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Thermodynamics of frost heaving: A thermodynamic proposition for dynamic phenomena

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A phenomenon of up-heaving during the freezing of water in porous materials is reviewed. A unique feature relevant to the phenomenon is that when water and ice are partitioned by a microporous material and are kept in a supercooled state, water moves from below to the ice bottom against a force of gravity, and gravitational potential energy is spontaneously produced. This phenomenon, which is unable to be explained by Newton's laws of dynamics, is found to be consistent with the second law of thermodynamics. It is suggested that matter in a system kept in a thermodynamically nonequilibrium state can move in a direction opposite to a force applied on the matter if the movement produces an increment of entropy in a whole system consisting of the system and local surroundings that interact with the system. The result is generalized and a simple thermodynamic proposition is proposed so as to account for emergence of dynamic motions in nonequilibrium systems. Some of the examples are discussed from this thermodynamic viewpoint. [S1063-651X(97)12909-9]

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I. INTRODUCTION

The growth of ice crystals from a soil surface has attracted scientists in various fields, e.g., physics, chemistry, geology, biology, agriculture, and civil engineering. The attractive feature is that an ice column grows upward as if it were a growing plant (see, e.g., Fig. 1). When the ice grows inside a freezing ground, the resultant upheaval of the surface is called frost heaving. Le Conte investigated this phenomenon for the first time [1]. Since then several experimental studies have been carried out (e.g., Taber [2], Fujita *et al.* [3], and Nakaya and Magono [4]). Characteristic features relevant to the frost heaving can be summarized as follows: (a) spontaneous separation of ice from a mixture of soil and water, (b) movement of water against a force of gravity, and (c) resultant production of potential energy against the gravity. Although several theoretical studies of frost heaving have been carried out [5–8], the cause of water movement is still debatable. In this paper, we shall not go into the details of the problems; e.g., soil properties, surface interactions, thermomolecular pressure, etc. Instead, a few fundamental features of frost heaving will be described in Sec. II. Then in Sec. III we shall see how this phenomenon can be explained by the second law of thermodynamics. It will be shown that Newton's second law of dynamics is not applicable to a system that is kept far from its thermodynamic equilibrium. In the nonequilibrium system, matter can advance to recover the equilibrium even though a force applied on the matter is in the opposite direction. The result is generalized, and a simple thermodynamic proposition is presented so as to account for spontaneous emergence of dynamic motions in nonequilibrium systems. Some of the examples, e.g., Carnot engine, Bénard thermal convection, and global circulation of the Earth's atmosphere, are to some extent discussed from this viewpoint.

II. FROST HEAVING

A schematic picture of frost heaving is shown in Fig. 2. Ice and water are partitioned by a porous material that is permeable to water. It has been confirmed that the material can be a thin membrane filter [9] or a grass filter [10,11] or even a single narrow capillary [12]. Thus it is needless to consider the complicated properties of soils. It is empirically known that the key factor is related to the size of pores (cf. [2,3]). If the size is large enough, say larger than 0.1 mm, frost heaving hardly takes place. Instead, if the size is small enough, say less than 1 μm, ice can be grown upward from the material. Figure 1 shows such an example. In this experiment, a microporous filter (Millipore filter, Millipore Intertech, P.O. Box 255 Bedford, MA 01830, USA, mean pore diameter 0.05 μm) is used as the material. The growth process has been investigated in an earlier publication [9]. Here it should be noted that water is kept in a supercooled state since ice does not propagate through the pores of the filter. Under this state, the water is driven through the filter, freezes at the ice bottom, and thus the ice grows upward (Fig. 1). Jackson *et al.* [5,13] presented a theoretical explanation for the nonpropagation of ice into the pore capillaries. They explained lowering of the freezing temperature of the ice in the capillaries by the Gibbs-Thomson effect. According to the Gibbs-Thomson effect, maximum supercooling maintained by pores with a diameter of 0.05 μm is 2 K (cf. [9]); it means ice cannot propagate through the pores if the ambient temperature is higher than 271.15 K (-2 °C).

An important fact relevant to the frost heaving is the existence of a thin water layer between ice and a solid surface at temperatures below the normal freezing point. Faraday first suggested the possibility of a water layer on the ice surface in order to explain several mechanical properties of ice, such as regelation [14]. The existence of such a water layer was observed under an optical microscope at a contact area between ice and a glass plate at temperatures as low as

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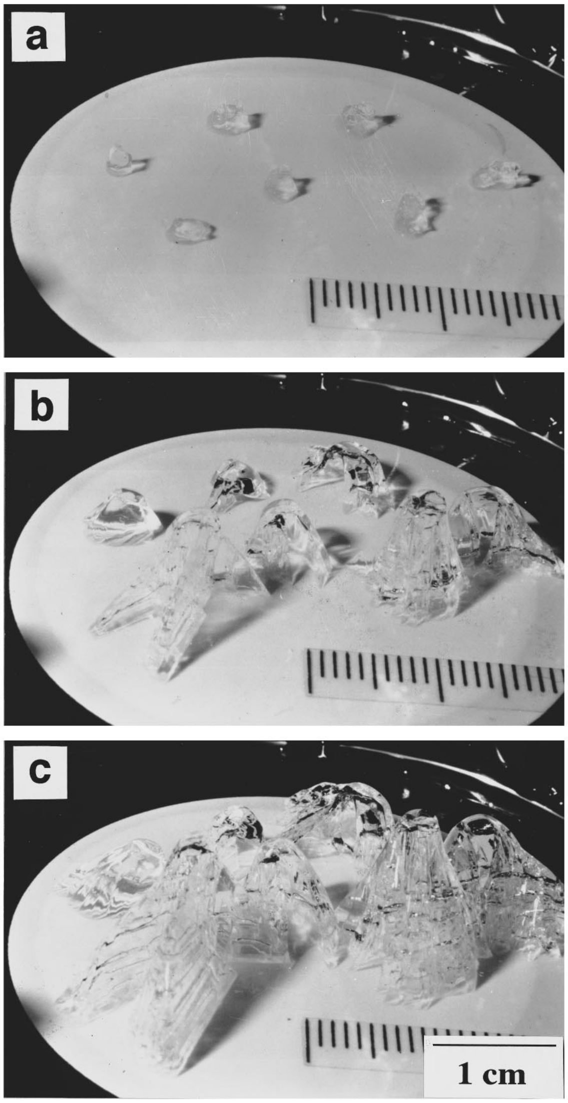

FIG. 1. Successive photographs of the ice growth on a microporous filter (Millipore filter, pore diameter 0.05 μm); (a) seeding of ice particles, (b) 3 h, and (c) 5 h after the seeding. The room temperature was -0.5 ± 0.1 °C.

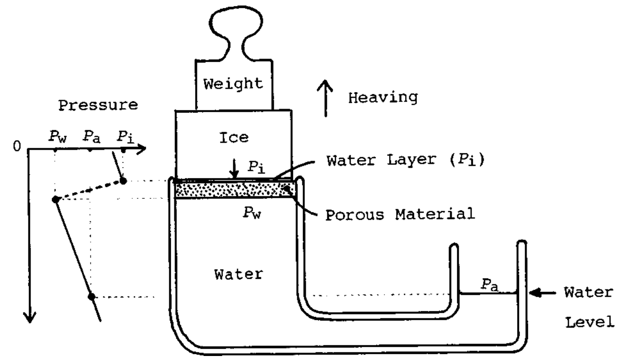

FIG. 2. Schematic illustration of frost heaving. Ice and water are partitioned by a microporous material that is permeable to water. A thin water layer is existing between the ice bottom and the material surface and freezing takes place at the upper surface of the layer. Water pressure at just below the material (p_w) is lower than the standard atmospheric pressure, whereas pressure at the water layer (p_i) is higher than the atmospheric pressure. Thus $p_w < p_i$. The water is nevertheless drawn into the water layer against the pressure increase ($p_i - p_w$), if it is kept in a certain supercooled (nonequilibrium) state. Consequently gravitational potential energy is spontaneously produced.

-30 °C [15]. Kuroda [7] presented a thermodynamic explanation for the existence of the water layer and discussed kinetic process at the water layer. A review on this subject was recently published by Dash *et al.* [16].

The most important feature of frost heaving is shown in Fig. 2, i.e., water moves *against* a pressure increase, and gravitational potential energy is spontaneously produced. As shown in Fig. 2, the water level in the right-hand side of the U-shaped tube is set lower than the level of the porous material (e.g., a filter). Thus, owing to the hydrostatic balance in the gravity field, the water pressure at the bottom of the filter, p_w, is less than the standard atmospheric pressure, p_a: $p_w < p_a$. On the other hand, pressure at the bottom of the ice, p_i, is a sum of ice weight and an extra weight (if loaded) divided by the area of the ice bottom plus the atmospheric pressure. Thus $p_i > p_a$. Because of the mechanical balance at the ice bottom, pressure of the water layer has to be p_i. So water has to flow *against* an increase in pressure ($p_i - p_w$) as indicated with a dashed line in a pressure diagram in Fig. 2. In fact, water flows if it is kept in a certain supercooled state (see Fig. 1). Water flows into the layer, freezes at the ice bottom, and thus the ice is pushed upward. This is the fundamental feature of frost heaving. This could be a paradox if one tried to work with Newton's second law of dynamics. There is no reason in Newton's dynamics for a mass to move *against* an external force. (Strictly speaking, the force consists of a pressure term and a gravity force applied to a mass of a liquid parcel under consideration. The direction of both forces is *opposite* to the direction of the water movement.) Some attempts assuming a *reduction* of water pressure at the water layer, which could explain a water flow into the layer (e.g., [16]), could not explain the mechanical balance at the water layer; i.e., the water layer should have a *higher* pressure to support the ice (see Fig. 2). Neither Newton's laws nor Navier-Stokes' equations for fluid dynamics can account for the water movement during frost heaving. This has been a center of debates on the matter of frost heaving.

If there were only Newton's laws, there could never have been any motion in the Earth. Newton himself was aware of the problem. By reason of viscosity of fluids and friction in their parts, motion is much more apt to be lost than gotten, and is always upon the decay (p. 398 [17]). He suspected an *active* principle by which bodies can be driven into motion, yet he did not specify it (p. 402 [17]). We shall in due course present an *active* principle by which frost heaving, as well as others, can be driven into motion.

So far several experimental studies have been carried out to find the maximum pressure produced by frost heaving. Radd and Oertle [18] carried out freezing experiments of soils under different loads on ice. They found a relation between the maximum overburden pressure on ice ($p_i - p_a = 0$ to 17 MPa) and degree of supercooling at the freezing front at a static state at which the heaving is suppressed. Biermans *et al.* [10] did a simple experiment such as Fig. 2, using a glass filter as the material. The experimental vessel was immersed in a liquid bath which was held at a constant

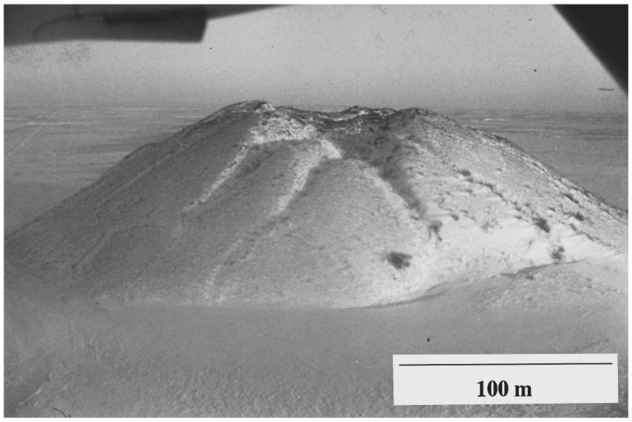

FIG. 3. A heaving mountain, called pingo, in Mackenzie delta in the Canadian Arctic (69.40° N, 133.08° W). The height of the mountain is 50 m, and the basal diameter is 300 m. The photograph was taken from an airplane in March 1989.

temperature below the freezing point, thereby keeping it in a supercooled state. In their experiment, water side pressure was set lower than the atmospheric pressure ($p_w - p_a = 0$ to -80 kPa), and a relation was found between the negative water pressure and the degree of supercooling at the static state. We shall refer to this static state as a metastable-static state, since the water phase is kept in a supercooled state, i.e., thermodynamically metastable (nonequilibrium). The two aforementioned results can be summarized into a single relation for the metastable-static state:

$$\Delta T_{ms} = \frac{T_e}{L} (\Delta p_i v_i - \Delta p_w v_w), \tag{1}$$

where $\Delta T_{ms} = T_e - T_{ms}$ is the degree of supercooling at the freezing front at the metastable-static state, T_e is the phase equilibrium temperature of ice and water (273.15 K) under the standard atmospheric pressure ($p_a = 101.3$ kPa$=1$ atm), L is the latent heat of fusion of ice per molecule, v_i is the molecular volume of ice, v_w is the molecular volume of water, $\Delta p_i = p_i - p_a$ and $\Delta p_w = p_w - p_a$ are pressures of ice and water measured against the standard atmospheric pressure. If the supercooling ΔT is greater than ΔT_{ms} and is less than the maximum degree maintained by the pores, then freezing and heaving will take place. This equation has an important meaning for civil engineers and geologists in cold climate regions. According to Eq. (1), one degree of supercooling could heave a weight of 11 kg on a ground of 1 cm^2 (cf., e.g., [18]). This is a source of motive power for dynamics in the cold regions. It is so powerful that rocks, buildings, and even mountains can be heaved up (see Fig. 3). The fundamental feature of frost heaving is shown in Fig. 2. It is easy to stop the heave. If a large hole is made in the porous material, or the soils are replaced with a coarser material such as sand, then water can never be kept in a supercooled state and it freezes without doing any work. The fundamental features of frost heaving can be summarized as (a) when water and ice are partitioned by a microporous material, water can be kept in a supercooled state, (b) the water is then driven through the material toward the ice bottom against an applied force, and potential energy against the force is spontaneously produced, and (c) an empirical relation Eq. (1) is found to exist under the metastable-static state.

III. A THERMODYNAMIC PROPOSITION

We shall here consider a proposition that matter in a system kept in a thermodynamically nonequilibrium state can move in a direction opposite to a force applied to the matter if the movement produces an increment of entropy in a whole system consisting of the system and local surroundings that interact directly with the system. The movement against the force results in production of potential energy, which is ready to be converted into kinetic energy. The proposition can, therefore, be seen as an *active* principle by which spontaneous emergence of dynamic motions in nonequilibrium systems may be explained. We shall examine the proposition with respect to frost heaving.

A. Entropy change during frost heaving

Let us consider a whole system that consists of a system, in which an ice column is grown upward and potential energy may be extracted, and of a surrounding thermal reservoir, whose temperature is isothermally controlled at T ($T < T_e$). Although it is not a general case, this situation has been realized in some experiments [9,10], and is suitable for our simple consideration. Let us then consider that a certain small amount of water molecules, dn, is drawn into the water layer and captured at the surface of ice lattice. Since the water movement against a pressure increase results in production of potential energy, a part of the latent energy released by the recovery of molecular bonds may be converted into the potential energy, δE. The rest of the energy will change into heat, δQ, i.e., random thermal motion of molecules. Then the conservation law for energy (the first law of thermodynamics) should hold as

$$L dn = \delta E + \delta Q. \tag{2}$$

Equation (2) means that a part of the latent heat (internal energy) of the supercooled water is converted into potential energy.

The entropy change in the whole system is given by a sum of that in the system and that in the thermal reservoir:

$$dS_{\mathrm{whole}} = dS_{\mathrm{sys}} + dS_{\mathrm{res}}, \tag{3}$$

where dS_{whole}, dS_{sys}, and dS_{res} are the entropy change of the whole system, that of the system, and that of the thermal reservoir, respectively. Entropy of the system will decrease owing to the ordering process of water molecules at the ice surface. The entropy decrease due to the ordering process is, in principle, independent of the temperature. The amount of the entropy decrease is thus approximated by that at the phase equilibrium temperature as

$$dS_{\mathrm{sys}} = -S_m dn = -\frac{L}{T_e} dn, \tag{4}$$

where $S_m = L/T_e$ is entropy of melting of ice per molecule.

The heating δQ at the freezing interface results in a rise in temperature around the interface, and the resultant temperature gradient causes heat conduction from the interface to the thermal reservoir. When we consider a steady state, the heat released at the interface is completely drained into the reservoir. The entropy increase of the system due to the heating is then negligible, whereas that of the thermal reservoir is given by the heating divided by its temperature as

$$dS_{\mathrm{res}}=\frac{\delta Q}{T}. \tag{5}$$

By substituting Eqs. (4) and (5) into Eq. (3), and eliminating δQ using Eq. (2), we get

$$dS_{\mathrm{whole}}=\frac{L\Delta T}{T_e T}\,dn-\frac{\delta E}{T}, \tag{6}$$

where $\Delta T=T_e-T$ is the supercooling of the thermal reservoir. The first term represents an increment of entropy due to the freezing of the supercooled water, and the second term represents a reduction of entropy due to extraction of potential energy from the latent heat. The first term corresponds to a decrease of Gibbs free energy (or chemical potential) due to freezing of supercooled liquid. The free energy is related to entropy of a whole system in a specific condition of constant temperature and constant pressure. We do not use free energy in this paper since the pressure condition (Fig. 2) is far from uniform.

B. Potential energy produced by frost heaving

Let us evaluate the amount of potential energy produced by frost heaving. There are two relevant processes. First, the water molecules dn move from the zone with low pressure (p_w) to the water layer with high pressure (p_i) against the pressure difference (see Fig. 2). The resultant production of potential energy is the pressure difference (p_i-p_w) times their volume ($v_w dn$). Therefore $\delta E_1=(p_i-p_w)v_w dn=(\Delta p_i-\Delta p_w)v_w dn$. Second, the water molecules in the water layer should expand their volume by freezing for a certain amount, $(v_i-v_w)dn$, against the overburden pressure Δp_i. The production of potential energy by this expansion is $\delta E_2=\Delta p_i(v_i-v_w)dn$. Thus the total amount of potential energy produced by the movement and the freezing is

$$\delta E=\delta E_1+\delta E_2=(\Delta p_i v_i-\Delta p_w v_w)dn. \tag{7}$$

One may suspect a contribution to the potential energy by the upward movement of the water mass against gravity. This contribution has already been taken into account by the lowness of the water pressure ($\Delta p_w<0$) so long as the pressure is measured at just below the freezing front (see Fig. 2). With increasing overburden (ice) pressure and decreasing water pressure, the potential energy produced by frost heaving will increase.

C. The cause of frost heaving

The thermodynamic proposition considered here is that water movement against an external force can take place provided that the movement produces an increment of entropy in the whole system. By substituting Eq. (7) into Eq. (6), the proposition is rewritten in the form

$$dS_{\mathrm{whole}}=\left\{\frac{L\Delta T}{T_e}-(\Delta p_i v_i-\Delta p_w v_w)\right\}\frac{dn}{T}\geqslant 0. \tag{8}$$

The proposition (8) states that frost heaving should proceed ($dn>0$) when the sum in the curly parentheses is a positive value, in other words, when the supercooling is larger than the empirical degree at the metastable-static state (1); i.e., $\Delta T>\Delta T_{ms}$. On the contrary, melting ($dn<0$) should take place when $\Delta T<\Delta T_{ms}$. The static state ($dn=0$) is expected when $\Delta T=\Delta T_{ms}$. The thermodynamic proposition (8) is thus consistent with the experimental results ([10] and [18]). It is concluded that the water movement during frost heaving is caused not by a mechanical *force*, but by a requirement of the second law of thermodynamics, i.e., a tendency to increase entropy in the whole system which has been kept in a thermodynamically nonequilibrium state.

IV. DISCUSSION

In general, phase change in a nonequilibrium system (e.g., freezing of supercooled liquid) is an irreversible process through which a certain amount of entropy is produced in a whole system connected with the system [the first term in Eq. (6)]. By making a link to this intrinsically irreversible process, potential energy can be extracted from internal energy (heat) even though this extraction reduces a certain amount of entropy in the whole system [the second term in Eq. (6)]. Let dS_{irrev} denote an increment of entropy in a whole system by an irreversible process of this kind. Then the proposition (6) is rewritten in a general form, viz.,

$$dS_{\mathrm{whole}}=dS_{\mathrm{irrev}}-\frac{\delta E}{T}\geqslant 0, \tag{9}$$

where E is a total amount of energy available for dynamic motions (i.e., potential energy, kinetic energy, work, electric energy, etc.) except for the internal energy such as heat. The intrinsically irreversible process can be a heat flow from hot to cold, diffusion of molecules from dense to sparse, or phase change in a nonequilibrium system. It is our usual experience that the dynamic forms of energy tend to dissipate into heat by viscosity of fluids, by friction of material surfaces, or by imperfect elasticity of solids. The dissipation of the dynamic forms of energy is, by itself, a spontaneous change since a certain amount of entropy ($-\delta E/T>0$) is produced. The dynamic motions thus come to rest. However, according to the proposition (9), we can expect spontaneous emergence of a dynamic motion ($\delta E>0$), if the motion is linked to an intrinsically irreversible process of higher entropy production ($dS_{\mathrm{irrev}}>\delta E/T$). The proposition (9) is thus seen as an *active* principle by which spontaneous emergence of dynamic motions can be accounted for.

A typical example which produces dynamic forms of energy from heat is a steam engine discussed by Carnot [19]. The steam engine is operated with a hot thermal reservoir and a cold thermal reservoir. A heat flow (δQ) from the hot reservoir (T_h) to the cold reservoir (T_c) is an intrinsically irreversible process by which a certain amount of entropy is produced. The amount is given by a sum of that gained by the cold reservoir and that lost from the hot reservoir, such as,

$$dS_{\mathrm{irrev}}=\frac{\delta Q}{T_c}-\frac{\delta Q}{T_h}=\frac{T_h-T_c}{T_hT_c}\;\delta Q. \tag{10}$$

Since $T_h>T_c$, $dS_{\mathrm{irrev}}>0$. Then according to the proposition (9), a certain amount of energy (δE) in a dynamic form (e.g., work) can be extracted from a thermal reservoir (T). By substituting Eq. (10) into Eq. (9), we get

$$dS_{\mathrm{whole}}=\frac{T_h-T_c}{T_hT_c}\;\delta Q-\frac{\delta E}{T}\geqslant 0. \tag{11}$$

If the energy conversion is made from the hot reservoir, then $T=T_h$. The efficiency of a steam engine is defined as a ratio of the converted energy to the total heat flow from the hot reservoir: $\eta=\delta E/(\delta Q+\delta E)$. By substituting the relation (11), we get $\eta\leqslant(T_h-T_c)/T_h$; that is what is called maximum efficiency found by Carnot [19]. If the extraction is made from the cold reservoir, then $T=T_c$, and the efficiency is $\eta'=\delta E/\delta Q$. Then using the relation (11), again we get the same maximum efficiency: $\eta'\leqslant(T_h-T_c)/T_h$. Since the proposition (11) does not depend on the place of the energy extraction, it seems to be a general expression for the operation of an engine. It is explicitly shown in Eq. (11) that the production of dynamic forms of energy is possible along a heat flow from hot to cold.

It seems to the present author that another typical example of dynamic phenomena in nonequilibrium systems is thermal convection investigated by Bénard [20]. Although numbers of investigations have been carried out on this subject, we have no solid physical theory that is capable of expressing the complete process of thermal convection (e.g., [21]). The difficulties may be related to nonlinearity of dynamic equations and the resultant complexity of the solution [22]. Apart from the complex behaviors of the dynamic equations, Félici [23] and Sawada [24] suggested that the state of thermal convection is stabilized at a state with a maximum rate of entropy increase through convective heat transport from a hot reservoir to a cold reservoir. The stabilization at the maximum rate of entropy increase has been confirmed by numerical simulation of Bénard-type convection (e.g., [25]). Further investigation is needed to verify the thermodynamic proposition for the evolution of thermal convection in relation to the change of a mode of kinetic motions of the fluid. Here it should be noted that global scale thermal convection of the Earth's atmosphere (the general circulation) is also regulated at a state of maximum rate of entropy increase through convective energy transport from the Earth's surface to outer space [26]. The general circulation of the atmosphere is a major source for dynamic motions in the present Earth; e.g., winds, cyclones, rainfalls, river streams, ocean currents, etc. The energy supply to the Earth's surface is currently maintained by shortwave radiation from the hot sun (5770 K). It is therefore reasonable to say that the dynamic phenomena in the present Earth are, in general, maintained by the tendency to increase entropy in the universe which has been kept in a large thermal nonequilibrium state.

V. CONCLUDING REMARKS

In this paper, we have discussed the mechanism of frost heaving which has not been explained by Newton's laws of dynamics. It appears that the water movement during frost heaving is caused not by a mechanical force but by a thermodynamic tendency to increase entropy in a whole system which has been kept in a supercooled (nonequilibrium) state. The result obtained from this case study is generalized, and a thermodynamic proposition is proposed so as to account for the occurrence of dynamic phenomena in thermodynamically nonequilibrium systems. Carnot engine, Bénard thermal convection, and global convection of the Earth's atmosphere are shown to be akin to frost heaving of an ice column in this respect.

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