ORDER AND DISORDER IN NATURE

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Keywords:order,disorder,entropy,fluctuation,phasetransition,latent heat, phase diagram, critical point, free energy, spontaneous symmetry breaking, open system, convection current, Bernard cell, crystalline solid, lattice structure, lattice vibration, phonon, magnetization, Curie point, ferro-paramagnetic transition, magnon, correlation function, correlation length, order parameter, critical exponent, renormalization group method, non-equilibrium process, Navier-Stokes equation, Reynold number, Rayleigh number, Prandtl number, turbulent flow, Lorentz model, laser.

Contents

1. Introduction
2. Structure of Solids and Liquids
2.1.Crystalline Structure of Solids
2.2.Liquids
3. Phase Transitions and Spontaneous Broken Symmetry
3.1.Spontaneous Symmetry Breaking
3.2.Order Parameter
4. Non-equilibrium Processes
Acknowledgements
Glossary
Bibliography
Biographical Sketch

Summary

Order-disorder problems are a rapidly developing subject not only in physics but also in all branches of science. Entropy is related to the degree of order in the structure of a system, and the second law of thermodynamics states that the system should change from a more ordered state to a less ordered one as long as the system is isolated from its surroundings.

Phase transitions of matter are the most well studied order-disorder transitions and occur at certain fixed values of dynamical variables such as temperature and pressure. In general, the degree of order of the atomic or molecular arrangement in matter will change by a phase transition and the phase at lower temperature than the transition temperature is more ordered than that at higher temperature. Also some symmetries shared by the phase at higher temperature will not be shared by the phase at lower temperature, so that the symmetry breaking can characterize the phase transition.

Phase transitions are classified into the first order transition and higher order transitions. The latter are also called critical phenomena. Internal energy and entropy of a system change discontinuously at the transition point in the first order transition, but not in higher order transitions. However, quantities such as specific heat will behave

anomalously near the transition point and it is found that the anomalous behavior is quite similar for diverse kinds of critical phenomena. This universality leads to a unified description of critical phenomena based upon spatio-temporal correlations of fluctuations in relevant quantities which grow near the critical point. The renormalization group method provides such a unified description with great success.

Phase transitions are transitions of a closed system in which in- and out-flows of energy or matter are exactly compensated to each other so that the system remains in thermal equilibrium. Open systems into which fluxes of energy or matter enter can exhibit ordered states far from thermal equilibrium. Fluid system is a well studied open system which exhibits order-disorder transitions under influence of an external heat flux.

A fluid contained in a vessel heated from below moves from a quiescent state to a convection flow state consists of vortices, and finally moves to turbulent flow state through some transient states as the strength of the heat flux increases. Each transition seems to occur at a critical value of the flux strength which depends upon other environmental conditions such as the shape of the vessel. Although the transitions between states far from thermal equilibrium are very complex, some dimensionless parameters such as Rayleigh number can roughly characterize the transitions, suggesting a more unified description of these transitions become available in future.

1.Introduction

In one of the previous chapters (see *Physical Systems and Laws*), we discussed the law of the energy conservation and the law of increase of entropy, both of which are strictly valid for physical processes in any isolated system and consequently govern all physical phenomena occurring in nature. We can look at physical phenomena as processes in which one kind of energy is transformed into other kinds of energy, thereby keeping the total energy of the system unchanged. Entropy is a quantity to determine the direction of change of states of an isolated system, and the system always changes in the direction of increasing its entropy (the second law of thermodynamics).

Entropy is related to the degree of order in the structure of a system, and the second law of thermodynamics means that the system always changes from a more ordered state to a less ordered state in any isolated system. However, if we look at actual physical phenomena, there are many of them in which an ordered state evolves out of a disordered state.

For example, a crystal which has an ordered array of atoms can be nucleated in a liquid solution or in a molten mass and can grow to a larger crystal by a continuous supply of fresh atoms from its surroundings to build it outward, layer upon layer of ordered atoms. Also a fluid like water can exhibit an ordered and beautiful flow pattern under appropriate conditions. When the layer of a fluid is contained between one hot plate below and another cold plate above, a macroscopically ordered structure of flow of fluid often appears that is heavily dependent upon the temperature gradient in the fluid and upon other surrounding conditions. A typical flow pattern when the layer is thin is shown in Fig.1, where the unit of the ordered pattern is called the Bernard cell.
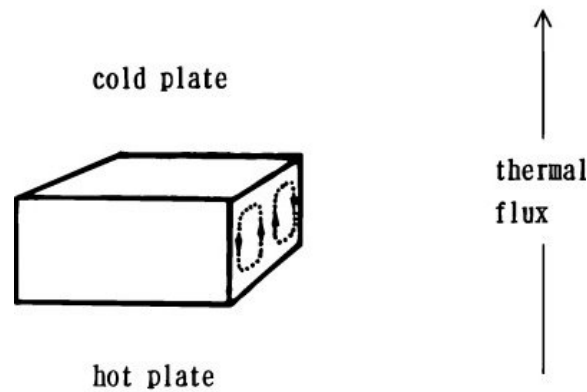
Figure 1. Bernard cells

At first sight, all these phenomena seem to be contradicting to the second law of thermodynamics, since they imply birth of a more ordered state out of a less ordered state. However, if we look into how these ordered states are formed out of disordered ones, crystals grow by getting matters from its environments and giving off heat to them, and the Bernard flow is formed and maintained through constant flow of heat from its environments to keep the temperature gradient in the fluid. All these systems are not an isolated system but an open system interacting with its environments through exchange of matter and energy. If we consider the net system including the environments, the entropy of the whole system always increases according to the second law of thermodynamics.

Matter consists of a huge number of atoms and molecules. In order to form an ordered structure of matter or to form an ordered flow of fluid, a large number of the constituents of it have to cooperate by certain means to form the ordered structure as a whole. Here we shall consider how cooperative relations among the constituents of a system are realized and how an ordered structure is born and maintained in a system composed by a large number of constituents.

In Fig.2 we show many people swimming in a pool. When the pool is heavily crowded with swimmers, they might swim along concentric circles in either clockwise or anticlockwise direction so that they can avoid colliding with each other. An instructor watching pool conditions for safety might order that the swimmers should swim in a circle either clockwise or anticlockwise. Or every swimmer may learn by oneself how to swim without interfering with others, and eventually becomes to swim in a circle. In both cases, an ordered pattern of the movement of swimmers emerges. If everybody watches others nearby and swims in about the same way in its speed and direction with his neighbors, then an ordered pattern of the movement will be eventually formed.
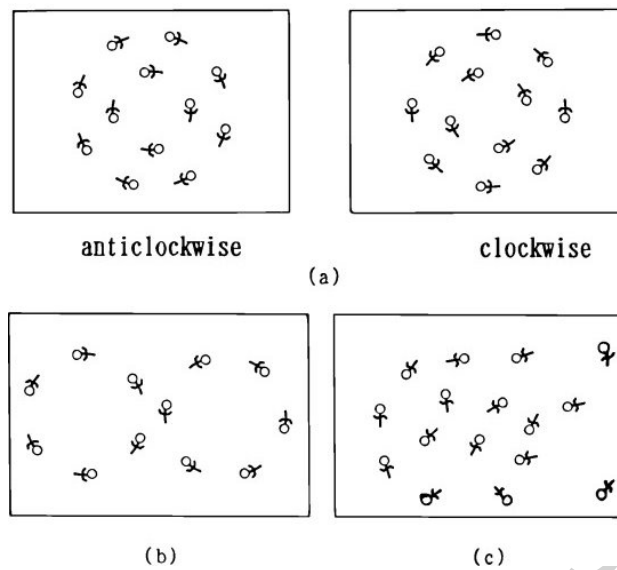
Figure 2. Patterns formed by swimmers in a pool

An ordered structure of matter will be formed in a similar way. To arrange atoms in an ordered structure by exerting an external force on them corresponds to the presence of an instructor who orders people how to swim. To form an ordered structure only through inter-atomic interactions without having external forces corresponds to the case of having no instructor. The latter case is called the self-organization or the spontaneous formation of an order.

Fig.2a shows a concentric movement of swimmers in either clockwise or anti-clockwise direction. Fig.2b shows an ordered pattern in which a half of swimmers swim in the left-half of the pool anticlockwise along concentric circles and the others swim in the right-half of the pool clockwise along concentric circles. Clearly there could be many other ordered movements in which everyone can swim without interfering with other swimmers.

If everybody is asked to swim faster, a larger space is needed for each swimmer so that one can swim without changing too rapidly its direction of motion. Thus, the pattern in Fig.2a will be preferred than the pattern in Fig.2b, and the former pattern is likely to be realized through self-organization. On the contrary, if everybody is allowed to swim very slowly, any ordered pattern might have a chance to be realized. Even one can swim randomly in any direction without interfering with his neighbors and no large scale ordered pattern of movements of the swimmers appears as shown in Fig.2c.

The pattern which is finally realized through self-organization seems to be heavily dependent upon initial condition how a small group of people started to swim in the pool. If a few people happened to start to swim in clockwise direction, a pattern of all the swimmers moving in clockwise direction would be finally formed. On the contrary, if the group of people started to swim in anticlockwise direction, then all the swimmers will become to swim in anticlockwise direction. Therefore, which one of the ordered patterns is realized depends upon a small scale fluctuation at the beginning, if it can grow to a large scale through self-organization.

In general, it is not easy to change an ordered pattern from one to another. If a small number of people tried to change the direction or speed of swimming by chance, they would immediately interfere with some of their neighbors who are swimming in a manner specified by the existing ordered pattern. Therefore, they are forced to go back to swim in the manner in accord with the pattern formed by the majority of the swimmers.

If it happened that many swimmers change their movements in a coherent manner at the same time, a new ordered pattern might be formed. However, the likelihood for such an instantaneous coherent change of movements of many swimmers to occur is negligibly small, unless we have an instructor to order the change. Thus, any ordered pattern once formed is likely to be stable against disturbances or fluctuations, or there is strong resistivity for change of order if the number of constituents forming the ordered pattern is sufficiently large.

Formation of ordered patterns by swimmers in a pool illustrates basic ways in formation of ordered states of a system composed of many constituents. Existence of fluctuations, appropriate conditions for the growth of them to an ordered structure of a large scale, and stability of the ordered pattern against small disturbances are common features observed in formation and maintenance of order in general.

In Fig.2a we showed two ordered patterns in which everybody swims in clock-wise direction or anticlockwise direction. These two patterns are equivalent to one another and there should be no preference for either one of them to occur. Which one is finally chosen in reality depends on into which direction a few people started to swim at the beginning. In another word it was determined by chance. However, once one of the patterns is established, it would be difficult to reverse the direction of movements of people as was explained before.

The equivalence of the two patterns represents the left-right symmetry of the underlying laws which govern the formation of ordered patterns. Once, for example, a clockwise circulation is established and maintained by the swimmers, a change of the pattern into an anticlockwise circulation is not likely to occur, because any small fluctuation in the swimming pattern cannot easily grow to a large scale. This means that the left-right symmetry is broken in reality. This kind of symmetry breaking is called spontaneous symmetry breaking and is widely found in diverse kinds of the ordered system. Clearly the spontaneous symmetry breaking is more strictly valid for larger systems with many more constituents, because coherent fluctuations among the constituets are more unlikely to occur for larger systems.

In order to describe the cooperative phenomena of atoms or molecules and the way to change the degree of order of atomic or molecular arrangement, we shall consider phase transitions of matter in general. Any substance can display at least three phases, which are the solid, liquid, and vapor. And phase transitions from one phase to another can take place under appropriate conditions.

The most familiar example of the phase transitions are those of water, which can exist in the form of water vapor, liquid water, or ice. Water consists of the water molecules, but the molecular arrangement differs for the three different phases. In the gas phase, the molecules are far apart from each other and move around almost independently from each other in random fashion. In the solid phase, the molecules are arranged in a very orderly array. Each atom has a definite equilibrium location in the regular array of atoms and it can only move around with small displacements from its equilibrium position. In the liquid phase the situation is intermediate, being neither as orderly as in the solid nor as random as in the gas.

In the solid or liquid phase, the water molecules are close to one another and always under mutual strong influence, but in the liquid phase they are still free to move past each other over long distances. Fig.3 illustrates the difference in the molecular arrangement between the solid and liquid phases.
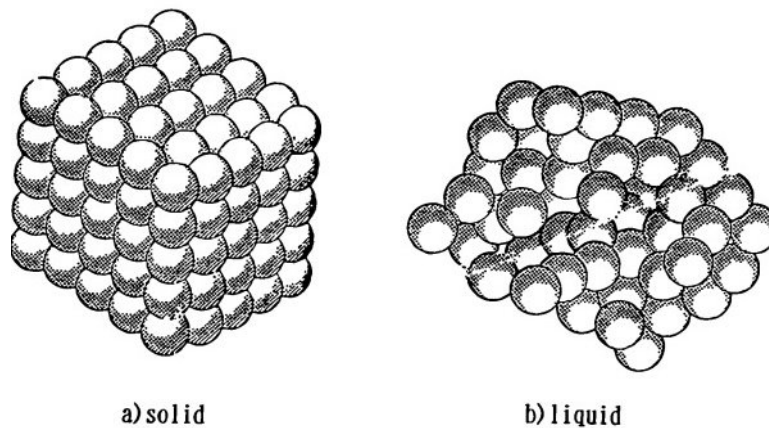
a) solid   b) liquid

Figure 3. Molecular arrangement in solid and liquid

In general, as the temperature of a substance is increased, it changes first from the most orderly solid form to the liquid form which is of an intermediate degree of order. As the temperature is further increased, it changes from the liquid form to the gas form which is the most disordered one. It is known that these changes from one phase to another take place at a fixed temperature called the phase transition temperature.

As we know, water changes from the solid ice form to the liquid water form at 0°C and changes from the liquid water form to the gaseous form at 100°C at the normal pressure of 1 atmosphere. The transition temperatures depend on the pressure, and, in particular, that for the liquid-gas phase transition depends very sensitively on the pressure.

At the transition temperature two phases coexist in thermal equilibrium. At 0°C ice and liquid water coexist and at 100°C liquid water and gaseous water coexist If we keep heating ice at 0°C, the fraction of liquid form of water keeps increasing until all of ice melts away into liquid water, while the temperature of water remains at 0°C as long as ice remains. Only after the solid-liquid phase transition is completed, the temperature of water begins to rise beyond 0°C.

When a substance changes from one phase to another at the transition temperature, either absorption or liberation of heat energy takes place. When ice melts into liquid water, a certain amount of heat is absorbed by ice. On the contrary, when liquid water freezes into ice, an equal amount of heat is liberated from water. The heat absorbed or liberated from a substance when it undergoes a phase transition is called the latent heat of the substance. Existence of the latent heat means that the structure of the substance differs in different phases, and that the structural change of the substance is accompanied by a change in energy which appears as the latent heat of the phase transition.

The three phases differ from each other not only in their macroscopic properties such as matter density and plasticity for deformation of shape, but also in their way of arranging atoms or molecules. Snow flakes are known to exhibit beautiful crystalline shapes, some of which are shown in Fig.4. All of the shapes are basically hexagonal but they differ from each other in details, so that it can be stated that no two snow flakes are identical in their shapes.
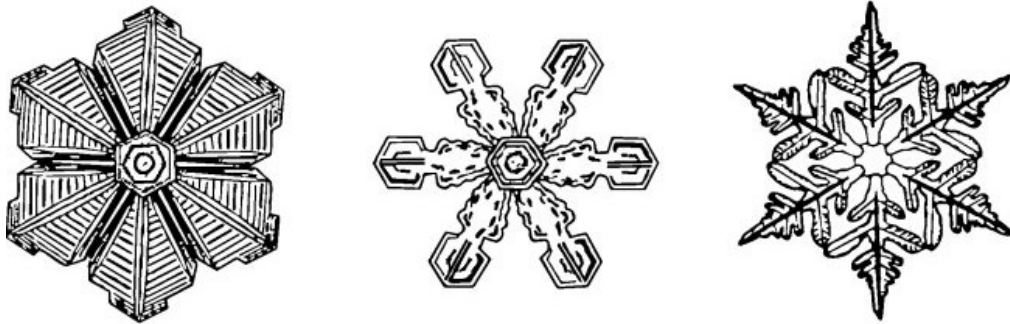
Figure 4. Examples of crystalline shapes of snow flakes

The Figure 5 is the phase diagram of water which shows the phase of water for given values of temperature *T* and pressure *P*. Various lines, or boundaries, in the phase diagram separate the different phases, and each point on these lines gives the pressure and temperature when a phase transition occurs. If we increase temperature of water under a constant pressure of 1 atmosphere along a dotted line shown in the figure, water changes from the solid ice to the liquid water at 0°C by crossing the melting line and then from the liquid water to the water vapor at 100°C by crossing the vapor-pressure line as shown in the figure.

The vapor-pressure line separates the liquid phase from the gas phase. The line ends up at a critical point *B*, whose coordinates are *P* = 218 atmospheric pressure and *T* = 374°C. Beyond this critical point there seems to be no distinction between the liquid and gas phases. We can go over the top of the critical point from one to another phase without any abrupt change occurring everything remains completely smooth for change of temperature or pressure. This means that liquids are just simply dense gases, and under high pressures beyond that of the critical point there is no distinction between the two phases.
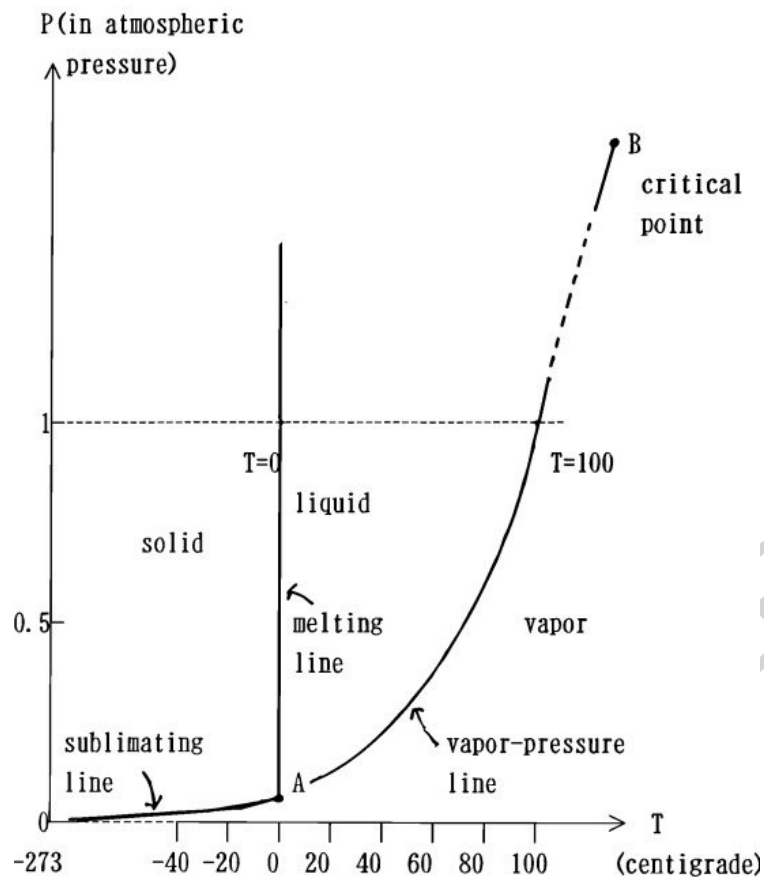
Figure 5. The phase diagram of water

At pressures below that of the critical point, a discontinuous change of volume or density of water takes place in the liquid-gas phase transition and the associated change in energy corresponds to the latent heat. At pressures beyond the critical point no such discontinuous change of volume or density occurs and the latent heat vanishes.

Contrary, for the liquid-solid transition line or the melting line there is no critical point where the line ends up. The difference in structures of solid and liquid persists up to infinitely high pressures. The structural difference between the two phases is in the degree of order of the arrangement of atoms or molecules and the energy difference due to the change of order appears as the latent heat in the phase transition.

At low pressure and temperature there is a line called the sublimating line, which separates a gas directly from a solid. The three lines, the vapor-pressure line, the melting line and the sublimating line, meet at a common point A called the triple point The values of P and T at the triple point of water are $P = 0.006$ *atmospheric pressure* and $T = 0.0098°C$. At low pressures below that of the triple point, the gaseous phase condenses directly into the solid phase without passing through the liquid phase.

A phase transition that displays a sudden state variation accompanied with a latent heat is called the first order phase transition. Not only water but many other substances undergo the first order phase transition at appropriate values of temperature and

pressure. Also there are other types of the phase transition which do not display a sudden change of states and do not have the latent heat. They are called higher-order phase transitions (see *Physical Systems and Laws* for further details of higher-order phase transitions).

In a first order phase transition, there occurs an entropy change ΔS of a system due to absorption or liberation of the latent heat ΔQ; $\Delta S = \Delta Q/T$ The entropy of the system increases ($\Delta S > 0$) when the latent heat is absorbed ($\Delta Q > 0$), and it decrease ($\Delta S < 0$) when the latent heat is liberated ($\Delta Q < 0$). Entropy is a quantity to measure the degree of order of a system. The entropy of a system increases when the system undergoes a phase transition from a solid to a liquid, from a liquid to a gas, or from a solid to a gas, because a latent heat is absorbed in the phase transition. On the contrary, the entropy decreases in a reversed phase transition because of liberation of the latent heat. These entropy changes show that the solid phase is the most ordered phase and the gaseous phase the most disordered phase of matter.

We know through our experiences that a mass of ice does not melt away rapidly into liquid water or a mass of liquid water does not freeze rapidly into ice. In general, it takes time to complete a first order phase transition from one to another phase. The two phases coexist during the transition and they are in thermodynamic equilibrium with one another.

When a portion of ice melts into liquid water, an amount of heat equivalent to the latent heat is absorbed by that part of ice and thus cools ice around. Likewise, when apart of a mass of liquid water freezes into ice, an amount of heat is liberated by that part of water and warms up liquid water around. Thus the presence of the latent heat works against the phase transition and keeps the temperature of water constant during the phase transition until it is completed.

We know that we have to put in a large amount of heat from outside to melt a mass of ice and that water in a pond does not freeze quickly even in cold weather below 0°C. There is resistivity against phase transitions due to the presence of the latent heat Water has a particularly large latent heat among substances; the latent heat for the solid-liquid phase transition is about 80 kcal/kg and that of the liquid-gas phase transition is about 540 kcal/kg at 1 *atmospheric pressure*. The large values of the latent heat explain why it takes a long time to complete a phase transition of water. At the normal atmospheric pressure, the entropy change in the liquid-gas phase transition is much larger than that in the liquid-solid transition for water as indicated by the much larger latent heat in the former transition. This is true for most substances, which means that the disorder introduced by evaporation is greater than the disorder introduced by melting at the normal atmospheric pressure.

Now, we shall consider the underlying reason for why a particular phase is chosen for given values of temperature and pressure. In general, any dynamical system has two mutually opposing tendencies for change of states of the system. One is to decrease its internal energy as much as possible so that the system would become more stable. The other is to increase its entropy as much as possible so that the system would be in a more disordered state. These two are certainly contradictory to each other, and the

system must make a compromise of the two tendencies in a certain specific way to choose a state to be realized.

First we shall illustrate the tendency that a system prefers to decrease its internal energy. In Fig.6 we show a potential energy which has peaks and valleys as a function of the spatial coordinates. If we place a small ball at rest at a certain position on a slope of the potential, the ball will start falling down the slope and, after moving back and forth repeatedly by passing through one of the potential minima, it will finally stop at the position of the minimum. The mechanical energy of the ball becomes minimal and the initial energy of the ball was lost by frictions.
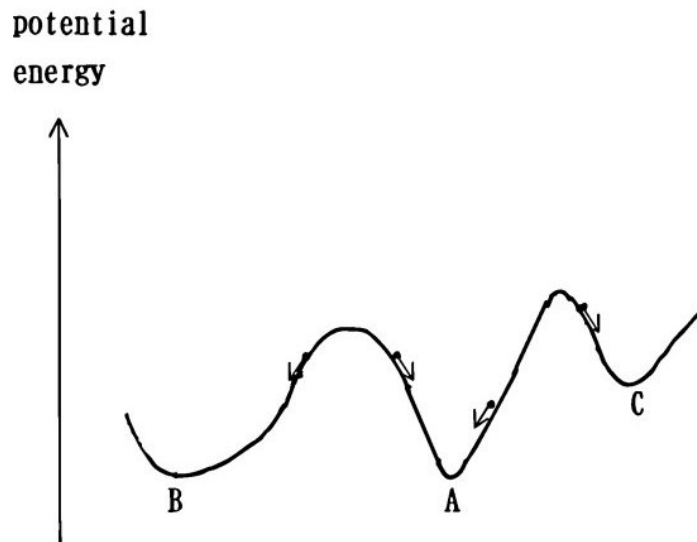

Figure 6. A potential with peaks and valleys

In Fig.7 we show a typical inter-atomic potential energy as a function of the inter-atomic distance. In general, at short distances the inter-atomic force is strongly repulsive as indicated by the rapidly decreasing potential with increasing distances. While at large distances the force becomes attractive as indicated by the gradually increasing potential with increasing distances. At an appropriate inter-atomic distance the potential energy is minimum, which gives the equilibrium distance between the two atoms.

When a large number of atoms are placed close together, the minimum energy state corresponding to equilibrium requires that the atoms are in an ordered array with inter-atomic distances corresponding to the equilibrium distance of the inter-atomic potential energy. There is evidence in nature that atoms are indeed arranged in this way and form a crystalline structure in solid.
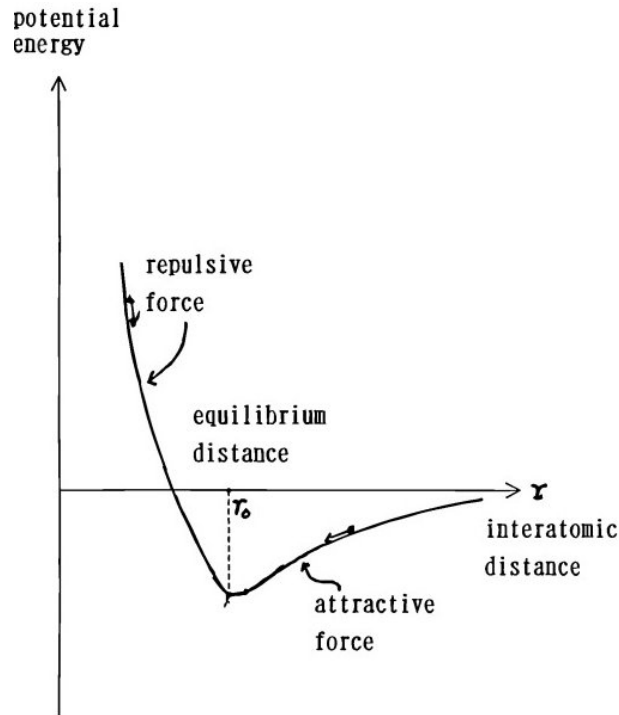
Figure 7. A typical inter-atomic potential as a function of the inter-atomic distance

In a crystalline structure the atoms are arrayed in a regular, systematic, recurring pattern with a long range order. As examples of the crystalline structures, we show unit cells of the cubic structures of crystals in Fig.8. These structures are called the cubic lattice, the body centered cubic lattice and the face centered cubic lattice. The crystalline structure is formed by the periodic repetition of identical unit cells in space. The inter-atomic distance in the crystalline structure is determined to minimize the inter-atomic potential and pack atoms as dense as possible, and therefore the crystalline structure depends on the inter-atomic forces.

(a)   (b)   (c)

a) cubic lattice   b) body centered   c) face centered
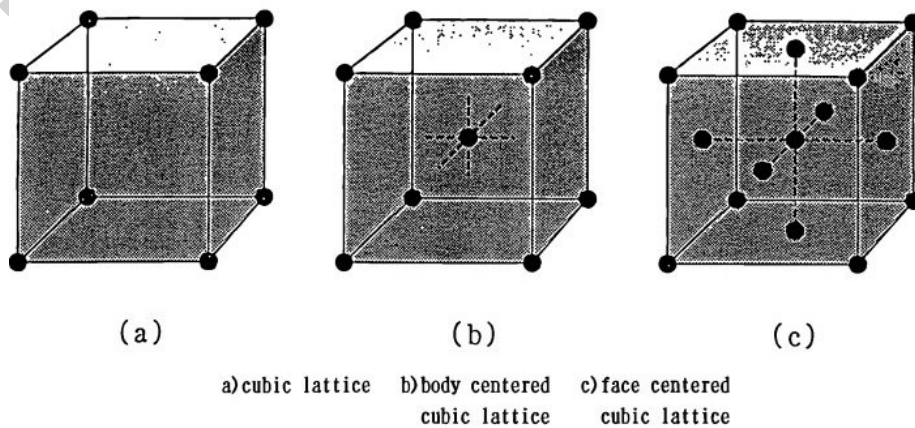   cubic lattice   cubic lattice

Figure 8. The unit cells of the cubic structures of crystals

In an ordered array of atoms in large scale, atoms do not interact with distant atoms and adjust their positions only referring to those of their neighboring atoms so that the inter-atomic potential energy becomes minimal. Thus, the formation of a crystalline structure is quite similar to the formation of a moving pattern of swimmers in a pool, where each individual swimmer adjusts his way of swimming only referring to those of his neighbors. No external force is needed for the formation of crystalline structures and they are formed by the self-organization of the constituent atoms through the inter-atomic forces.

Next, we shall consider the second tendency in change of a system to increase its entropy. Any system composed by a large number of constituents will increase its entropy by dispersing its energy into more degrees of freedom of motion and change into more disordered states. In general, there exist a large number of microstates for a given macrostate of the system and we cannot differentiate them from each other by any macroscopic measurement. These microstates must be realized with an equal probability according to the fundamental postulate of statistical thermodynamics (see *Physical Systems and Laws – Statistical Physics*). Therefore, a macrostate with the largest multiplicity of microstates is more likely to be realized in thermal equilibrium, and the system should evolve into that macrostate.

Since entropy is defined as a quantity proportional to the logarithm of the number of microstates for the given macrostate and is a measure of degree of order of the system, the second law of thermodynamics means that any isolated system tends to evolve into more disordered states. This is clearly opposite to the first tendency of the system to change into more stable and ordered states.

The concepts of order and disorder are related to the entropy of a system. In the case of disorder the number of microstates for a macrostate of a system is so large that one cannot tell which one of the microstates is realized at a given time, and we are almost ignorant about the states of individual atoms or molecules. In the case of order there exists correlation displayed by the states of the individual atoms or molecules and the number of microstates for a given macrostate is smaller as the order of the state increases. For example, in the extreme case of zero entropy, the number of microstates is 1 and one can know the microscopic arrangement of atoms or molecules from the values of macroscopic variables of the system.

In Fig.9 we show schematically motion of atoms (or molecules) in a solid or a liquid. Each atom has a kinetic energy whose average value is specified by the temperature of the system and moves about its equilibrium position randomly. In solid, atoms cannot move too far from their equilibrium positions and keep more or less the ordered array of atoms. In liquids, atoms can move to far distances and move rather freely thereby keeping the density of atoms constant

There are two causes for random motion of atoms in a solid or liquid. One is the uncertainty principle which prohibits an atom to stay at a definite position at rest. Thus the atom is forced to move around. The position of an atom is determined by the probability distribution specified by its wave function and the position would change

from time to time if we repeatedly measure the position. The other cause is thermal motion of atoms, whose kinetic energy increases with temperature of the solid or liquid.
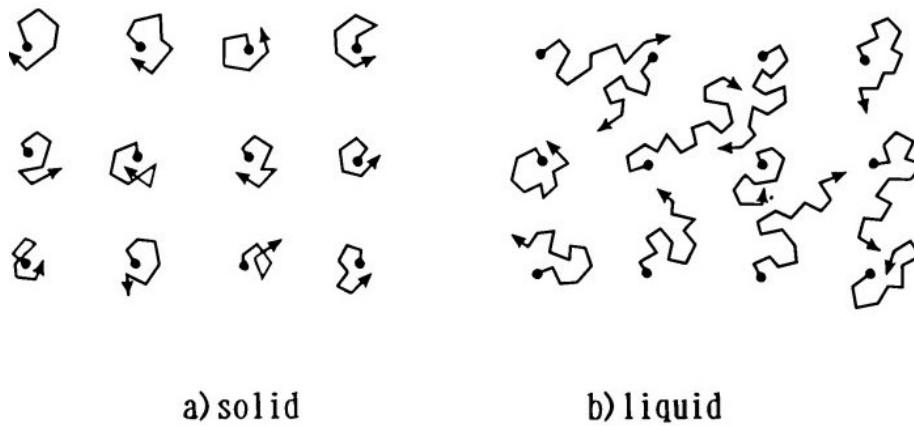

a) solid   b) liquid

Figure 9. Motion of atoms in solid or liquid

At extremely low temperatures, motion of atoms due to the uncertainty principle dominates and at higher temperatures thermal motion dominates. In solids, the motion due to the two causes is not strong enough for atoms to move far from their equilibrium positions and the stability tendency dominates over the tendency to increase entropy, while, in liquids, atoms move far from their equilibrium positions so that the system can increase its entropy due to the possibility of atoms being anywhere in space.

In general, atoms or molecules are packed densely in liquids and solids. For example, the size of a molecule in volume is about one half of the volume of the substance per molecule for water or ice. In spite of this close packing, atoms or molecules in a liquid can move to far distances just like a man could walk through the crowd of people in a heavily crowded street

At the liquid-solid phase transition temperature, random motion of atoms is mainly due to thermal motion for most substances. Only exception is helium, for which motion due to the uncertainty principle is significant because of the small mass of the helium atom and dominates over thermal motion at low temperatures. Since the inter-atomic force is very weak for helium and the minimum motion of the atoms required by the uncertainty principle is significant, helium is known not to become a solid even at absolute zero temperature under the normal pressure.

Now, we are ready to discuss what phase a system would take for given values of temperature and other thermodynamical variables which specify a macrostate of the system. In thermal equilibrium, the system is constantly exchanging energy with its surroundings (heat reservoirs), and thus the energy of the system is not conserved but fluctuates about its average value related to the temperature of the system.

In classical physics the probability for finding the system in a state with energy E is given by Maxwell-Boltzmann's distribution function and is proportional to the

Botzmann factor $\exp(-E/kT)$ (see *Physical Systems and Laws*). The entropy *S* of the system for a given macrostate is $\Omega = \exp(S/k)$, where Ω is the number of microstates for the given macrostate. Then, the probability for finding a macrostate with energy *E* and entropy *S* is proportional to the product of the two factors, $\exp(-E/kT)$ and Ω:

$$\Omega \exp(-E/kT) = \exp(-F/kT) \tag{1}$$

Here *F* is the Helmholtz free energy defined by

$$F = E - TS \tag{2}$$

From Eq.(1) we can infer that the macrostate with minimum value of *F* has the highest probability and thus is most likely to be realized. In particular, when the number of the constituents of the system is very large, the amount of change of the free energy for a small change of the macroscopic variables is much larger than *kT*, and probabilities for finding the system in macrostates other than one with minimum value of *F* will be exceedingly small and can be safely neglected in thermal equilibrium. In Fig.10 we show the energy, entropy and free energy of a substance as a function of temperature for the solid and liquid phases. Both the energy and entropy increase with temperature for the both phases and their values of the liquid are larger than those of the solid.
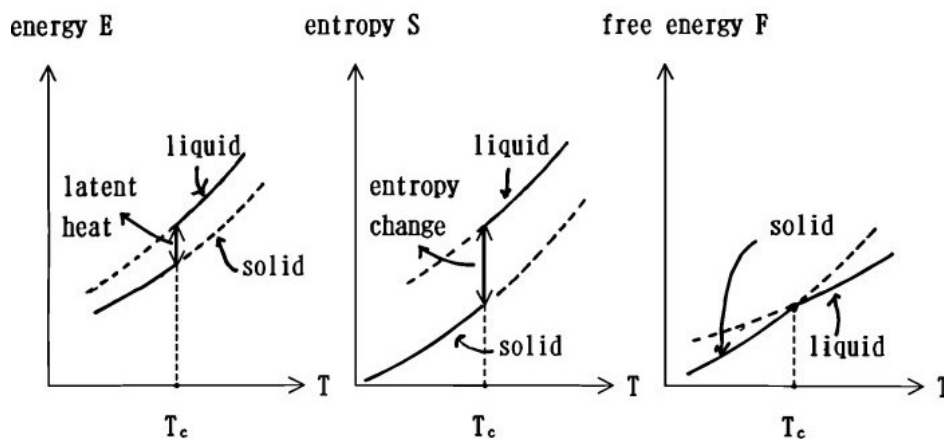

Figure 10. The energy, entropy and free energy as a function of temperature

For low enough temperatures we obtain *F* ~ *E* so that the free energy is smaller for the solid phase than for the liquid phase. At high enough temperatures the free energy is dominated by −*TS* so that *F* is smaller for the liquid phase than for the solid phase. Therefore, at a certain intermediate temperature T_c the free energy *F* must become the same for the two phases. The temperature T_c is the transition temperature for the liquid-solid phase transition, and below T_c the substance takes the solid phase and above T_c the liquid phase. The difference in energy between the two phases at T_c is equal to the latent heat, and the difference in entropy at T_c means that there occurs a sudden change in order of the structure associated with the liquid-solid phase transition. The larger entropy of liquids signifies that they are more disordered than solids.

The underlying principle for the formation of order in matter is the principle of least free energy. The free energy can be calculated in principle by knowing the number of microstates for a given macrostate and the energy determined by inter-atomic forces. Thus we obtained the basic understanding on what phase a substance takes for given values of the thermodynamical variables of the system in thermal equilibrium.

We know that there exists resistivity for change of political systems, change of laws and regulations, change of our customs for living, change of standard models of industrial products, or any change of social systems. In this respect natural phenomena are not exceptions. For instance, in the first order phase transitions the latent heat prevents rapid change of phase to occur and two phases coexist during the phase transition.

In physics, there is always resistivity against change of an ordered state of a system into another state. When we lower the temperature of a substance below the transition temperature, it can happen that the substance remains in the original phase without undergoing a phase transition. When we keep cooling a substance, the phase transition from gas to liquid or from liquid to solid does not necessarily occur and the temperature of the substance would keep decreasing beyond the transition temperature. This phenomenon is called supercooling. Conversely, when we raise the temperature of a substance beyond the transition temperature, it can happen that the substance remains in the original phase with its temperature still increasing. This phenomenon is called superheating. In the both cases, the substance is not in the state of the least free energy but remains in a state with higher free energy.

For a phase transition to occur some fluctuations from the uniformity of the system must exist and these must grow beyond a certain critical magnitude to govern the whole system. For instance, when liquid water boils, small bubbles of water vapor are formed here and there. M any of the bubbles would disappear soon without growing, and only those which grew beyond a certain critical size can grow further and form water vapor. When water is not clean and contains dirt, bubbles are most likely formed either around the dirt particles as the center or at the boundaries between the water and the container, and then grow further. On the contrary, very clean water evenly warmed is not easily boiled and can stay in the superheated state for a while.

When atmospheric water vapor condenses into water droplets and an aggregate of the droplets form a cloud in the sky, it is known that fine particles or dusts of sizes from 10^{-3} to 10 *microns* floating in the atmosphere act as nuclei of water droplets formed. This means that for the gas-liquid transition to occur we need fluctuations from uniformity or presence of impurities. The phase transition cannot occur under completely uniform and fluctuationless circumstances.

Next, we shall discuss some intimate relations between the degree of order and the symmetry property of arrangement of atoms or molecules in a substance. A crystalline structure in solid is an ordered structure with a regular and recurring arrangement of atoms. As shown in Fig.11 the array of atoms has axes of orientation. In certain directions atoms are arrayed with equal distances and in other directions no atoms are arrayed. Contrary to this, in liquid atoms are constantly moving and change their

positions thereby keeping the density of atoms constant If we average the distribution of atoms over a short but finite period of time, atoms in the liquid are equally placed in all directions and distances. This means that translational and rotational symmetries are broken in solid but not in liquid.
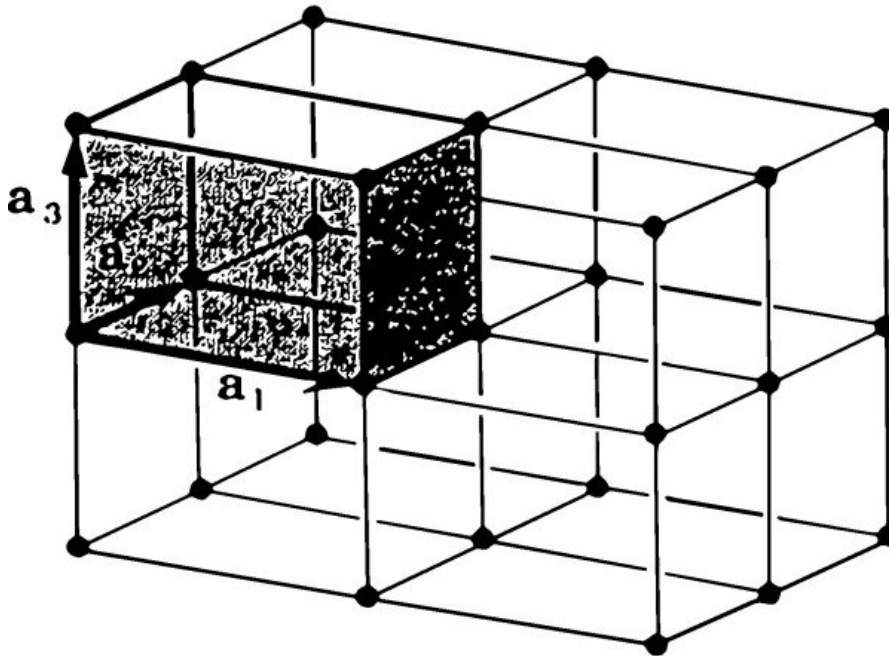

Figure 11. The array of atoms in solid phase

When we observe array of atoms from a fixed point in space, the array has rotational symmetry if there is no preferred direction in the arrangement of atoms. Thus the liquid has rotational symmetry under rotations by any angle about any axis. This full rotational symmetry is broken in solid. However, as described in an earlier chapter (see *Physical Systems and Laws – Symmetry Principles and Conservation Laws*), a solid exhibits a certain restricted rotational symmetry under rotations. For example, the simple cubic lattice structure of a solid has axial symmetry under rotations by 90 degrees about any of the three axes passing through the center of the unit cells as shown in Fig.12. Other lattice structures also have its own rotational symmetry which depends upon the lattice structure. None of the lattice structures of solid can have full rotational symmetry, while that of liquid has full rotational symmetry.

In general, when a system undergoes a phase transition, symmetry properties of the structure of the system will change. In most cases it has been shown that the structure of the system in a phase realized at higher temperature exhibits more symmetry than that of the other phase realized at lower temperature. This means that some symmetry becomes broken when a system undergoes a phase change from one phase at higher temperature to another one at lower temperature. So it seems that a more ordered state has less symmetry than a less ordered state and certain symmetry properties must be changed in the phase transition between the two. We shall discuss more about

spontaneous symmetry breaking associated with phase transitions in a later chapter (see *Physical Systems and Laws*).
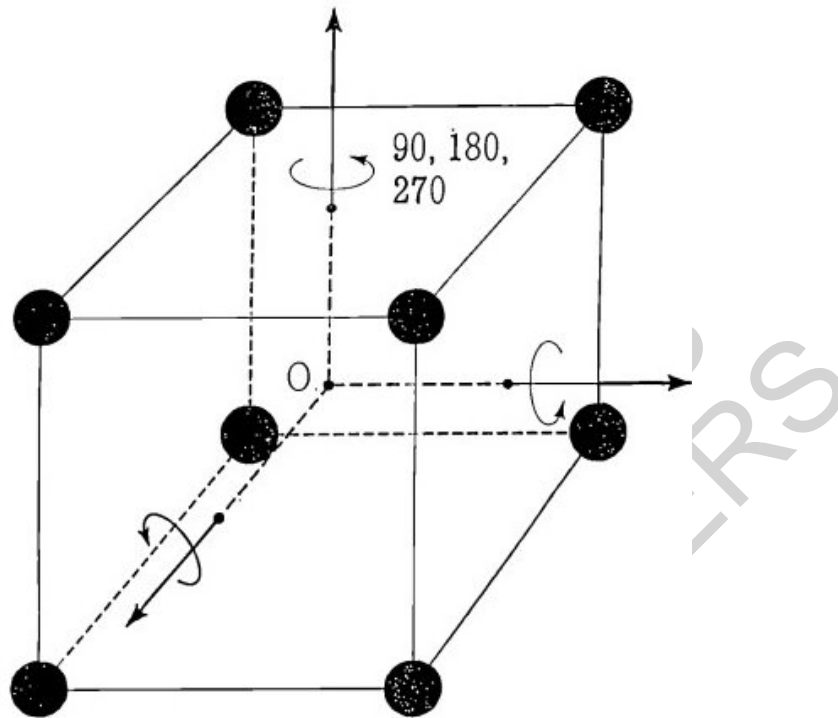

Figure 12. The simple cubic lattice and its three rotational axes

So far we have discussed the phase transitions, particularly those of water. A phase transition occurs at a definite value of temperature for a given value of pressure as was shown in the phase diagram for water. However, as everybody knows, liquid water can evaporate from its surface even at temperatures below the transition or boiling temperature, and the liquid and gas phases coexist at these temperatures.

In Fig.13, we show water contained in a vessel with a movable cylinder attached to it, so that the effective volume of the vessel can be changed by moving the cylinder up or down. Fig.13a shows the case that all the volume of the vessel is filled with liquid water with no empty space left in the vessel. Fig.13b shows the case when the cylinder is pulled up a little so that a fraction of liquid water evaporates from its surface and the liquid and vapor water coexist with a boundary surface between them. Fig.13c shows the case when we pulled up the cylinder sufficiently high so that all of the liquid water evaporate and became vaporized. These phenomena are widely observed for a wide range of temperature.

Although volume change of liquid or solid with pressure is small for most substances, volume of gas depends much on pressure. Fig.13 shows what phase water would take for given values of volume and temperature, but not for given values of pressure and temperature. The coexisting state of the liquid and gas phases in Fig.13b can be

understood based on the phase diagram where temperature and volume are chosen as state variables.
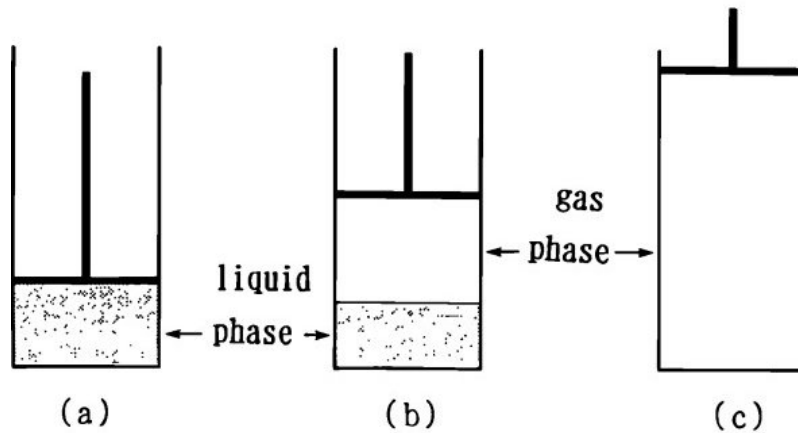

Figure 13. Water contained in a vessel with a movable cylinder attached to it

In an earlier chapter (see *Physical Systems and Laws – Statistical Physics*) we discussed two kinds of free energies and showed that the Helmholz free energy *F* is minimum for fixed values of temperature and volume, while the Gibbs free energy *G* is minimum for fixed values of temperature and pressure. The Gibbs free energy is

$$G = F - PV = E - TS - PV \tag{3}$$

For the solid-liquid transition the different choice of the free energy does not make much difference since volume does not change much under variation of pressure.

In Fig.14 we show motion of water molecules in the coexisting state of gas and liquid separated by a boundary surface. Each molecule in the liquid is moving randomly due to thermal motion, but most of the molecules remain in the liquid because of strong binding forces exerted by its neighboring molecules in the liquid. But some of energetic molecules can go out from the liquid through the boundary surface, thereby making itself free from the binding forces. Conversely, some energetic molecules in the gas can go through the surface into the liquid.

Thus, microscopically there is constant exchange of molecules between the two phases, although in average the net flow of molecules through the boundary is zero at thermal equilibrium. When the inflow and outflow of molecules through the boundary surface become balanced, the Gibbs free energies for the two phases become equal and a thermal equilibrium state is established as a coexisting state of the two phases separated by the boundary surface. The pressure of gas in this equilibrium state is called the saturation vapor pressure.

This is similar to the situation in which two countries having different political or economical system are neighbors. People will go out or come in through the border looking for better life or asking for political asylum. The basic cause for this movement

of people is the desire of people for freedom and stability for living, which might be compared to the requirement that the free energy must be minimized in thermal equilibrium of material systems.
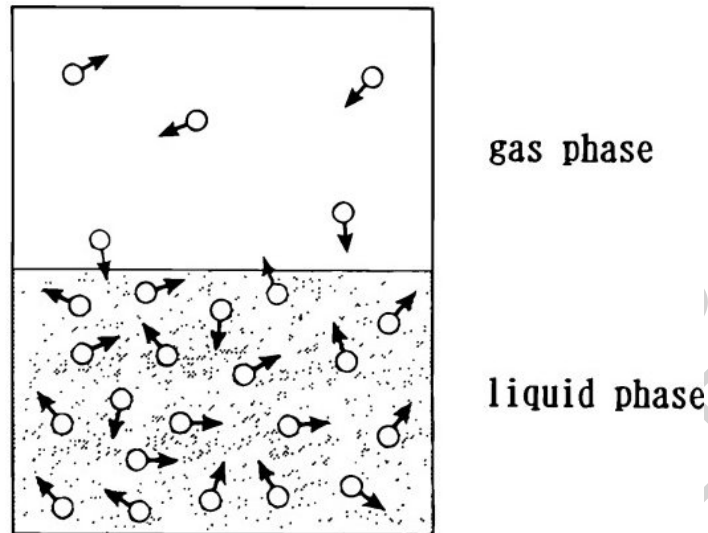

Figure 14. The coexisting state of liquid and gas

As time passed, the in- and out-flows of people cause change of states for living in the both countries and they become equal in conditions for living and an equilibrium state is realized as a coexisting state of the two countries separated by the border. By this time, the in- and out-flows of people become balanced in average and there will be no net flow of people through the border, although still movement of people across the border will continue as a kind of fluctuation.

The first order liquid-gas phase transition is not a change of the phase of a substance occurring through the boundary of the substance, but it occurs at every point within the substance. This is similar to a revolutionary change of the social system of a country by internal dynamics within the country and not a change caused by influence coming in through the border of the country. The similarity between the phase transition and the change of social systems is rather remarkable and can be explored further. However, there is a limitation in discussing quantitatively the change of social systems, because we may not be able to find and calculate a quantity equivalent to the free energy in physics.

In case of phase transitions of matter we considered the matter in thermal equilibrium with constant temperature through heat exchange with its environments (heat reservoirs). In equilibrium, although the system is exchanging constantly energy with its surroundings, every flux in one direction is compensated by another in the exact opposite direction so that the system remains in an invariant state in time. Contrary to this, there exist open systems in which fluxes entering the system move it to a state that

is far from thermal equilibrium and the new state seems to be characterized by more order.

Open systems which have been extensively studied both experimentally and theoretically are fluid systems and laser systems. Here we shall consider fluid systems which are often cited as a paradigm of the transition from order to disorder (turbulence) or disorder to order under influence of external flux of heat or energy. The best known phenomenon showing order in this context is the Rayleigh-Bernard or Bernard convection current

A fluid contained in a vessel is heated from below. Heat comes into the fluid from its bottom layer and goes away from its top layer into outer surroundings of the vessel. A temperature gradient will be established inside the fluid, and there arises a constant upward flow of heat by thermal conduction. When the temperature gradient is less than a certain critical value, the heat entered into the fluid from the bottom will be transferred to upper layers by thermal conduction and then disposed to the surroundings from the top layer. All the heat coming in will be disposed without accumulation and an equilibrium flow of heat and an equilibrium temperature gradient in the fluid will be established.

The fluid itself is at rest and the gravitational instability due to the colder and more dense fluid being above the hotter and less dense fluid is balanced by the viscous forces of the fluid which prevents the fluid to move and heat diffusion to disperse heat to surroundings.

When the temperature gradient exceeds the critical value, the fluid is set in motion. In this new regime hotter fluid will rise to upper layers, lose heat, and descend to lower layers and get heated again. The net effect of this motion is that the whole fluid will move and carry heat with it from bottom to top layers. This is called the convection current of the fluid.

Although the amount of heat transferred by thermal conduction increases with the temperature gradient, it saturates with sufficiently increasing values of the gradient. Therefore, if the incoming flow of heat from the bottom exceeds the maximum value of heat could be carried by thermal conduction, the fluid itself starts moving to carry heat with it from bottom to top layers.

There are varieties of ordered flow of fluid induced by an external thermal flux depending on the strength of the flux and the shape and size of the vessel containing the fluid. In Fig.15 we show a typical macroscopic ordered flow of fluid in a rectangular vessel. The flow develops a pattern of parallel cylindrical rolls (vortices) called the Bernard cells. This is obviously a space-time ordering process induced by the external thermal flux. Adjacent vortices rotate in the opposite directions to each other so that the flow of the fluid in the intermediate region between the two vortices is smooth,

Obviously, the fluid motion is very similar to the motion of swimmers in a crowded pool described before. In Fig.16 we show two flow patterns consist of three Bernard's cells. These are equivalent to each other except the directions of motion of the fluid are

opposite. Which one of the patterns is actually realized depends upon initial fluctuations which grow to a large scale.
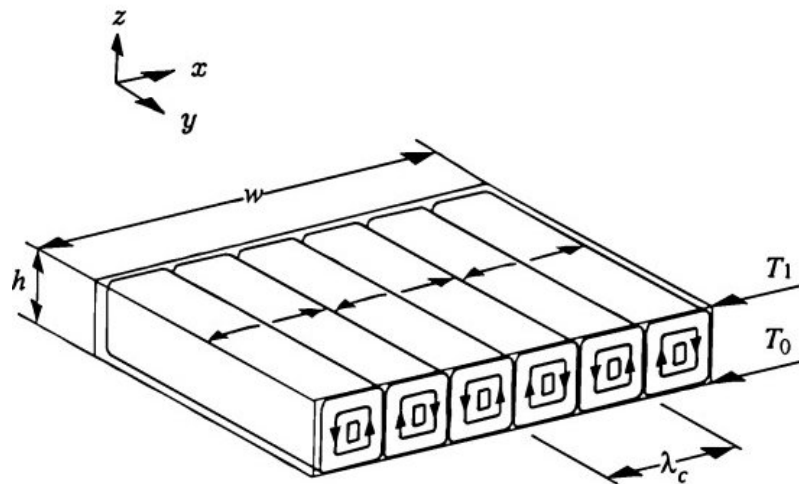

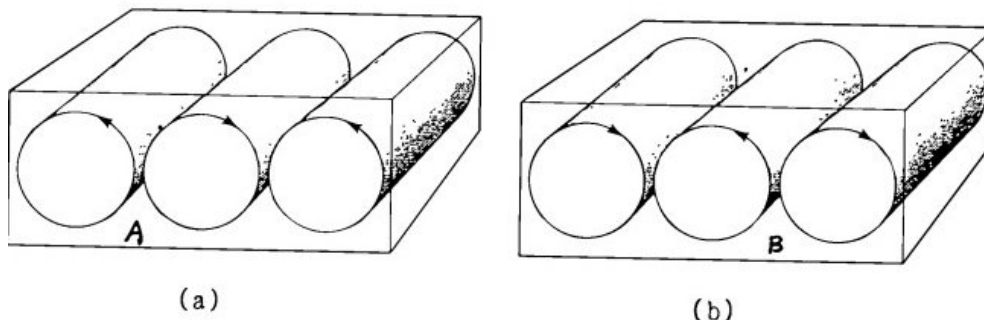Figure 15. The Bernard cells in a rectangular vessel

Figure 16. Two flow patterns with three Bernard's cells

Consider a hot droplet formed in the bottom layer of the fluid by thermal fluctuation. It has a lower density than the surrounding fluid and thus is pushed upwards by buoyancy. If the buoyancy is not counterbalanced by viscous forces and heat diffusion from the droplet to the environment, the droplet will move upwards and enter colder regions where the density is even higher, so that it keeps rising.

Such a hot droplet will be formed anywhere in the bottom layer of the fluid with more or less equal probability. If it is formed in region *A* of Fig.16 the resulted vortex patterns will be one shown in Fig.16a and, if it is formed in region *B*, the pattern will be one in Fig.16b, The underlying laws of motion of the fluid is left-right symmetric and there is no preference for either one of the two patterns occurring, but the choice is made by initial fluctuations, i.e., by chance. However, once one of the patterns is formed, it is difficult to change it to the other pattern, thus the left-right symmetry is spontaneously broken.

When an amount of heat ΔQ is brought into the fluid from the bottom layer at temperature T_1 and the same amount of heat goes out from the upper layer at temperature T_2 ($< T_1$), the amount of entropy $\Delta S = \Delta Q/T_2 - \Delta Q/T_1 > 0$ is taken away from the fluid into its environment or the fluid gets the negative entropy $-\Delta S$ from its surroundings. Thus, inevitable entropy increase due to the convection current of the fluid is compensated by this feeding of negative entropy from the environment to the fluid, which can stabilize the fluid motion in spite of the fluid being in a state far away from its thermal equilibrium, The same reason may apply for biological order by which the unique and highly ordered structures and functions are kept in biological livings.

As the external flux continues to increase, the fluid motion becomes turbulent and it reaches a chaotic state formed by uncorrelated and unpredictable local states. In some cases the transition takes place passing through several successive ordered patterns with its own instabilities which can grow when the flux exceeds a certain critical value. We will discuss more about this in a later chapter (see *Particles and Fields*).

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Biographical Sketch

Gyo Takeda, Professor Emeritus of Tokyo University and Tohoku University, was born in Tokyo l924. His speciality is the theory of Particle physics and nuclear physics and he also carries out research into neuroscience. He is known as one of the collaborators of Prof. S. Tomonaga's works on the relativistic renormalized theory of quantum electrodynamics. After graduating from Physics Department, University of Tokyo, he has served as an Associate professor, Kobe University, Professor and Director, Institute for Nuclear Studies, University of Tokyo, Professor of Physics and Dean of Faculty of Science, Tohoku University, and a Professor, General Education, Tohoku Gakuin University. Also he served as a research associate of University of Wisconsin and Brookhaven National Laboratory, USA, during the period of 1952-l955 and as a visiting professor of University of Wisconsin and University of California, Berkley, during the period of 196l-l963. He was a member of High Energy Physics Committee of IUPAP(International Union of Pure and Applied Physics) during the period of l973-l978 and served as the Chairman of the Organizing Committee of the l7th International High Energy Physics Conference held in Tokyo, l978. He has published many textbooks on general physics, quantum field theory, particle physics, and neuroscience all in Japanese.