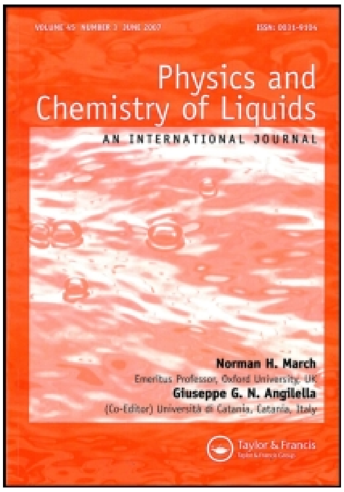

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Singh, R. N.(1997) 'Chemical and Topological Order in the Vicinity of Phase Separation', Physics and Chemistry of Liquids, 34: 4, 249 — 253
To link to this Article: DOI: 10.1080/00319109708030569
URL: http://dx.doi.org/10.1080/00319109708030569

Phys. Chem. Liq., 1997, Vol. 34, pp. 249–253
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Letter

CHEMICAL AND TOPOLOGICAL ORDER IN THE VICINITY OF PHASE SEPARATION

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(Received 7 January 1997)

A statistical thermodynamic model is used to establish a link between the chemical order, topological order and the concentration fluctuations in the nearest neighbour shell of a binary mixture. The topological order related to density fluctuations is found to play the dominant role in the process of phase separation.

Keywords: Coordination number; segregation

The physical significance of the topological order in the critical region of the phase separation entails considerable importance in the light of results that have been obtained from the pioneering experiments of Hensel and coworkers [1–2]. The neutron diffraction experiments by these authors on expanded fluid Cs exhibit a significant decrease in the coordination number as one approached the critical point of the liquid vapour interface. Liquid Rb also shows similar features. Following it, March and coworkers [3–4] suggest that coordination number tends to 2 at the critical point of the phase boundary.

In this note we provide a short discussion related to chemical short range order parameter (α_1), concentration fluctuations [$S_{cc}(0)$] in the long wavelength limit and the coordination number (z) as one approaches to the critical region of the phase separation in a binary mixture. Consider a binary mixture consisting of A and B atoms. If A and B atoms prefer to remain self coordinated (i.e. A-A pair or B-B pair) over the heterocoordinated pair (i.e. A-B pair), then such a mixture is termed as segregating mixture. Phase separation is an extreme condition of segregation. In order to quantify it, we consider the Warren-Cowley [5–6] short range order parameter, α_1, for the first neighbour shell which is defined in terms of conditional probabilities,

$$\begin{aligned} P_{AB} &= C_A(1-\alpha_1) \\ P_{BA} &= C_B(1-\alpha_1) \end{aligned} \tag{1}$$

where $P_{i,j}$ defines the probability that i atoms exist at site 2 as a nearest neighbour of a given j atom at site 1. Obviously, $C_A P_{BA} = C_B P_{AB}$. Equation (1) provides an immediate insight into the local arrangement of atoms in the mixture. For random distribution of atoms, $P_{AB} = C_A$, then $\alpha_1 = 0$. If $\alpha_1 > 0$, A-A or B-B pairs of atmos are preferred over A-B pairs as nearest neighbour, and for the converse case $\alpha_1 < 0$. By taking a probabilistic approach one can easily show that the limiting values of α_1 lie in the range,

$$\begin{aligned} -\frac{C_A}{C_B} \le \alpha_1 \le 1 \quad \text{for} \quad C_A \le \frac{1}{2} \\ -\frac{C_B}{C_A} \le \alpha_1 \le 1 \quad \text{for} \quad C_A \ge \frac{1}{2} \end{aligned} \tag{2}$$

For $C_A = C_B = \frac{1}{2}$, one has

$$-1 \le \alpha_1 \le 1 \tag{3}$$

The minimum possible value, $\alpha_1^{\min} = -1$, means complete ordering of A-B pairs in the mixture, whereas the maximum value, $\alpha_1^{\max} = +1$, suggests that the A-A and B-B pairs in the mixture are totally segregated. For segregation α_1 varies from 0 to + 1, the latter value conforms to the phase separation.

By virtue of the basic thermodynamic relations, α_1 and the concentration fluctuations, $S_{cc}(0)$, in the long wavelength limit are directly related. If atoms A and B are assumed to be located at sites of lattice, the grand partition function of the system is then written as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) e^{(\mu_A N_A + \mu_B N_B - E)/K_B T} \tag{4}$$

where $q_i(T)'s(i = A, B)$ are the partition functions associated with inner and translational degrees of freedom of atom i and $\mu_i's$ are the chemical potentials. N_A and N_B are the number of A and B atoms in the alloy with the configurational energy E. The grand partion function (4) can be solved by lattice-model theory for different sizes of the cluster of atoms [7 – 8]. It readily provides an expression for X_{AB} (probability that one lattice site of a nearest neighbour pair is occupied by an A atom and the other by a B atom),

$$X_{AB} = \frac{2C_A C_B}{(\beta + 1)} \tag{5}$$

where
$$\beta = \left\{1 + 4C_A C_B\left(e^{\frac{2w}{zK_BT}} - 1\right)\right\}^{\frac{1}{2}} \tag{6}$$

where w is the order energy and z is the coordination number of the first shell. The conditional probability P_{AB} is related to $X_{AB}(X_{AB} = C_B P_{AB})$, therefore

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{7}$$

On the other hand, equation (4) can also be linked to basic thermodynamic relations to obtain an expression for excess free energy of mixing, i.e.

$$\frac{G_M^{xs}}{NK_BT} = C_A \ell n\ \gamma_A + C_B \ell n \gamma_B \tag{8}$$

with
$$\gamma_A = \left\{\frac{\beta - 1 + 2C_A}{C_A(\beta + 1)}\right\}^{\frac{1}{2}z}; \quad \gamma_B = \left\{\frac{\beta + 1 - 2C_A}{C_B(1 + \beta)}\right\}^{\frac{z}{2}} \tag{9}$$

The concentration fluctuations, $S_{cc}(0)\left\{= NK_BT(\frac{\partial^2 G_M}{\partial c^2})^{-1}_{T,P,N}\right\}$, therefore becomes

$$S_{cc}(0) = \frac{C_A C_B}{1 + \frac{1}{2}z(\beta^{-1} - 1)} \tag{10}$$

Now, on eliminating β from (7) and (10), one has a desired relation between α_1 and $S_{cc}(0)$.

$$\alpha_1 = \frac{(S^* - 1)}{S^*(z-1)+1}, S^* = \frac{S_{cc}(0)}{C_A C_B} \tag{11}$$

Equation (11) provides a desired link between the short range order(α_1), the coordination number (z) and the concentration fluctuations $[S_{cc}(0)]$ in the nearest neighbour shell of binary mixture. The inter-dependence of α_1, z and $S_{cc}(0)$, is depicted in Figure 1. In the region of heterocoordination $(\alpha_1 < 0), \alpha_1$ decreases with decreas-

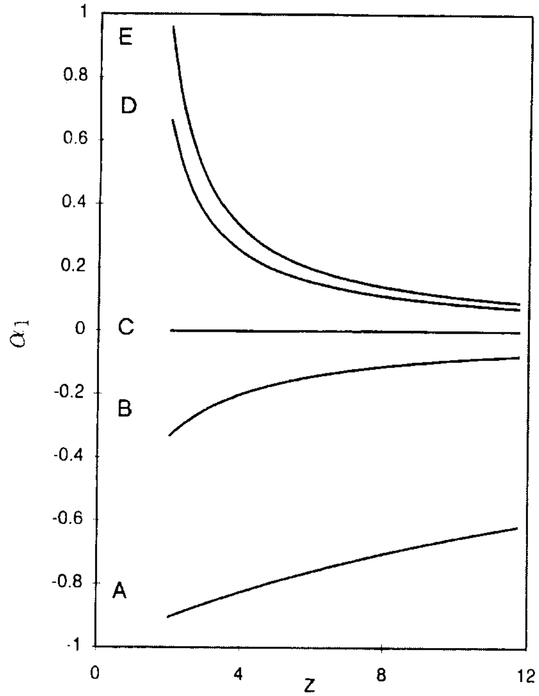

FIGURE 1 Variation of short range order parameter (α_1) with coordination number (z) in the first coordination shell of a binary mixture for different values of concentration fluctuations: Curves A, B, C, D and E refer to $S_{cc}(0)/C_A C_B = 0.05, 0.5, 1.0, 5.0$ and 50 respectively.

ing z for a given fluctuation. On the other hand α_1 increases with decreasing z in the region of homocoordination ($\alpha_1 > 0$) for a given $S_{cc}(0)$. However, for a given z, the increase in concentration fluctuations increases α_1. In phase separating region, increase in α_1 is more dramatic at low z.

The increase in α_1 in the segregating region is distinctively visible as z decreases below 6. For z tending to 2, α_1 increases sharply towards its maximum possible value, i.e., 1 and hence implying a total segregation for large $S_{cc}(0)$. For a given high concentration fluctuations, the degree of segregation in the mixture is dictated by z. We may recall that z is determined from the number density structure factors $S_{NN}(q)$. This suggests that in the region of phase separation, the role of density fluctuations becomes significantly important. Both density and concentration fluctuations share the responsibility to infuse phase separation.

For considerable large concentration fluctuations ($S_{cc}(0) \to \infty$), equation (11) implies,

$$\alpha_1 = \frac{1}{z-1} \tag{12}$$

Obviously for $z=2$, one gets $\alpha_1 = +1$, conforming to the total segregation or phase transformation. At this stage, it is of interest to recall the neutron diffraction results of Hensel and coworkers on expanded fluid Cs and Rb. It was observed that $z \to 2$ as one approaches the critical point of the liquid-vapour interface. It is, therefore, not unlikely that density fluctuations could be ultimately responsible for phase separation.

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