from the critical point where the correlation length is still smaller than this structural length scale, one can observe mean-field behaviour. Ultimately, in the nearest vicinity of the critical point, the correlation length becomes dominant and one should expect Ising singular behaviour. Such a crossover is observed in polymer solutions, where the structural length scale is controlled by the molecular weight of polymer, and in aqueous salt solutions, where the range of Ising behaviour can be tuned by the salt concentration. The structural length diverges at a tricritical point. Crossover to mean-field tricriticality can be naturally incorporated into a universal scaling description of polymer solutions.

It is commonly accepted that complex fluids, such as polymer and micellar solutions, microemulsions and solutions of electrolytes asymptotically close to the appropriate critical points exhibit the same universal behaviour as simple fluids. In other words, all fluids, simple and complex, belong to the same universality class, namely that of the three-dimensional Ising model [1]. Critical-point universality originates from the long-range nature of the order-parameter fluctuations. Close enough to the critical point the correlation length of critical fluctuations becomes so large that microscopic details of short-range intermolecular interactions become unimportant. However, as the distance from the critical point increases, one should expect a crossover to classical mean-field (van-der-Waals-like) behaviour. The range of classical behaviour should increase with increase of the range of intermolecular forces. Such an expectation is confirmed by a numerical study of the three-dimensional Ising lattice with a variety of interaction ranges tuned by the coordination number [2]. However, in ordinary fluids with short-range intermolecular forces, the crossover to classical critical behaviour is never completed in the critical domain. The critical domain is characterized by the parameter $\tau = (T - T_c)/T \ll 1$, the reduced difference between the temperature T and the critical temperature T_c. In practice, one can consider $\tau \approx 10^{-2}$ or a few kelvins around an ordinary critical temperature as the critical domain. In simple fluids at $\tau \approx 10^{-2}$ the correlation length is about 2–5 nm, which is much larger than the characteristic microscopic length scale (of the order of a molecular size). The fluctuations become unimportant outside the critical region only. In contrast, in complex fluids, one observes sometimes almost pure classical behaviour in the critical domain [3, 4]. Thus, the range of Ising-like universal behaviour in complex fluids can be so narrow that experimentally it is difficult to achieve. More typically, the physical properties of complex fluids in the critical region exhibit some kind of intermediate (crossover) non-universal behaviour rather than asymptotic behaviour [5–9]. The questions

arise: (i) What can we learn about complex fluids from the shape of the crossover? (ii) What physical features drive the crossover and control the crossover temperature τ_x?

A natural phenomenological approach to the crossover problem in complex fluids is to assume that the critical behaviour in such systems is affected by a competition between the correlation length, ξ, of the critical fluctuations and an additional length ξ_D associated with a supramolecular structure or/and with long-range interparticle interactions. When the correlation length dominates, the system enters the Ising critical regime. When the length ξ_D is larger than ξ, the critical fluctuations are not important. The length ξ_D may be associated with an additional (non-critical) order parameter and will diverge at a tricritical or a multicritical point of some kind that emerges as a result of coupling between the order parameters. With small logarithmic corrections, the tricritical behaviour is almost mean-field-like [10]. Thus, if the system is close to the tricritical point, one should expect a crossover to mean-field tricriticality.

A sensitive test of the shape of the crossover behaviour is obtained from analysis of the effective exponent of the susceptibility χ, defined as $\gamma_{eff} = -\mathrm{d}\log\chi/\mathrm{d}\log\tau$, and from the effective critical exponent of the order parameter φ defined as $\beta_{eff} = \mathrm{d}\log\varphi/\mathrm{d}\log\tau$. The exponent γ_{eff} exhibits crossover from its classical value $\gamma = 1$ ($\tau \gg \tau_x$) to its Ising value $\gamma \simeq 1.24$ ($\tau \ll \tau_x$). Analogously, β_{eff} changes from its classical value $\beta = 0.5$ to its Ising value $\beta \simeq 0.325$. Anisimov *et al* [7] have shown that the crossover behaviour in many complex fluids can be quantitatively described by a crossover function based on the 'renormalization group matching' theory [11, 12] that contains two independent parameters: a rescaled coupling constant $\bar{u}$ which reflects the strength and the range, $\bar{\xi}_0$, of molecular forces ($\bar{u} \sim \bar{\xi}_0^{-4}$ [13]) and a 'cutoff' inverse length, Λ, which in complex fluids is assumed to be inversely proportional to the structural length ξ_D. The product of $\bar{u}$ and of the ratio $\bar{\xi}_0/\xi_D$ determines the so-called Ginzburg number $N_G \simeq 0.03(\bar{u}\bar{\xi}_0/\xi_D)^2$ which serves as the crossover scale. Independently, the difference $(1 - \bar{u})$ determines the shape of the crossover: the larger $\bar{u}$, the sharper the crossover. If N_G is small and $(1 - \bar{u})$ is small or negative, the crossover behaviour is both pronounced and sharp. The crossover temperature τ_x can be defined as the inflection point of $\gamma_{eff}(\tau)$: in practice, $\tau_x \simeq 10N_G$.

If is important to emphasize the physical difference between approaching mean-field behaviour due to the long-range nature of the molecular forces (small $\bar{u}$, while $\bar{\xi}_0/\xi_D$ is not small) and that due to a small ratio ξ_0/ξ_D (i.e. the ratio $\xi_D/\bar{\xi}_0$ is large, while $\bar{u}$ is not necessarily small). In both cases the Ginzburg number is small. The former case is the conventional crossover to mean-field *critical* behaviour. Complete crossover of such a kind has been observed in the three-dimensional Ising model [2, 13]. The latter case of large and eventually diverging ξ_D may correspond to approaching a special kind of mean-field behaviour, namely *tricritical* mean-field behaviour. A typical and conceptually well understood example is the crossover to theta-point *tricriticality* in polymer solutions [14, 15]. Possibly, a mean-field-like multicriticality determines the nature of crossover phenomena in ionic solutions as well [16].

This approach has been proved for high molecular weight polymers in low molecular weight solvents. The structural length scale ξ_D in polymer solutions can be identified with the radius of gyration. It has been shown by Melnichenko *et al* [8] that the susceptibility of polystyrene solutions in deuterocyclohexane does exhibit a sharp crossover to mean-field behaviour with τ_x corresponding to the temperature at which the correlation length becomes equal to the radius of gyration. As the radius of gyration diverges in the infinite molecular weight limit, the critical temperature approaches the theta temperature Θ and τ_x vanishes. Povodyrev *et al* [14] have developed a crossover Flory model modified by fluctuations to describe phase separation in polymer solutions. In the Flory model $\xi_D \sim N^{1/2}$ [17] with N being the degree of polymerization. Thus the crossover temperature $\tau_x \sim N^{-1/2}$.
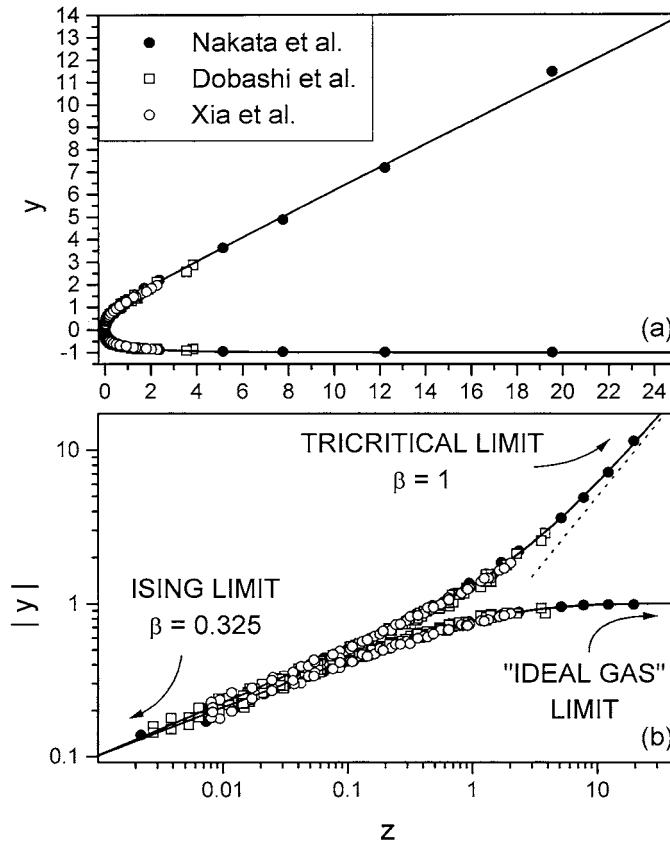
Figure 1. Universal scaled phase coexistence in polymer solutions: (a) plotted in a linear scale, (b) plotted in a logarithmic scale. Symbols are the experimental data for 16 different systems with a variety of polymer molecular weights [18–20]. The solid curve is predicted by the crossover theory [15] based on a six-term Landau expansion renormalized by fluctuations.

A spectacular demonstration of scaling and crossover to tricriticality in polymer solutions can be done without assumptions and restrictions implied by any particular equation of state. In figure 1 the rescaled experimental phase co-existence data are presented in linear (a) and logarithmic (b) scales for different polymer systems with various molecular weights of polymers: polystyrene in methylcyclohexane, polystyrene in cyclohexane and polymethylmethacrylate in 3-octanone obtained by Dobashi *et al* (nine samples with polymer molecular weight from 10^4 to 7.2×10^5) [18], Nakata *et al* (two samples with polymer molecular weights 2×10^5 and 1.6×10^6) [19], and Xia *et al* (five samples with polymer molecular weights from 4.9×10^4 to 6×10^5) [20], respectively. The solid curve represents the universal crossover description based on a six-term Landau expansion renormalized by fluctuations [15]. The universal description is formulated in terms of the scaling variable $z = C|\tau|/\phi_c$ and the scaling function $y(z) = A(\phi - \phi_c)/B_0\phi_c^\beta$, where ϕ is the volume fraction of polymer, ϕ_c the critical volume fraction, C the asymptotic slope of the polymer-rich branch of the coexistence curve, B_0 the asymptotic critical amplitude according to $\phi - \phi_c \simeq \pm B_0|\tau|^\beta$ and the constant A is defined as $B_0\phi_c^{\beta-1} \to A$ at $\phi_c \to 0$.

While polymer solutions demonstrate the crossover behaviour which is conceptually well understood, another class of complex fluids, ionic fluids, remains a subject of controversy. In
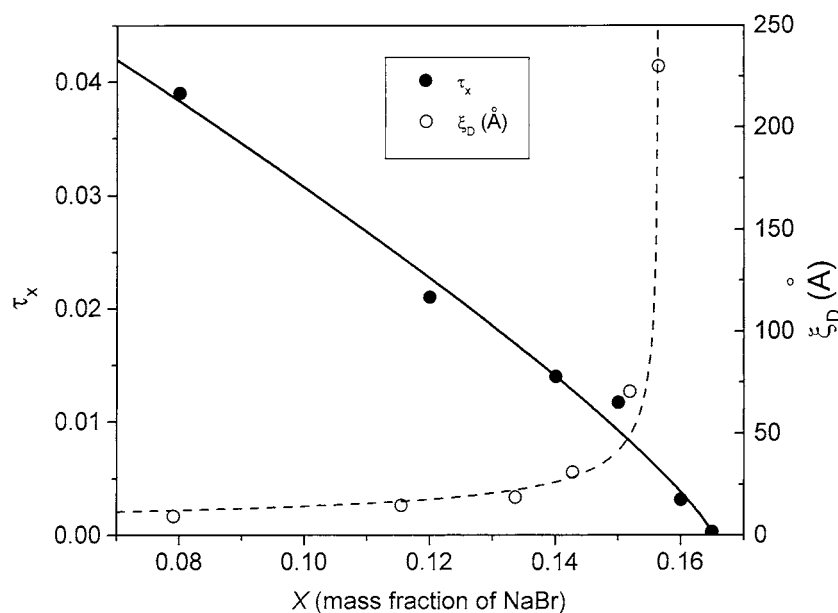
Figure 2. Crossover temperature τ_x and the crossover length scale ξ_D as a function of NaBr concentration X. The solid curve represents an empirical power law $\tau_x = 0.3(X_0 - X)^{0.8}$ with $X_0 = 0.1652$. The dashed curve represents a power law $\xi_D \sim (X_0 - X)^{-1/2}$.

spite of remarkable progress in the theoretical investigations of various models representing ionic systems [21–23] and impressive experimental achievements [24, 25], there is still no clear picture of ionic criticality. Phase separation in most fluids containing ions is driven by non-coulombic forces. This does not mean that ions play no role in the phenomenon, but it means the phase separation can occur even in the absence of ions. Examples are vapour–liquid separation of salty water or liquid–liquid separation of weakly dissociated organic solutes in water. The latter is referred to as 'solvophobic' phase separation and expected in solvents of high dielectric constant when coulombic forces are weak [24]. In aqueous solvophobic systems hydrogen bonding may also play an important role in driving the phase separation and causing more complex phase behaviour such as closed-loop phase diagrams and double critical points. This, however, does not make the criticality different from that in other solvophobic systems [26]. Results of experiments in 'coulombic' systems are ambiguous. While Narayanan and Pitzer [6] observed a sharp crossover to mean field for solutions of tetra-*n*-butylammonium picrate in low dielectric constant alcohols (the result was later confirmed by an explicit analysis [7]), some other coulombic systems do not exhibit any pronounced tendency to mean-field behaviour [27] or even show either mean-field [3, 4] or Ising [28, 29] behaviour in the same system depending on the sample source. In this respect, a complete crossover to mean-field critical behaviour recently observed in a typically solvophobic system, a ternary solution of 3-methylpyridine-water-sodium bromide [9], deserves special attention. This system exhibits a closed-loop miscibility gap which is widening with increase of the salt concentration. At low concentration of NaBr the susceptibility extracted from the light-scattering intensity exhibits almost Ising behaviour; however, with increase of the salt concentration the crossover to mean-field behaviour becomes more and more pronounced. Finally, at a concentration of 16.5 mass% NaBr the critical behaviour becomes almost perfectly mean-field-like. Figure 2 demonstrates the decrease of the crossover temperature τ_x with increase of the salt concentration and a
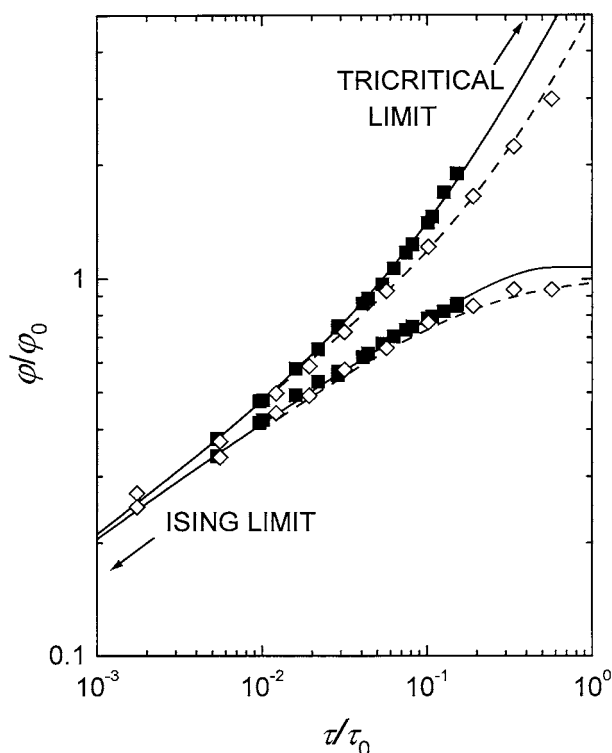
Figure 3. Comparison between the rescaled coexistence curves of dioxane–water–CuSo$_4$ and polystyrene–methylcyclohexane. Solid squares are experimental data for dioxane–water–CuSO$_4$ [31] and open diamonds are experimental data [18] for the polymer with the highest molecular weight (7.2×10^5). The solid curve represents the crossover predicted for the salt solution [16]. The dashed curve represents the crossover to tricriticality for polymer solutions [15].

divergence of the length ξ_D at the point where τ_x vanishes. It was assumed that the divergence of ξ_D is associated with the proximity to a multicritical point which emerges on the critical line presumably as a result of strong interaction between critical fluctuations and ions. It was speculated that this point may be identified with a so-called Lifshitz tricritical point in which two liquid phases coexist with a charge-density-wave phase [30] (see also [21, 23]).

It should be noted that the tricritical value of the susceptibility exponent γ is the same as the mean-field value $\gamma = 1$, so the crossover behaviour of the susceptibility alone does not allow us to distinguish between mean-field criticality and mean-field tricriticality. This is why the analysis of the crossover behaviour of the coexistence curve, similar to that presented for polymer solutions, plays a crucial role in revealing the possibility of tricriticality. In figure 3 the rescaled data for the coexistence curves of the polystyrene– (molecular weight $\simeq 7.2 \times 10^5$) methylcyclohexane system obtained by Dobashi *et al* [18] and of dioxane–water– (saturated) CuSO$_4$ obtained by Japas [31] are presented. The rescaling parameters used, as suggested by Izumi and Miyake [32], are $\varphi_0 = \phi_c \simeq 0.04$ (critical volume fraction) and $\tau_0 = (\Theta - T_c)/T_c \simeq 0.027$ for the polymer solution, while they are $\varphi_0 \simeq 0.03$ and $\tau_0 \simeq 0.18$ for the aqueous salt solution. The parameters for the aqueous solution were adjusted in such a way that the critical Ising limit ($\tau/\tau_0 \ll 1$) became the same as for the polymer solution. The similarity between the two curves is remarkable. Far away from the critical point ($\tau/\tau_0 \gg 1$),

the coexistence curves transform into the angle-like shape with the critical exponent $\beta \to 1$ corresponding to the tricritical limit. This result supports the assumption that the crossover to mean-field tricriticality may be a common phenomenon in concentrated aqueous salt solutions with lower critical points. Ions may stabilize the fluctuations of concentration and result in charge ordering and eventually in appearance of a multicritical point. The observed crossover in some 'coulombic' systems, possibly, may also be caused by coupling between coulombic and solvophobic interactions and by formation of a supramolecular structure. Evidence of a coarse structure at a scale of ~ 2 nm as well as sharp crossover to mean-field behaviour has been reported by Chieux [33] and Chieux and Sienko [5] for metal–ammonia solutions. To verify the assumption that this is a common reason for the crossover behaviour in ionic fluids, more systematic and accurate experiments are desirable.

Acknowledgments

References

[1] Fisher M E 1988 *Critical Phenomena (Lecture Notes in Physics 186)* ed F J W Hahne (Berlin: Springer) p 1
[2] Luijten E and Binder K 1988 *Phys. Rev.* E **58** R4060
[3] Singh R R and Pitzer K S 1990 *J. Chem. Phys.* **92** 6775
    Pitzer K S 1992 *Accounts Chem. Res.* **23** 373
[4] Zhang K C, Briggs M E, Gammon R W and Levelt Sengers J M H 1992 *J. Chem. Phys.* **97** 8692
[5] Chieux P and Sienko M J 1970 *J. Chem. Phys.* **53** 566
[6] Narayanan T and Pitzer K S 1995 *J. Chem. Phys.* **102** 8118
[7] Anisimov M A, Povodyrev A A, Kulikov V D and Sengers J V 1996 *Phys. Rev. Lett.* **75** 3146
    Anisimov M A, Povodyrev A A, Kulikov V D and Sengers J V 1995 *Phys. Rev. Lett.* **76** 4095
[8] Melnichenko Y B, Anisimov M A, Povodyrev A A, Wignall G D, Sengers J V and Van Hook W A 1997 *Phys. Rev. Lett.* **79** 5266
[9] Jacob J, Kumar A, Anisimov M A, Povodyrev A A and Sengers J V 1998 *Phys. Rev.* B **58** 2188
    Anisimov M A, Jacob J, Kumar A, Agayan V A and Sengers J V to be published
[10] Lawrie D and Sarback S 1984, *Phase Transitions and Critical Phenomena* ed C Domb and J L Lebowitz (London: Academic) p 1
[11] Nicholl J F and Bhattacharjee J K 1981 *Phys. Rev.* B **23** 389
[12] Nicholl J F and Albright P C 1985 *Phys. Rev.* B **31** 4576
[13] Anisimov M A, Luijten E, Agayan V A, Sengers J V and Binder K 1998 *Preprint* Cond-Mat/9810252
[14] Povodyrev A A, Anisimov M A and Sengers J V 1999 *Physica* A **264** 345
[15] Anisimov M A, Agayan V A and Gorodetskii E E to be published
[16] Gutkowski K, Anisimov M A and Sengers J V to be published
[17] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (New York: Cornell University)
[18] Dobashi T, Nakata M and Kaneko M 1980 *J. Chem. Phys.* **72** 6685
     Dobashi T, Nakata M and Kaneko M 1980 *J. Chem. Phys.* **72** 6692
[19] Nakata M, Dobashi T, Kuwahara N, Kaneko M and Chu B 1979 *Phys. Rev.* A **18** 2683
     Nakata M, Kuwahara N and Kaneko M 1975 *J. Chem. Phys.* **62** 4278
[20] Xia K Q, An X-Q and Shen W G 1996 *J. Chem. Phys.* **105** 6018

[21] Fisher M E 1994 *J. Stat. Phys.* **75** 1
[22] Fisher M E 1996 *J. Phys.: Condens. Matter* **8** 9103
     Fisher M E and Lee B P 1996 *Phys. Rev. Lett.* **77** 3561
     Lee B P and Fisher M E 1997 *Europhys. Lett.* **39** 611
[23] Stell G 1995 *J. Stat. Phys.* **78** 197
[24] Weingärtner H, Kleemeier M, Wiegand S and Schröer W 1995 *J. Stat. Phys.* **78** 169
[25] Levelt Sengers J M H, Harvey A H and Wiegand S *Equations of State for Fluids and Fluids Mixtures*
     ed J V Sengers and J White (Amsterdam: Elsevier) at press
[26] Narayanan T and Kumar A 1994 *Phys. Rev.* **249** 135
[27] Wiegand S, Kleemeier M, Schröder J M and Weingärtner H 1994 *Int. J. Thermophys.* **15** 1045
[28] Wiegand S and Levelt Sengers J M H, Zhang K J, Briggs M E and Gammon R W 1997 *J. Chem. Phys.* **106** 2777
[29] Wiegand S, Briggs M E, Levelt Sengers J M H, Kleemeier M and Schöer W 1998 *J. Chem. Phys.* **109** 9038
[30] Nabutovskii V M, Menov M A and Peisakhovich Yu G 1980 *Sov. Phys.–JETP* **52** 1111
     Nabutovskii V M, Menov M A and Peisakhovich Yu G 1980 *Phys. Lett.* A **79** 98
     Nabutovskii V M, Menov M A and Peisakhovich Yu G 1985 *Mol. Phys.* **54** 979
[31] Japas M L 1999 private communication
[32] Izumi Y and Miyake Y 1984 *J. Chem. Phys.* **81** 1501
[33] Chieux P 1991 *J. Physique Coll.* IV **C5** 373