

Effect of Gravity on the Equilibrium Mass Distribution of Two-Component Liquid Systems. The Observation of Reversed Diffusion Flow

H. L. Lorentzen and B. B. Hansen

University of Oslo, Oslo, Norway

At the conference the similarity between the *coexistence curves* of one-component and two-component systems has been stressed. The similarities between the two systems have to be extended to the *equilibrium mass distributions* in vertical containers.

In one-component systems it is well known that close to the critical point the mass distributions at equilibrium are represented by sigmoid curves in the height versus density diagrams. This is caused by the effect of gravity. The same applies to the two-component systems. Thus in a vertical container filled with mixture at critical conditions, homogeneous mixtures do not represent equilibrium. Due to the effect of gravity—also in the two-component systems—equilibria in the critical region are represented by sigmoid curves in the height versus composition diagrams. (See fig. 1.)

In the experimental part of this paper will be shown exposures of curves of mass distribution, which spontaneously developed in two-component liquid systems. They are representing equilibrium mass distributions. One of the observations which support this is the observation of transport of material through the layers of the equilibrium distributions. The transport was towards greater composition differences.

It will be shown in three different ways that the equilibrium mass distribution in the critical region cannot be the homogeneous mixtures, but distributions represented by sigmoid curves in the height versus composition diagram. The developments are founded on the low values of the gradient of the chemical potential ($d\mu/dc$) in the critical region.

According to classical thermodynamical view the gradient of the chemical potential is zero at the critical point:

$$\frac{d\mu}{dc} = 0. \quad (1)$$

Furthermore, according to modern views the gradient of chemical potential is the virtual force

producing diffusion. Therefore, when the gradient of the chemical potential is zero, also the diffusion coefficient will be zero.

Bjørn Bergsnov Hansen [1] and I determined the diffusion coefficient at critical density as function of the temperature distance from the critical for the two systems; succinonitrile-ethanol and triethylamine-water. We found the diffusion coefficients to be close to linear functions of the temperature distance from critical, $\Delta T = T - T_c$, and approaching zero at the critical temperature.

Determinations of the diffusion coefficients as function of the composition difference from critical $\Delta c = c - c_c$, as well as the temperature difference from critical ΔT has shown the following relationship to be basically correct.

$$D = k_1 \Delta T + |k_2 \Delta c^n| \quad (2)$$

where k_1 and k_2 are constants (k_2 not the same on both sides of the critical composition) and n is close to 3.

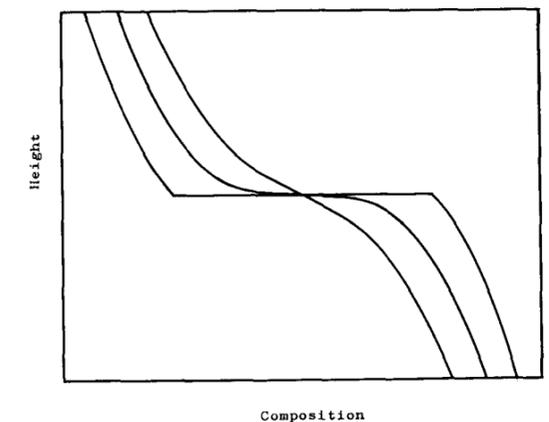


FIGURE 1. Schematic drawing of equilibrium mass distributions in the height versus composition diagram.

This is in agreement with theoretical considerations which Professor Joseph Mayer had pointed out to me [6].

When the diffusion coefficient approaches zero at the critical point the *thermal diffusion ratio* approaches infinite. In a binary system a temperature gradient leads to a flow which will ultimately separate the liquid in two layers. However, by this flow a composition gradient is built up and consequently a mass diffusion flow will counteract the effect of the temperature gradient. At the "Endzustand" the two effects are in balance. At the critical point the diffusion coefficient approaches zero and thus the composition gradient $\left(\frac{dc}{dh}\right)$ will approach infinite.

Studies of the thermodiffusions in the critical region of the system aniline-cyclohexane here have shown the Endzustände to be sigmoid curves with the greatest gradients at critical composition. The gradient increases where the temperature of the critical composition approaches the critical, and the gradient may well become infinite at this temperature. When this is so, it is obvious that, when the temperature gradient diminishes towards zero ($T = \text{constant}$) and the Endzustände goes towards that of an equilibrium, the mass distributions at this equilibrium will also be sigmoid curves in the height versus composition diagram.

In a binary mixture the molecules of the components will have different buoyancy relative to the mixture. Therefore, the molecules of one of the components will have a tendency to move upwards and the molecules of the other to move downwards in the liquid. Consequently, a composition gradient will develop and an inhomogeneous equilibrium distribution will be established, whereby these tendencies are balanced by diffusion flow towards homogeneity.

Because of the overwhelming influence of the diffusion flow such effect has not been observed at normal conditions. In the critical region, however, where the diffusion coefficients are very small, the effect will have to be remarkable, and at the critical point the effect will result in an equilibrium distribution of an infinitely great composition gradient.

In a liquid the potential energy increases with the height. In liquid mixtures—at equilibrium—the difference of potential energy of the layers at the various heights will be balanced by a change of the composition of the mixtures with height.

In a binary mixture the equilibrium condition will be governed by the equation

$$\frac{dx}{dh} = \frac{M_1 - \rho V_1}{d\mu_1/dx} \cdot g \quad (3)$$

where x is the mole fraction n_1/n_1+n_2 , h is the height, M is the molecular weight, ρ is the density of the mixture, V is the partial molar volume, $V_1 = (dV/dn_1)_{p,T,n_2}$, μ is the chemical potential and g the acceleration of gravity. When in the critical region $d\mu/dx$ is very small, dx/dh will be great.

Reversed diffusion flow. It was mentioned in the introduction that diffusion flow towards greater composition differences has been observed. Fick's law is founded on the observation that at normal conditions the Endzustände of the diffusion process is that of a homogeneous mixture. When, however, homogeneous mixtures do not represent equilibrium, the diffusion process will not go towards homogeneity, but towards the equilibrium condition.

Fick's law then may have to be rewritten in the form:

$$J = -D^* \left(\frac{dc}{dh} - \left(\frac{dc}{dh} \right)^0 \right) \quad (4)$$

where h is the direction of the diffusion flow in a vertical container. dc/dh is the concentration gradient of the liquid with respect to the height; dc/dh approaches the equilibrium distribution characterized for the temperature and composition in question by the gradient $(dc/dh)^0$ at equilibrium.

The term $\left(\frac{dc}{dh} - \left(\frac{dc}{dh} \right)^0 \right)$ of eq (4) will be negative when $(dc/dh)^0$ is greater than dc/dh . The flow J is then negative, and we will observe a "reversed diffusion flow."

Reversed diffusion flow can also be observed independent of the effect of gravity. If a mixture is left at a temperature of the coexistence curve the mixture may be split in two phases divided by a surface. This is schematically shown on figure 2. The lines AB and B'A' indicate equilibrium phases. When now the temperature is changed in the direction away from the critical temperature, then the compositions of the phases at the new temperature will be outside the compositions corresponding to the former temperature (dotted lines CD and D'C').

Generally the formation of the new phases will be introduced by fog formation. In some cases,

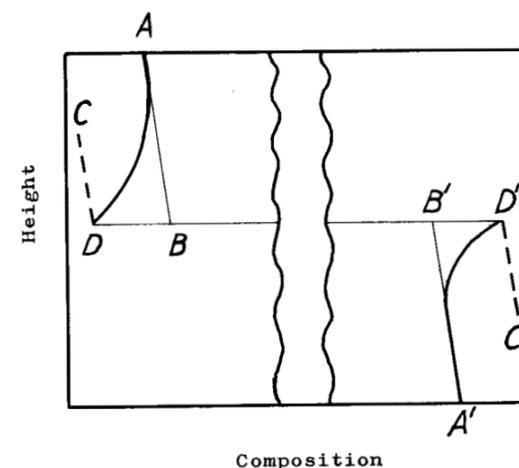


FIGURE 2. A schematic drawing of the mass distribution at two temperatures T_1 and T_2 .

T_1 is the temperature closest to the critical, and the lines AB and A'B' indicate the two phases at equilibrium at T_1 . The temperature difference between T_1 and T_2 is very small, and the dotted lines DC and D'C' indicate the equilibrium distribution at T_2 . When the temperature is changed from T_1 to T_2 , no fog is formed. A diffusion flow of material passing the surface DD' will be observed as mass distribution curves of the form AD and A'D'.

however, when the phases remain "undercooled," the formation of fog does not take place, and a diffusion flow of material will take place. The diffusion flow is crossing the surface border and is a "reversed diffusion flow" towards greater differences in composition.

The two arched curves at the surface together with the straight lines at greater distance from the surface show the distributions observed after a period of time at the new temperature.

I have not been able to make an exact determination of the form of the arched curves. The form appears, however, to be close to the error function curve observed by free diffusion.

Experimental Procedures

The average compositions of the mixtures were close to the critical compositions.

The liquid mixtures were sealed in all-glass containers—ca. 15 mm high and of about 5 mm² cross section area. The liquid mixture almost completely filled the container.

The container was placed in a thermostat which allowed the temperature to be controlled with an accuracy better than ± 1 mdeg [2]. The temperature was determined by means of a platinum resistance thermometer.

The compositions of the mixture at the various heights inside the container were determined by means of an integral optical system [3]. This allowed visual observations and photographic recordings, which actually are diagrams with the height in the container as ordinate and the optical density as abscissa.

In the region of the critical solution points, one observes that the mass transports towards equilibrium distributions are using the formation of fog as vehicle. Thereby droplets of compositions at densities different from that of the mother liquid are formed and move by buoyancy upwards or downwards in the liquid mixture. After a period of time the fog has disappeared and a new mass distribution can be observed.

When the temperature of a nearly homogeneous mixture of a composition close to the critical, and at a temperature outside the coexistence curve, is changed to one of the temperatures of the coexistence curve, the material of the sample is then brought to a state of unattainable instability. Two phases must then develop and they do so probably instantaneously by the formation of fog.

Figure 3 shows an example whereby a nearly homogeneous mixture of succinonitrile-ethanol was cooled to about 50 mdeg below the critical. When the fog had disappeared the composition of both phases were inhomogeneous and had the form of two arms of a sigmoid curve.

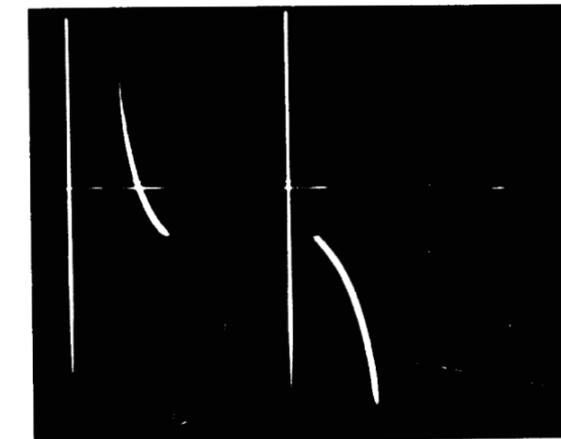


FIGURE 3. System: Succinonitrile-ethanol. Ordinate: Height in container. Abscissa: Composition. Straight vertical and horizontal lines are orientation lines.

Figure 3 shows the composition which appeared when the near homogeneous mixture of succinonitrile-ethanol had been cooled from a temperature above the critical down to a temperature of about 50 mdeg below the critical and the fog had disappeared.

Figure 3 is representative for a great number of observations also with other liquid systems which have been studied here.

Figure 3, however, does not represent the sole form which the phases may show when the fog disappears. In some cases only one of the phases may be smoothly sigmoid and the other closer to homogeneous. This is explained by convection flow in this phase during the establishment.

When the temperature of the mixture is *not* brought to the temperature of the coexistence curve, a redistribution of the material can not be enforced. It happened, however, that in a mixture of triethylamine-water the reestablishment took place also at a temperature outside those of the coexistence curve and in the temperature range reaching from the critical temperature to about 100 mdeg outside the coexistence curve.

The system triethylamine-water was studied at the lower critical solution point of the system. At a lower solution point the temperatures outside the coexistence curve are below the critical temperature, and the temperatures of the coexistence curve above.

During the general study of this system the sample was left for one night at a temperature outside the coexistence curve. Next day the arbitrary mass distribution curve was found to have been partly reformed into a smoothly formed arched curve in the diagram height versus composition.

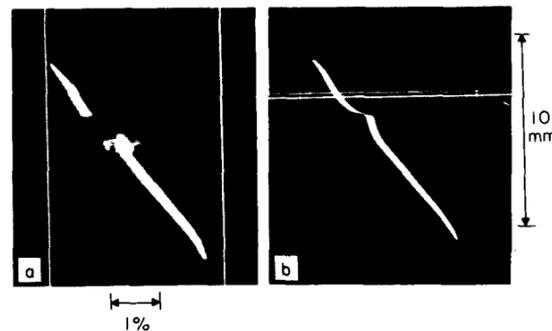


FIGURE 4. System: Triethylamine-water. Ordinate: Height in the container, scale shown on the right side of the figure. Abscissa: Composition of the mixture, scale unit below photograph 4.a.

Exposure 4.a shows the originally straight curve partly disrupted by layers of fog. Below this layer is another layer of fog, which, however, allows the light to pass and produces background illumination at these heights. Exposure 4.b shows the composition curve after the fog had disappeared. The curve has attained a regular arched form where the upper layer of fog had been. When making the exposure a, the horizontal orientation lines were not illuminated. The photographically recorded composition curves do not represent the entire column of the liquid mixture.

This surprising reformation of the mass distribution was then systematically studied, and Bjørn Bergsnov Hansen and I subsequently found a temperature treatment of the sample — which was sealed inside an all-glass cell — whereby we could reproduce the phenomenon ad libitum. The temperature of the thermostat was set at a temperature below the critical (outside of the coexistence curve). The cell was then removed from the thermostat, warmed to room temperature and cooled to about 10° below the critical and carefully tilted. Thereby a certain concentration gradient was established in the liquid mixture. (Typical is the lower curve of fig. 5.) The container was then reinserted in the thermostat and it was observed that the composition curve remained unbroken.

After periods of time of different duration at constant temperature a belt of fog was spontaneously formed at varying levels in the liquid (in all cases but one in the upper middle section of the liquid column). The belt was at first fractions of a millimeter thick and gradually developed upwards as well as downwards in the liquid.

Figure 4a shows a photograph made after the fog had appeared. The fog consisted of two layers separated by a sharp boundary. The upper layer of fog entirely veiled this part of the liquid. The lower layer of fog allowed the light to pass and disclosed that the mixture at these levels had attained nearly homogeneous compositions. The nature of this fog, however, was such that light was scattered, and at these levels a background illumination was observed.

30 min later the fog had disappeared and, where the upper layer of fog had been, the curve had attained a smooth arched shape leading downwards to a kink from which the curve by a near-vertical section continued into the original curve. (Fig. 4b.)

The smooth arched curves represent layers with defined composition gradients. The gradient increases towards critical composition, and must be regarded as a section of an equilibrium distribution curve.

As mentioned the fog started as a very thin belt, which grew broader with time. In one series of experiments the temperature was immediately lowered just as the fog appeared. Thereby the fog disappeared, and a comparison between the curve, before and after the fog disappeared, showed that the fog was first formed where the original gradient and the gradient of the developed arched curve were equal (fig. 5) [5].



FIGURE 5. System, ordinate, and abscissa as on figure 4, however, different scales.

Two photographs are mounted together by dislocation along the ordinate. The lower is the original composition curve before the development of fog. The upper curve shows the composition after the liquid mixture had been cooled and the fog had thus disappeared. Visual observation had disclosed that the formation of fog started at composition close to the left vertical orientation line, where the exposures show that the gradients of the original and the developed regular arched curves are the same.

The latter observation explains why the belt of fog appeared at compositions somewhat different from critical composition (in all cases but one at triethylamine richer mixtures).

The smooth arched curves which appeared after the fog had disappeared generally did not reach to the critical composition. When the system was left undisturbed at constant temperature after the fog had disappeared, the smooth arched curve grew in both directions. The form of the originally formed curve remained unchanged. It was, however, observed slowly to change its height in the container.

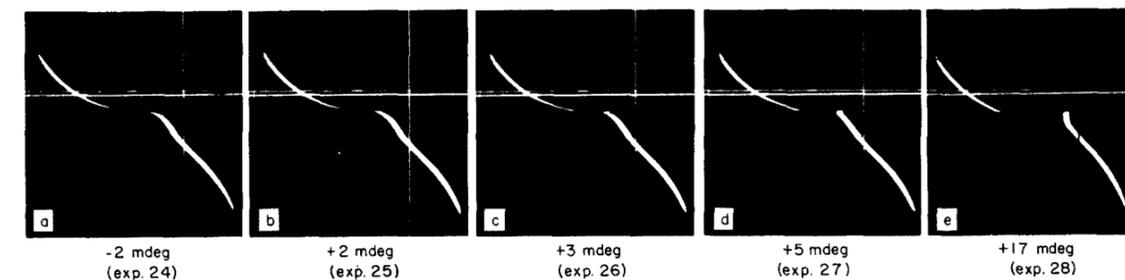


FIGURE 7. System, ordinate, abscissa and scales as on figure 4. Five photographs of the same series with stepwise increasing temperatures, mounted in successive sequence of time. The opening of the concentration curve in figure 7a is due to the optics of the apparatus. In figures 7b-e two phases are formed.

When enough time had gone, the smooth arched curve grew past the critical composition and passed a point of inflexion. From this point on the composition gradient decreased with increasing distance from critical composition. Maximum gradient was found at — or very close to — critical composition.

When the smooth arched curve was observed to grow in both directions this naturally was caused by an increase in the height of these layers upwards as well as downwards. This was a consequence of a transport of material through these layers, which transport was a diffusion flow towards increasing differences in composition, "reversed diffusion flow."

Figure 6 and figure 7 show exposures from two series in which the curves mentioned above had been established. (See legend.) In the series of figure 6 the temperature was lowered in steps (away from the critical). When the temperature changed, a fine fog veiled the regular arched section of the curve for a shorter period of time, and

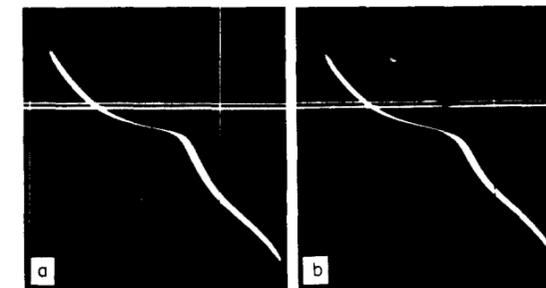


FIGURE 6. System, ordinate, abscissa and scales as on figure 4. Figure 6.a shows the regular arched curve developed to both sides of the critical composition during 10 hr at constant temperature, 41.5 mdeg below the critical. The temperature was then lowered to 53 mdeg below critical, and figure 6.b shows the composition curve after 7 hr at this temperature. The composition gradients had decreased in the layers of the smooth arched composition curve. A comparison of the "lower arm" of the curve does indicate that a diffusion towards greater composition differences has taken place (towards a continuation of the regular arched curve).

in this section the form of the curve changed basically by an increase of the composition gradients dc/dh .

Figure 7 shows exposures of a series with step-wise increase of temperature. Here too a faint fog was formed as in the series above. At the temperatures of the exposures 7a and 7b the smooth arched section of the curve changed basically at each step by a decrease of the gradients dc/dh at the various compositions.

At the step 7b the critical temperature is passed and the concentration curve is broken close to critical composition.

Exposure 7d is taken at a temperature 17 mdeg above critical. The left part of the curve is arched basically in the same way as shown on figures 1 and 3. The upper part of the right side leading to the surface dividing the phases is nearly vertical. The reason for this may be a convection flow in the lower phase during the establishment of this phase.

End Remarks

In the beginning of this paper it was said that the effect of gravity added to the analogy which is known to exist between the binary and the one-component systems. This may be further illuminated:

1. The presence of a temperature gradient in the binary systems leads to the Soret effect. In the one-component systems a temperature gradient will lead to mass distribution curves which will constitute isobars in the temperature-density diagram. In both cases it must however be remembered that the effect of the temperature gradient in the experiments will come in addition to the effect of gravity.

It may also be mentioned that when in the one-component systems the isobars are experimentally known, and also the gradient dp/dT at the critical density, the isotherms can be constructed. A similar relationship may be expected to hold in the binary systems between the Soret effect and the effect of gravity.

2. It was said that the effect of gravity in the binary systems was a necessary consequence of the small diffusion coefficient in the critical region, caused by the fall of the molecules of the heavier

component towards the bottom of the container. In the same way the known sigmoid form of the mass distribution curves in the one-component systems can be regarded as a consequence of the fall of the molecules balanced by a diffusion upwards. This leads to the conclusion that the diffusion coefficients also of the one-component systems are very small in the critical region and will apply to an equation analogous to eq (2).

Hirschfelder [4] and Prigogine [5] have pointed out that diffusion measurements are of fundamental importance for the study of liquid mixtures on the molecular level.

By experimental determination of the equilibrium mass distributions in mixtures, preferably in fields of increased acceleration, one should have an additional method for the study of liquid mixtures—not only in the region of the critical solution points, but also for the study of liquid mixtures in general.

The reestablishment of the mixtures were observed in 1957. Professor Joseph Mayer kindly reviewed the reports from the experiments and showed that the form of the new established curves were related to the gradient of the chemical potential and consequently to the diffusion coefficient as function of the temperature and composition. I am very much in debt to Professor Mayer, who thereby gave me the clue to the problems.

I also express my thanks to Professor Odd Hassel for his interest and assistance. Furthermore, I express my thanks to Professor E. G. D. Cohen and Dr. J. M. H. Levelt Sengers, who have reviewed my paper.

References

- [1] Hans Ludvig Lorentzen and Bjørn Bergsnov Hansen. *Acta Chem. Scand.* **12**, 139 (1958).
- [2] Hans Ludvig Lorentzen. *Acta Chem. Scand.* **7**, 1335 (1953).
- [3] Hans Ludvig Lorentzen. *Acta Chem. Scand.* **9**, 1724 (1953).
- [4] Hirschfelder, Curtiss, Bird, *Molecular Theory of Gases and Liquids*, p. 539 (John Wiley & Sons, Inc., New York, N.Y., 1964).
- [5] Prigogine. *The Molecular Theory of Solutions*, p. 51 (North-Holland Publ., 1957).
- [6] Professor Joseph Mayer, private correspondence (Chicago, June 21, 1957).

S. Katsura and B. Tsujiyama

Tohoku University, Sendai, Japan

1. Introduction

The properties of alloys of magnetic substance and nonmagnetic substance are investigated experimentally and theoretically as problems of dilute magnetism. Here we consider Ising spins of $S=1/2$ as a magnetic substance and the energy of the system is assumed to be given by a sum of exchange energies between nearest neighbor Ising spins, positive or negative, corresponding to ferro- and antiferromagnetic coupling. That is, the interaction energy between nonmagnetic ions and that between nonmagnetic ions and Ising spins are neglected. This restriction can easily be removed. The calculation based on the inclusion of the interaction energy of nonmagnetic ions will be carried out in future.

The idealization of the preparation of the system can be classified into two limiting cases. We denote the spin average by $\langle \rangle_s$ and the configuration average by $\langle \rangle_c$.

The free energy of the system which was heated at infinitely high temperature and was cooled infinitely rapidly up to temperature T is given by

$$F_Q = -kT \langle \ln \langle Z \rangle_s \rangle_c. \quad (1.1)$$

In this system the true thermal equilibrium is not realized and it is a free energy of an idealized quenched system in which ions are frozen randomly at their positions.

On the other hand, if the temperature and external parameters are varied infinitely slowly and true thermal equilibrium is realized, the free energy of the system is given by

$$F_A = -kT \ln \langle Z \rangle_{s,c}. \quad (1.2)$$

Although the interaction energy of the nonmagnetic ions are to be taken into account, the system corresponds to an idealized annealed system.

The distinction between these two cases has been discussed by Brout [1], Mazo [2], and Morita [3].

Quenched random dilute magnetism has been investigated by Behringer [4], Sato, Arrott and Kikuchi [5], Brout [1], Rushbrooke and Morgan [6], Elliott and Heap [7], and Abe [8]. In experiments ideal randomness in Brout's sense is not realized an actual "randomness" depends on the history of the preparation of samples. Experimental situation lies, more or less, between two idealized limiting cases. Hence it seems worthwhile to compare physical properties of those two systems for exactly solvable cases.

On the other hand, Syozi [9] investigated a two-dimensional decorated lattice model of dilute magnetism, where Ising spins locate on lattice points of regular two-dimensional lattice, and nonmagnetic atoms or Ising spins locate on middle points between nearest neighbor lattice points (fig. 1). He obtained exactly thermal properties of two-dimensional lattices by reducing its partition function to Onsager's partition function. We can get thermal and magnetic properties of the one-dimensional Syozi's model since the original Ising model of a one-dimensional system is known in a magnetic field. We will also compare properties of Syozi's model with above mentioned two cases.

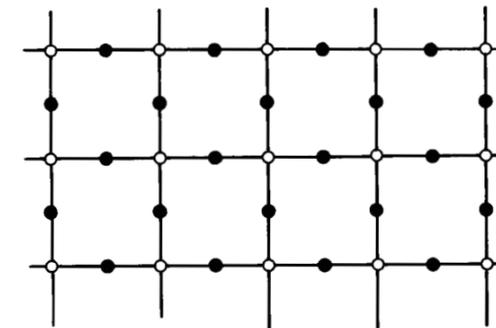


FIGURE 1. Syozi's decorated lattice model of dilute Ising model. ○ Ising spins. ● Ising spins or nonmagnetic atoms.