Liquid-Gas Transitions in Steady Heat Conduction

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We study liquid-gas transitions of heat conduction systems in contact with two heat baths under constant pressure in the linear response regime. On the basis of local equilibrium thermodynamics, we propose an equality with a global temperature, which determines the volume near the equilibrium liquid-gas transition. We find that the formation of the liquid-gas interface is accompanied by a discontinuous change in the volume when increasing the mean temperature of the baths. A supercooled gas near the interface is observed as a stable steady state.

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Introduction.—Liquid-gas transitions under constant pressure have been a classical subject of equilibrium thermodynamics [1]. In reality, however, a temperature gradient is formed, and thus the transition properties may be influenced by heat flow. As related experiments, enhanced heat conduction by condensation and evaporation was observed in turbulent systems [2,3]. In order to describe such nonequilibrium phenomena systematically, we first need to establish a thermodynamic theory for phase transitions under heat conduction.

As the simplest situation, we consider cases where the pressure and heat flux are spatially homogeneous, which is illustrated in Fig. 1. Specifically, let $T_c(p^{\rm ex})$ be the temperature for the liquid-gas transition in equilibrium under constant pressure $p^{\rm ex}$. When $T_c(p^{\rm ex})$ is between the temperatures of the baths [4], there is no reliable theory for determining the steady state even in the linear response regime. Indeed, the standard hydrodynamic equations [5] have many stationary solutions [6] once the liquid-gas interface is contained [7–10]. Furthermore, since the density profile has to be determined under the constraint of global mass conservation, the variational principle for selecting the steady state, if it exists, should be formulated for the whole system. Such a theory has not been reported yet.

Over the last two decades, statistical mechanics of nonequilibrium systems has progressed significantly [11–13] owing to the discovery of universal relations associated with the second law of thermodynamics [14–20]. As examples that may be related to the above problem, we point out extensions of thermodynamic relations [21–26], variational formulas associated with large deviation theory [27–31], representations of steady state probability densities [32–34], and inequalities stronger than the second law [35–38]. However, these results are not directly applicable to the analysis of liquid-gas transitions in heat conduction.

In this Letter, we generalize an equilibrium variational principle that determines the volume near the liquid-gas transition. Concretely, on the basis of local equilibrium thermodynamics in the linear response regime, we propose the equality (11) with a global temperature $\tilde{T}$, the main claim of this Letter, which corresponds to the generalized variational principle. This allows us to obtain the phase diagram of the heat conduction system, which can be examined in experiments.

Setup.—We study the system shown in Fig. 1. A heat bath of temperature T_1 is attached to the left end ($x = 0$) of the system, and a second heat bath of temperature T_2 to the right end ($x = L$), where $T_1 \le T_2$ is assumed without loss of generality. We focus on cases that $T_c(p^{\rm ex})$ is far below the liquid-gas critical temperature. The length L of the system is fixed throughout this Letter. Other boundaries are thermally insulating. The top plate is freely movable under constant pressure $p^{\rm ex}$. For simplicity, gravity effects are ignored.

We first consider the equilibrium case $T_1 = T_2 = T$. Let V and N be the volume of the system and the number of particles in moles. As an example, we take the van der Waals equation of state

$$p = \frac{RT\rho}{1 - b\rho} - a\rho^2 \tag{1}$$

and the heat capacity $C_V = \eta NR$, where R is the gas constant, a, b, and η are constants depending on the material, and $\rho = N/V$. Note that Eq. (1) represents even metastable states. The van der Waals free energy $F_{\rm vW}(T, V)$ [6] defined by $p = -\partial F_{\rm vW}(T, V)/\partial V$ is derived as

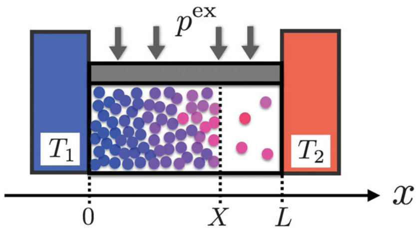

FIG. 1. Schematic illustration of experimental systems.

$$-NRT\log\left[T^{\eta}\left(\frac{V}{N}-b\right)\right]-a\frac{N^2}{V}+(c_1T+c_2)N, \quad (2)$$

where c_1 and c_2 are arbitrary constants that depend on the reference state for the entropy and the energy, respectively. Let ρ^L and ρ^G be densities corresponding to the liquid state and the gas state. The two densities satisfy $p(T,\rho^L)=p(T,\rho^G)=p^{\mathrm{ex}}$, with $\rho^L>\rho^G$. We then express the thermodynamic value of $V=N/\rho$, which is either $V=N/\rho^L$ or $V=N/\rho^G$, as $V_*(T,p^{\mathrm{ex}})$. For the following variational function with (T,p^{ex}) fixed:

$$\mathcal{G}_{\mathrm{eq}}(V;T,p^{\mathrm{ex}})\equiv F_{\mathrm{vW}}(T,V)+p^{\mathrm{ex}}V, \quad (3)$$

$V_*(T,p^{\mathrm{ex}})$ is characterized by the variational principle $\mathcal{G}_{\mathrm{eq}}(V_*(T,p^{\mathrm{ex}});T,p^{\mathrm{ex}})\le\mathcal{G}_{\mathrm{eq}}(V;T,p^{\mathrm{ex}})$ for any value of V. There exists a $T_c(p^{\mathrm{ex}})$ value at which $V_*(T,p^{\mathrm{ex}})$ is discontinuous as a function of T [6]. This singular behavior corresponds to the liquid-gas transition in equilibrium systems, and it is described by the thermodynamic Gibbs free energy $G(T,p^{\mathrm{ex}})\equiv\mathcal{G}_{\mathrm{eq}}(V_*(T,p^{\mathrm{ex}});T,p^{\mathrm{ex}})$. For hard spheres with long-range attractive interactions, $T_c(p^{\mathrm{ex}})$ is exactly determined by means of the variational principle with Eqs. (2) and (3) [39,40].

Main result.—We consider steady heat conduction states. We set $\Delta\equiv T_2-T_1>0$ and $\epsilon\equiv\Delta/T_1$. We focus on the linear response regime where $\epsilon\ll 1$. Since gravity effects are ignored, the heat conduction state is homogeneous in directions perpendicular to x. We choose the mean temperature $T_m\equiv(T_1+T_2)/2$ as a control parameter. Let X be the position of the interface between the liquid region $0\le x<X$ and the gas region $X<x\le L$. That is, for a given value of $T(x)$, we set $\rho(x)=\rho^L(x)$ in $x<X$ and $\rho(x)=\rho^G(x)$ in $x>X$, where the pressure balance equation

$$p(T(x),\rho(x))=p^{\mathrm{ex}} \quad (4)$$

holds. Note that $\rho(x)$ is discontinuous only at the interface $x=X$. The continuous temperature profile is determined by the conductivity $\kappa(T,\rho)$. Explicitly, $T(x)$ satisfies

$$-\kappa(T(x),\rho(x))\partial_x T=J, \quad (5)$$

where J is constant in x, $T(0)=T_1$, and $T(L)=T_2$. In this manner, $T(x)$ and $\rho(x)$ are determined from Eqs. (4) and (5) for a given X value. Since the volume V of the system is obtained by

$$\frac{V}{L}\int_0^L dx\rho(x)=N, \quad (6)$$

V has a one-to-one correspondence to X. Thus, the solutions $T(x)$ and $\rho(x)$ satisfying Eqs. (4) and (5) may be parametrized by V. We express the solutions and the interface position as $T(x;V)$, $\rho(x;V)$, and $X(V)$, respectively. For the steady state value V_*, we set $X_*=X(V_*)$. Furthermore, we define $X_*=0$ or $X_*=L$ when the space is filled with either gas or liquid, respectively. We next propose a formula for determining V_*.

Since local thermodynamic quantities characterize the steady heat conduction state in the linear response regime, a candidate for the variational function is

$$\frac{V}{L}\int_0^L dx[f(T(x;V),\rho(x;V))+p^{\mathrm{ex}}], \quad (7)$$

which is the natural extension of the right-hand side in Eq. (3). Here, $f(T,\rho)=F_{\mathrm{vW}}(T,V)/V$, and we ignore the free energy in the liquid-gas interface. Then, in order to identify fixed parameters, we use the fact that V_* has to be independent of c_1 and c_2 in Eq. (2). Since the variational equation should be independent of c_1 and c_2, we require that

$$\frac{V}{L}\int_0^L dx[c_1T(x;V)\rho(x;V)+c_2\rho(x;V)] \quad (8)$$

be kept constant with respect to the variation in V. This means that $V\int_0^L dxT(x;V)\rho(x;V)/L$ is a fixed parameter. Since this is proportional to the temperature averaged over all particles, we define a global temperature,

$$\tilde{T}=\frac{\int_0^L dxT(x;V)\rho(x;V)}{\int_0^L dx\rho(x;V)}. \quad (9)$$

The integral (8) is expressed by $(c_1\tilde{T}+c_2)N$, whose form is the same as the last two terms of Eq. (2). Thus, the variational function is expressed as

$$\mathcal{G}(V;\tilde{T},p^{\mathrm{ex}},\Delta)\equiv\frac{V}{L}\int_0^L dx[f(T(x;V),\rho(x;V))+p^{\mathrm{ex}}], \quad (10)$$

with $(\tilde{T},p^{\mathrm{ex}},\Delta)$ fixed.

The main claim of this Letter is that the equality

$$\left.\frac{\partial\mathcal{G}(V;\tilde{T},p^{\mathrm{ex}},\Delta)}{\partial V}\right|_{V=V_*}=O(\epsilon^2) \quad (11)$$

holds for the steady state value V_*. Here, V_* is assumed to satisfy a scaling relation that the thermodynamic state in the liquid or the gas region persists for $(N,\Delta)\to(\lambda N,\lambda\Delta)$ with $1\ll\lambda\ll\epsilon^{-1}$ [6]. The derivation of Eq. (11) is given in the paragraphs including Eqs. (12) and (13). Using Eq. (11), we can determine $V_*(\tilde{T},p^{\mathrm{ex}})$ and X_* as follows. First, we plot $\mathcal{G}(V;\tilde{T},p^{\mathrm{ex}},\Delta)$ as a function of $X=X(V)$. When this graph shows a local minimum at $X=X_*$ in $0<X<L$, we find the interface at $x=X_*$ because Eq. (11) is satisfied. When there is no local minimum, X_* is determined as either $X_*=0$ or $X_*=L$, which minimizes $\mathcal{G}$. Note that, for equilibrium cases where $T_1=T_2=T$, there is no local minimum when $T\ne T_c(p^{\mathrm{ex}})$. The slope of $\mathcal{G}$ as a function of X changes its sign at $T=T_c(p^{\mathrm{ex}})$. It is then found that $X_*=L$ for $T<T_c(p^{\mathrm{ex}})$ and $X_*=0$ for $T>T_c(p^{\mathrm{ex}})$.

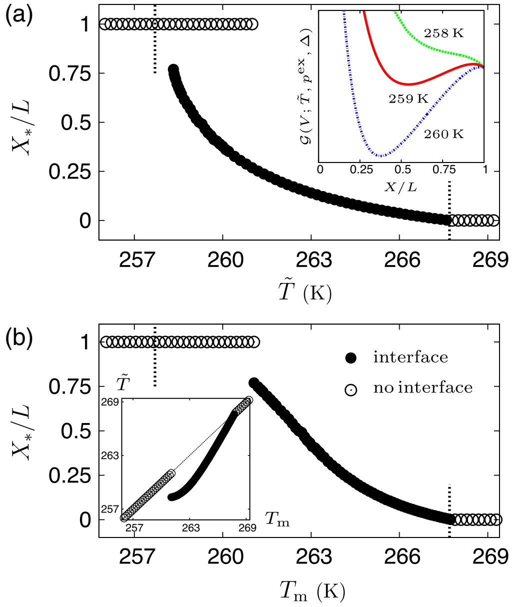

FIG. 2. Interface position X_* (the filled circles) as a function of (a) $\tilde{T}$ and (b) T_m. The open circles represent $X_* = L$ and $X_* = 0$. The dotted lines are $T_m = 257.7$ K [corresponding to $T_2 = T_c(p^{\rm ex})$] and 267.7 K [corresponding to $T_1 = T_c(p^{\rm ex})$], where $T_c(p^{\rm ex}) = 262.7$ K. The inset of (a) shows examples of the variational function with local minimum in $0 < X < L$ for higher $\tilde{T}$ values. The inset of (b) shows a graph of the map from T_m to $\tilde{T}$. The parameter values are $a = 0.365$ Pa m^6/mol and $b = 4.28 \times 10^{-5}$ m^3/mol of the van der Waals equation for CO_2 [41]. $C_V = 5NR$, where $R = 8.31$ J/K mol, and $\kappa = 0.1$ W/m K in the liquid branch $\rho > \rho_c$ and $\kappa = 0.02$ W/m K in the gas branch $\rho < \rho_c$, where $\rho_c = 10^4$ mol/m^3 referring to the database [42]. $N = 1$ mol without loss of generality, $p^{\rm ex} = 4.0 \times 10^6$ Pa and $\Delta = 10$ K.

Example.—Figure 2(a) shows the graph of the interface position X_* as a function of $\tilde{T}$ for the system with $T_c(p^{\rm ex}) = 262.7$ K. Since $\tilde{T}$ is not an experimentally controllable parameter, we employ T_m so as to predict phenomena in experiments. The relation between $\tilde{T}$ and T_m is shown in the inset of Fig. 2(b). When there is no interface, $\tilde{T} = T_m + O(\epsilon^2)$ holds [6]. By using the relation in the inset, we draw a graph of X_* as a function of T_m in Fig. 2(b). We find that the transition from $X_* = L$ to $0 < X_* < L$ is discontinuous. Since $T_2 > T_c(p^{\rm ex})$ on the right side of the left dotted line in Fig. 2, the whole system is filled with liquid even when T_2 is slightly larger than $T_c(p^{\rm ex})$. This means that the superheated liquid is stable near the right boundary. On the other hand, as $T_1 - T_c(p^{\rm ex}) \to 0$, which is indicated by the right dotted line in Fig. 2, the liquid region disappears continuously.

The discontinuous transition is connected to the standard liquid-gas transition when $\Delta \to 0$. However, the nature of the discontinuous transition is rather different. First, if the local temperature of the interface were always identical to the equilibrium transition temperature $T_c(p^{\rm ex})$, X_* would change continuously. Thus, the discontinuous transition implies that $T(X_*) - T_c(p^{\rm ex}) \neq 0$, which is indeed observed in the top panel of Fig. 3. For the chemical potential $\mu(T,\rho) \equiv [f(T,\rho) + p(T,\rho)]\rho^{-1}$, we plot its profile $\mu(T(x;V_*),\rho(x;V_*))$ as a function of x in the bottom panel of Fig. 3. We then find the discontinuous jump at the interface $x = X_*$. This means $T(X_*) - T_c(p^{\rm ex}) \neq 0$ because $T_c(p^{\rm ex})$ is characterized by $\mu(T_c(p^{\rm ex}),\rho^G) = \mu(T_c(p^{\rm ex}),\rho^L)$. The position $\tilde{x}$ satisfying $T(\tilde{x}) = T_c(p^{\rm ex})$ is obtained from the crossing point of the two curves $\mu(T(x;V_*),\rho^G(x))$ and $\mu(T(x;V_*),\rho^L(x))$, as shown in Fig. 3. It should be noted that, in the region $X_* < x < \tilde{x}$, the supercooled gas is observed as a stable steady state.

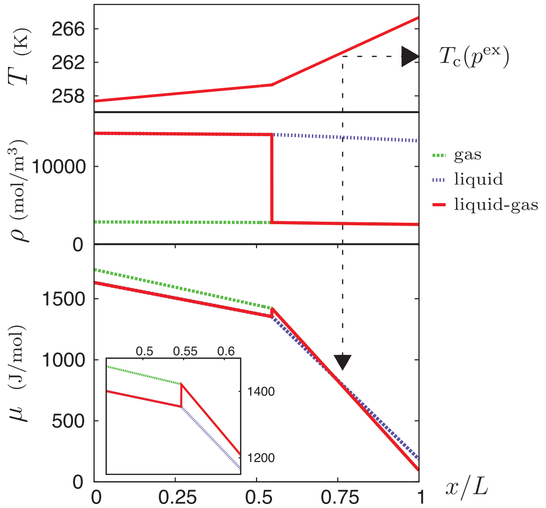

FIG. 3. Profiles of local thermodynamic variables for $\tilde{T} = 259.0$ K and $T_2 - T_1 = 10.0$ K ($T_1 = 257.36$ K, $T_2 = 267.36$ K). The temperature $T(x;V_*)$, the density $\rho(x;V_*)$, and the chemical potential $\mu(x;V_*) = \mu(T(x;V_*),\rho(x;V_*))$ are shown with red lines in the top, middle, and bottom panels, respectively. The green lines correspond to $\rho^G(x)$ and $\mu(T(x;V_*),\rho^G(x))$ in the middle and bottom panels, and the blue lines correspond to $\rho^L(x)$ and $\mu(T(x;V_*),\rho^L(x))$. The inset of the bottom panel is the close-up view of the chemical potential profiles around the interface. The liquid-gas interface exists at $X_*/L = 0.547$. The constants c_1 and c_2 are chosen as $c_1 = -113.45$ J/mol K and $c_2 = 7400$ J/mol.

Outline of the derivation of Eq. (11).—There are two key steps in the derivation of Eq. (11). The first step is that, when there is no singularity of $\rho(x;V)$ in the region $I = [x_1, x_2]$, the integration of a local quantity $\phi(T(x),\rho(x))$ over region I is estimated as

$$\int_{x_1}^{x_2} dx \phi(T(x;V),\rho(x;V)) = |I| \phi(T_m^I, \bar{\rho}^I) + O(\epsilon^2), \quad (12)$$

which follows from the trapezoidal rule for the integral after the change of the integration variable from x to T. Here, $T_m^I \equiv [T(x_1;V) + T(x_2;V)]/2$, $\bar{\rho}^I \equiv \int_{x_1}^{x_2} dx \rho(x;V)/|I|$ and $|I| = x_2 - x_1$. The relation (12) indicates that a nonuniform system with $(T(x;V), \rho(x;V))$ is equivalent to an equilibrium system with $(T_m^I, \bar{\rho}^I)$. We employ (12) with $\phi = f$ or $\phi = \rho T$.

Next, we consider the case in which the density is discontinuous at $x = X$. Since there is no singularity in the liquid region $0 \leq x < X$ or the gas region $X < x \leq L$, we apply Eq. (12) to each region. We use L and G, respectively, as the quantity superscripts. By letting N_*^{L-G} and T_{m*}^{L-G} as the steady state values, it is assumed that the thermodynamic state in the liquid region, $(p^{\mathrm{ex}}, T_{m*}^L, N_*^L)$, can be invariant under the scale transformations $(\Delta, N) \to (\lambda\Delta, \lambda N)$, with $1 \ll \lambda \ll \epsilon^{-1}$, which corresponds to the extension of the gas region [6]. This scaling assumption is expressed as $T_m^L(p^{\mathrm{ex}}, N_*^L, \lambda\Delta, \lambda N) = T_m^L(p^{\mathrm{ex}}, N_*^L, \Delta, N) = T_{m*}^L$. Similarly, the scaling relation for keeping the thermodynamic state in the gas region is also assumed. From these relations and $T_{m*}^G - T_{m*}^L = \Delta/2$, we obtain

$$T_{m*}^{L-G} = T_c(p^{\mathrm{ex}}) \mp \frac{\Delta}{2}\frac{N_*^{L-G}}{N} + O(\epsilon^2). \tag{13}$$

This is the second key step in the derivation of Eq. (11).

To evaluate the left-hand side of Eq. (11), we consider $\mathcal{G}(V; \tilde{T}, p^{\mathrm{ex}}, \Delta) = \mathcal{G}^L + \mathcal{G}^G$. We estimate $\mathcal{G}^L$ and $\mathcal{G}^G$ using Eq. (12) and take the variation $V \to V + \delta V$ in $\mathcal{G}$ by fixing $\tilde{T}$, p^{ex} and Δ. The variation δV induces δN^G, δN^L, δT_m^G, δT_m^L, δV^G, and δV^L. The straightforward calculation using Eq. (13) leads to $\mathcal{G}(V_* + \delta V; \tilde{T}, p^{\mathrm{ex}}, \Delta) - \mathcal{G}(V_*; \tilde{T}, p^{\mathrm{ex}}, \Delta) = O(\epsilon^2)$. This ends the proof of Eq. (11) [6].

Concluding remarks.—The result of our theory is schematically summarized as a phase diagram in Fig. 4. We emphasize that either the supercooled gas or the superheated liquid becomes stable as a local equilibrium state in heat conduction. This striking phenomenon is a consequence of the discontinuous transition from the liquid to the liquid-gas coexistence state. Even without quantitative measurements, observing this qualitatively new phenomenon in experiments and numerical simulations would be very stimulating. Before ending this Letter, we present a few remarks.

As a different approach to determining the position of the liquid-gas interface, the density-gradient dependent pressure

$$\frac{1}{2}d_1\xi^2(\partial_x\rho)^2 - d_2\xi^2\partial_x^2\rho + d_3 J\xi\partial_x\rho \tag{14}$$

may be added to the left-hand side of Eq. (4), where ξ is the width of the interface. For equilibrium cases in which $J = 0$, $d_1 = -\rho^2\partial(\rho^{-2}d_2)/\partial\rho$ is derived according to the van der Waals theory [8]. When this relation is applied to Eq. (14) for the heat conduction states, the interface temperature turns out to deviate from $T_c(p^{\mathrm{ex}})$ through the influence of the d_3 term [6]. While the density-gradient terms (14) are required to describe the density profile inside the interface, the variational principle (11) determines the profile outside the interface. When the density profile inside the interface is not our concern, a density-gradient term is not necessary in the variational functional (10). It should be noted that, for equilibrium cases, the density-gradient dependent pressure is systematically obtained from the free energy functional with the density-gradient term. It will be an important future subject to explore such a unified theory for heat conduction states.

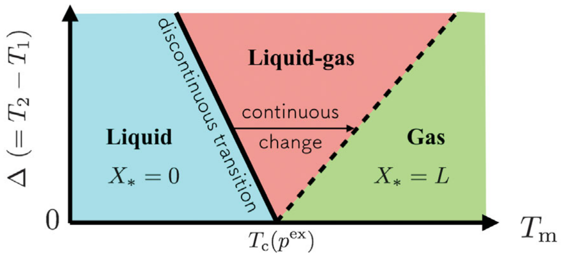

FIG. 4. Schematic phase diagram in the heat conduction system under constant pressure.

Next, we remark on future theoretical studies. Since we focus on the linear response regime, we may use representations of the probability distribution and the variational principles for the steady state [32–34,43–46]. It is a challenging problem to derive Eq. (11) on the basis of these results. Related to this problem, one may study more general experimental configurations than Fig. 1. The variational function $\mathcal{G}$ can be similarly defined for such cases, but the variational problem cannot be easily solved because of the complicated geometry of the interface. Another possible study is to seek an extended form of thermodynamics. The liquid-gas coexistence predicted in this Letter may be interpreted as a phase separated by a first-order transition. We conjecture that the transition is characterized by the singularity of the generalized free energy $G(\tilde{T}, p^{\mathrm{ex}}, \Delta) \equiv \mathcal{G}(V_*(\tilde{T}, p^{\mathrm{ex}}, \Delta); \tilde{T}, p^{\mathrm{ex}}, \Delta)$ that satisfies the fundamental relation in thermodynamics $dG = -S_* d\tilde{T} + V_* dp^{\mathrm{ex}}$ for each Δ value, where S_* is the spatial integration of the local entropy density [47]. This framework differs from previous theories [48–52]. When constructing generalized thermodynamics, we should carefully study the manner of contact [53–56]. Last but not least, we wish to extend our theory to describe thermodynamic phases of active matter [57,58] and phase transitions in turbulent flow [2,3]. Although our theory is firmly formulated in the linear response regime, a framework using global quantities, which is our key concept, may be developed for the study of phenomena far from equilibrium. It would be quite interesting to discover new phenomena as the result of such a framework for general settings with various materials.

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