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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Liquid-gas transitions in steady heat conduction

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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 $T_{\text{ex}}(p^\text{ex})$ be the temperature for the liquid-gas transition in equilibrium under constant pressure $p^\text{ex}$. When $T_{\text{ex}}(p^\text{ex})$ 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 $\bar{T}$, 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 $T_1 \leq T_2$ is assumed without loss of generality. We focus on cases that $T_{\text{ex}}(p^\text{ex})$ 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 $p^\text{ex}$. 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

$$p = \frac{RT\rho}{1 - b\rho} - a\rho^2 \quad (1)$$

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

$$-NRT \log \left[ \frac{V}{N} - b \right] - a\frac{N^2}{V} + (c_1 T + c_2)N \quad (2)$$

FIG. 1: Schematic illustration of experimental systems.
where $c_1$ and $c_2$ are arbitrary constants that depend on the reference state for the entropy and the energy, respectively. Let $\rho^L$ and $\rho^G$ be densities corresponding to liquid state and gas state. The two densities satisfy $p(T, \rho^L) = p(T, \rho^G) = p^{ex}$ with $\rho^L > \rho^G$. We then express the thermodynamic value of $V = N/\rho$, which is either $V = N/\rho^L$ or $V = N/\rho^G$, by $V_\kappa(T, \rho^{ex})$. For the following variational function with $(T, \rho^{ex})$ fixed:

$$G_{eq}(V; T, \rho^{ex}) = F_{eq}(V; T) + \rho^{ex}V,$$

(3)

$V_\kappa(T, \rho^{ex})$ is characterized by the variational principle $G_{eq}(V_\kappa(T, \rho^{ex}); T, \rho^{ex}) \leq G_{eq}(V; T, \rho^{ex})$ for any $V$. There exists $T_c(p^{ex})$ at which $V_\kappa(T, \rho^{ex})$ is discontinuous as a function of $T$ [40]. This singular behavior corresponds to the liquid-gas transition in equilibrium systems, and it is described by the thermodynamic Gibbs free energy $G(T, \rho^{ex}) \equiv G_{eq}(V_\kappa(T, \rho^{ex}); T, \rho^{ex})$. For hard spheres with long-range attractive interaction, $T_c(p^{ex})$ is exactly determined by means of the variational principle with [2] and [33] [43].

**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 $x$ [44]. 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 $0 \leq x < X$ and the gas region $X < x \leq L$. That is, for a given $T(x)$, we set $\rho(x) = \rho^L(x)$ in $x < X$ and $\rho(x) = \rho^G(x)$ in $x > X$, where the pressure balance equation

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

(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

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

(5)

where $J$ is constant in $x$, and $T(0) = T_1$ and $T(L) = T_2$. In this manner, $T(x)$ and $\rho(x)$ are determined from [29] and [33] for a given $X$. Since the volume $V$ of the system is obtained by

$$V_\kappa(T, \rho^{ex}) = \int_0^L dx \rho(x) = N,$$

(6)

$V$ has one-to-one correspondence with $X$. Thus, the solutions $T(x)$ and $\rho(x)$ satisfying [29] and [33] 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 $V_\kappa$, we set $X_\kappa = X(V_\kappa)$. Furthermore, we define $X_\epsilon = 0$ or $X_\epsilon = L$ when the space is filled with either gas or liquid, respectively. We next propose a formula for determining $V_\kappa$.

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

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

(7)

which is the natural extension of the right-hand side in [33]. Here, $f(T, \rho) = F_{W}(T, V)/V$ and we ignore the free energy in the liquid-gas interface. Then, in order to identify fixed parameters, we use the fact that $V_\kappa$ has to be independent of $c_1$ and $c_2$ in [2]. Since the variational equation should be independent of $c_1$ and $c_2$, we impose that

$$\frac{V}{L} \int_0^L dx \left[ c_1 T(x; V) \rho(x; V) + c_2 \rho(x; V) \right]$$

(8)

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

$$\tilde{T} = \frac{V}{L} \int_0^L dx \left[ f(T(x; V), \rho(x; V)) + p^{ex} \right]$$

(9)

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

The main claim of this Letter is that the equality

$$\frac{\partial G(V; \tilde{T}, \rho^{ex}, \Delta)}{\partial V} \bigg|_{V = V_\kappa} = O(\epsilon^2)$$

(11)

holds for the steady state value $V_\kappa$. Here, $V_\kappa$ is assumed to satisfy a scaling relation that the thermodynamic value of the system in the liquid or the gas region persists for $(N, \Delta) \rightarrow (\lambda N, \lambda \Delta)$ with $1 \ll \lambda \ll \epsilon^{-1}$ [45]. The derivation of (11) is given in the paragraphs including [12] and [13].

Using [11], we can determine $V_\kappa(\tilde{T}, \rho^{ex})$ and $X_\kappa$ as follows. First, we plot $G(V; \tilde{T}, \rho^{ex}, \Delta)$ as a function of $X = X(V)$ [46]. When this graph shows a local minimum at $X = X_\kappa$ in $0 < X < L$, we find the interface at $x = X_\kappa$ because (11) is satisfied. When there is no local minimum, $X_\kappa$ is determined as either $X_\kappa = 0$ or $X_\kappa = L$ which minimizes $G$. Note that, for equilibrium cases $T_1 = T_2 = T$, there is no local minimum when $T \neq T_c(p^{ex})$. The slope of $G$ as a function of $X$ changes its sign at $T = T_c(p^{ex})$ [47]. It is then found that $X_\kappa = L$ for $T < T_c(p^{ex})$ and $X_\kappa = 0$ for $T > T_c(p^{ex})$.

**Example.**— Fig. 2(a) shows the graph of the interface position $X_\kappa$ as a function of $\tilde{T}$ for the system with $T_c(p^{ex}) = 262.7$ 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 $T_m$.
we plot its profile the chemical potential continuous transition implies that ways identical to the equilibrium transition temperature First, if the local temperature of the interface were al-

nature of the discontinuous transition is rather different. system is filled with liquid even when 

line in Figs. 2, the liquid region disappears continuously.

T < X in the bottom panel of Fig. 3 We then find the dis-

continuous jump at the interface x = X∗. This means T(X∗) − Tc(pex) ≠ 0, because Tc(pex) is characterized by μ(Tc(pex), ρc) = μ(Tc(pex), ρc∗). The position x̄ satisfying T(x̄) = Tc(pex) is obtained from the crossing point of the two curves μ(T(x); ρc) and μ(T(x); ρc∗), as shown in Fig. 3. It should be noted that in the region X∗ < x < x̄, the super-cooled gas is observed as a stable steady state.

Outline of the derivation of (11). There are two key steps in the derivation of (11). The first step is that when there is no singularity of ρ(x; V) in the region I = [x1, x2], the integration of a local quantity φ(T(x), ρ(x)) over the region I is estimated as

\[ \int_{x_1}^{x_2} dx \phi(T(x); V, \rho(x)) = |I| \phi(T_{m}, \bar{\rho}) + O(\varepsilon^2), \quad (12) \]

which follows from the trapezoidal rule for the integral after the change of the integration variable from x to T. Here, T_{m} \equiv (T(x_1); V) + (T(x_2); V)/2, \bar{\rho} \equiv \int_{x_1}^{x_2} dx \rho(x; V)/|I| and |I| = x_2 − x_1. The relation (12) means that a non-uniform system with (T(x); V, \rho(x; V)) is equivalent to an equilibrium system with (T_m, \bar{\rho}). We employ (12) with φ = f or φ = ρT.
Next, we consider the case that 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 \((12)\) to each region. We put $L$ and $G$ as the superscript on quantities, respectively. 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, $(p^{ex}, T_{m*}, N_{*}^{L})$, can be invariant under the scale transformation $(\Delta, N) \rightarrow (\Delta, \lambda N)$ with $1 < \lambda < e^{-1}$, which corresponds to the extension of the gas region \([51]\). This scaling assumption is expressed as $T_{m*}^{L}(p^{ex}, N_{*}^{L}, \Delta, \lambda N) = T_{m*}^{G}(p^{ex}, N_{*}^{G}, \Delta, N) = T_{m*}^{G}$. 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

$$T_{m*}^{L/G} = T_{m*}^{c}(p^{ex}) \mp \Delta N_{*}^{L/G} \frac{1}{2 N} + O(\varepsilon^{2}).$$

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

To evaluate the left-hand side of \((11)\), we consider $G(V; T, p^{ex}, \Delta) = G^{L} + G^{G}$. We estimate $G^{L}$ and $G^{G}$ using \((12)\), and take the variation $V \rightarrow V + \delta V$ in $G$ by fixing $T$, $p^{ex}$ and $\Delta$. The variation $\delta V$ induces $\delta N^{G}$, $\delta N^{L}$, $\delta T_{m*}^{G}$, $\delta T_{m*}^{L}$, $\delta V^{G}$ and $\delta V^{L}$. The straightforward calculation using \((13)\) leads to $G(V_{*} + \delta V; T, p^{ex}, \Delta) - G(V_{*}; T, p^{ex}, \Delta) = O(\varepsilon^{2})$. This ends the proof of \((11)\) \([52]\).

Concluding Remarks.— The result of our theory is schematically summarized as the phase diagram in Fig. 4. We emphasize that either the super-cooled gas or super-heated 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 determine the position of the liquid-gas interface, the density-gradient dependent pressure

$$\frac{1}{2} d_{1} \xi^{2} (\partial_{x} \rho)^{2} - d_{2} \xi^{2} \partial_{x}^{2} \rho + d_{3} J \xi \partial_{x} \rho$$

may be added to the left-hand side of \((12)\), where $\xi$ is the width of the interface. For equilibrium cases $J = 0$, $d_{1} = -\rho^{2} (\rho^{2} d_{1} / \partial \rho$ is derived according to the van der Waals theory \([8]\). When this relation is applied to \((14)\) for the heat conduction states, the interface temperature turns out to deviate from $T_{c}(p^{ex})$ by the influence of the $d_{3}$ term \([52]\). 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 is an important future subject to have such a unified theory for heat conduction states.

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 \([32, 34, 54–57]\). It is a challenging problem to derive \((11)\) on the basis of these results. Related to this problem, one may study more general experimental configurations than Fig. 4. The variational function $G$ 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 $G(T, p^{ex}, \Delta) \equiv G(V_{*}(T, p^{ex}, \Delta); T, p^{ex}, \Delta)$ that satisfies the fundamental relation in thermodynamics with the global temperature $T$ \([58]\). This framework is different from previous theories \([59, 63]\). When constructing generalized thermodynamics, we should carefully study the manner of contact \([64, 67]\). Last but not least, we wish to extend our theory to describe thermodynamic phases of active matter \([59, 68]\) 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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When both the temperatures of the baths are larger (or smaller) than \( T_c(p^\alpha) \), the system is filled with the gas (or liquid).

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The stationary solutions of the standard hydrodynamic equations are obtained from Eqs. (29), (3), and (9). These are parametrized by the interface position.

A solution is uniquely selected, for example, if the interface temperature is equal to \( T_c(p^\alpha) \), which is equivalent to the application of the equilibrium van der Waals theory to heat conduction states. However, the validity of this assumption is not established yet. See also the discussion in the paragraph involving (1).

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The van der Waals free energy \( F_{vW}(T, V, N) \) is not a thermodynamic free energy. Indeed, it is not a convex function in \( V \). Instead, \( F_{vW}(T, V, N) \) may be interpreted as a mesoscopic free energy obtained by integrating microscopic degrees of freedom in ranges less than the nucleation size.

The result \( V_c(T, p^\alpha) \) is equivalent to that obtained by the Maxwell construction (the equal area law) from the
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gases, respectively. Note that these may be applied even 
to metastable states. Then, from the experimental data, 
a mesoscopic free energy \( F_{\text{vW}}(T, V) \) is obtained in a cer-
tain range of \( V \), which is sufficient to apply our theory 
to general cases.

[44] We assume that bubbles or droplets are not observed.

[45] The thermodynamic state in the liquid region is described 
by the pressure, the mean temperature and the particle 
number of the liquid, as shown from (12).

[46] For \( (T_1, T_2) \), we calculate (11) and (12), which yields the 
value of \( G(V; T^*, p^*; \Delta) \).

[47] In the conventional variational principle of equilibr ium 
cases, the pressure of the system is not fixed to 
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Supplemental Material for  
Liquid-gas transitions in steady heat conduction

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I. DERIVATION OF (11)

We derive (11) in the main text. In this section, we explicitly describe the dependence of $G$ on $N$, while we omit it in the main text. For $G(V; \tilde{T}, p^\text{ex}, \Delta, N)$ defined by

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

we show

$$\frac{\partial G(V; \tilde{T}, p^\text{ex}, \Delta, N)}{\partial V} \bigg|_{V=V^*} = O(\epsilon^2).$$  

(S2)

In the above, $f(T, \rho) = F_{\text{vW}}(T, V, N)/V$.

We first note the following equivalence relation for cases that there is no singularity of $\rho(x)$ in $I = [x_1, x_2]$. For a local quantity $\phi$, let $\Phi^I$ be

$$\Phi^I \equiv \frac{V}{|I|} \int_{x_1}^{x_2} dx \phi(T(x; V), \rho(x; V)),$$  

(S3)

where $|I| = x_2 - x_1$. Then, $\Phi^I$ satisfies

$$\Phi^I = V \phi(T^I_m, \bar{\rho}^I) + O(\epsilon^2),$$  

(S4)

where

$$T^I_m = \frac{T(x_1) + T(x_2)}{2},$$  

$$\bar{\rho}^I = \frac{1}{|I|} \int_{x_1}^{x_2} dx \rho(x).$$  

(S5)

(S6)

This means that the space-integrated quantities over the region $I$ for the nonuniform system with $(T(x; V), \rho(x; V))$ is equivalent to the thermodynamic quantities for the equilibrium system with $(T^I_m, \bar{\rho}^I)$. The proof of (S4) is given in Sec. 1A. In particular, by setting $\phi = \rho(x; V)T(x; V)$, we obtain

$$\tilde{T} = T_m + O(\epsilon^2)$$  

(S7)

for systems without any singularity of $\rho(x; V)$ in $[0, L]$.

Now, we consider the heat conduction system in which the density is discontinuous at $x = X$, while there is no singularity in each region $0 \leq x < X$ or $X < x \leq L$. We refer $0 \leq x < X$ to as the liquid region and $X < x \leq L$ to as the gas region, respectively. We express quantities defined in these regions by putting the superscript L or G on them. Note that there are fixing conditions,

$$N^L + N^G = N,$$  

$$V^L + V^G = V,$$  

$$\tilde{T}^L N^L + \tilde{T}^G N^G = \tilde{T} N.$$  

(S8)

(S9)

(S10)

The last condition is due to the definition of $\tilde{T}$ given in the main text as (9). We then write

$$G = G^L + G^G,$$  

(S11)
where

\( G^L = \frac{V}{L} \int_0^X dx[f(T(x; V), \rho(x; V)) + p^{ex}] \), \hspace{1cm} (S12)

\( G^G = \frac{V}{L} \int_X^L dx[f(T(x; V), \rho(x; V)) + p^{ex}] \). \hspace{1cm} (S13)

In the present setting, the volumes \( V^L \) and \( V^G \) for the respective regions satisfy

\( V^L/X = V^G/(L-X) = V/L \). \hspace{1cm} (S14)

Therefore, each variational function is expressed consistently with the definition \([S1]\) as

\( G^L = G(V^L; \tilde{T}^L, p^{ex}, \Delta^L, N^L) = \frac{V^L}{X} \int_0^X dx[f(T(x; V), \rho(x; V)) + p^{ex}], \hspace{1cm} (S15)\)

\( G^G = G(V^G; \tilde{T}^G, p^{ex}, \Delta^G, N^G) = \frac{V^G}{L-X} \int_X^L dx[f(T(x; V), \rho(x; V)) + p^{ex}], \hspace{1cm} (S16)\)

where \( \Delta^L = T(X) - T_1 \) and \( \Delta^G = T_2 - T(X) \). Since there is no singularity in the respective regions, we can use the equivalence relation \([S3]\). Then, we obtain

\( G^L = V^L[f(T^L_m, \rho^L_t) + p^{ex}] + O(\epsilon^2), \hspace{1cm} (S17)\)

\( G^G = V^G[f(T^G_m, \rho^G_t) + p^{ex}] + O(\epsilon^2), \hspace{1cm} (S18)\)

where \( T^L_m = (T_1 + T(X))/2, T^G_m = (T_2 + T(X))/2, \rho^L_t = N^L/V^L, \) and \( \rho^G_t = N^G/V^G \).

Recalling that \( T^L_m/G = T^L/G + O(\epsilon^2) \), the fixing condition \([S10]\) leads to

\( \tilde{T} = \frac{T^L_m N^L + T^G_m N^G}{N} + O(\epsilon^2). \hspace{1cm} (S19)\)

Then, by noting

\( T^G_m - T^L_m = \frac{\Delta}{2}, \hspace{1cm} (S20)\)

we express \( T^L_m \) and \( T^G_m \) as

\( T^L_m = \tilde{T} - \frac{\Delta N^G}{2N} + O(\epsilon^2), \hspace{1cm} (S21)\)

\( T^G_m = \tilde{T} + \frac{\Delta N^L}{2N} + O(\epsilon^2). \hspace{1cm} (S22)\)

We consider the variation \( V \rightarrow V + \delta V \) for \( G \) with fixing \( \tilde{T}, p^{ex}, \) and \( \Delta \). The variation \( \delta V \) induces \( \delta N^G, \delta N^L, \delta T^G_m, \delta T^L_m, \delta V^G, \) and \( \delta V^L \), where the fixing conditions lead to

\( \delta N^G = -\delta N^L, \hspace{1cm} (S23)\)

\( \delta V^G = -\delta V^L + \delta V, \hspace{1cm} (S24)\)

\( \delta T^G_m = \delta T^L_m = \frac{\Delta}{2N} \delta N^L. \hspace{1cm} (S25)\)

By using \([S14]\) and \([S18]\), we obtain

\[ G(V + \delta V; \tilde{T}, p^{ex}, \Delta, N) - G(V; \tilde{T}, p^{ex}, \Delta, N) = F_{vw}(T^L_m + \delta T^L_m, V^L + \delta V^L, N^L + \delta N^L) + F_{vw}(T^G_m + \delta T^G_m, V^G + \delta V^G, N^G + \delta N^G) \]

\[ - F_{vw}(T^L_m, V^L, N^L) - F_{vw}(T^G_m, V^G, N^G) + p^{ex} \delta V + O(\epsilon^2). \hspace{1cm} (S26)\]

We define the chemical potential

\[ \mu(T, \rho) = \frac{\partial F_{vw}(T, V, N)}{\partial N} \hspace{1cm} (S27)\]
with $\rho = V/N$, and the van der Waals entropy

$$S_{\text{vW}}(T, V, N) = -\frac{\partial F_{\text{vW}}(T, V, N)}{\partial T}. \quad (S28)$$

By noting the pressure balance

$$p(T^L_m, \rho^L) = p(T^G_m, \rho^G) = p^{ex}, \quad (S29)$$

is transformed into

$$\mathcal{G}(V + \delta V; \tilde{T}, p^{ex}, \Delta, N) - \mathcal{G}(V; \tilde{T}, p^{ex}, \Delta, N) = \left[ -(S^L + S^G) \frac{\Delta}{2N} + \mu^L - \mu^G \right] \delta N^L + O(\epsilon^2), \quad (S30)$$

where $S^L \equiv S_{\text{vW}}(T^L_m, V^L, N^L)$, $S^G \equiv S_{\text{vW}}(T^G_m, V^G, N^G)$, $\mu^L \equiv \mu(T^L_m, \rho^L)$ and $\mu^G \equiv \mu(T^G_m, \rho^G)$.

We next consider $\mu^L - \mu^G$ by interpreting $\mu$ to be a dependent variable of $(T, p)$, $\rho = \rho(T, p)$. There exists the transition temperature $T_c(p^{ex})$ for given $p^{ex}$ such that the density is discontinuous, i.e.,

$$\rho(T_c(p^{ex}) - 0, p^{ex}) \neq \rho(T_c(p^{ex}) + 0, p^{ex}), \quad (S31)$$

whereas the chemical potential is continuous as

$$\mu(T_c(p^{ex}), \rho(T_c(p^{ex}) - 0, p^{ex})) = \mu(T_c(p^{ex}), \rho(T_c(p^{ex}) + 0, p^{ex})). \quad (S32)$$

Using this equality, we express $\mu^L - \mu^G$ as

$$\mu^L - \mu^G = \mu(T^L_m, \rho(T^L_m, p^{ex})) - \mu(T_c(p^{ex}), \rho(T_c(p^{ex}) - 0, p^{ex}))$$

$$- \mu(T^G_m, \rho(T^G_m, p^{ex}))) + \mu(T_c(p^{ex}), \rho(T_c(p^{ex}) + 0, p^{ex})). \quad (S33)$$

We also note that the Gibbs-Duhem relation $Nd\mu = -S_{\text{vW}}dT + Vdp^{ex}$ leads to

$$\frac{S_{\text{vW}}(T, V)}{N} = -\frac{\partial \mu(T, \rho(T, p))}{\partial T}. \quad (S34)$$

Here, since there is no singularity for respective regions $0 \leq x < X$ and $X < x \leq L$, we can estimate the first line and the second line in (S33) separately. Substituting (S34), we obtain

$$\mu^L - \mu^G = \frac{s(T^L_m, \rho(T^L_m, p^{ex}))}{\rho^L}(T_c(p^{ex}) - T^L_m) + \frac{s(T^G_m, \rho(T^G_m, p^{ex}))}{\rho^G}(T^G_m - T_c(p^{ex})) + O(\epsilon^2), \quad (S35)$$

with $s(T, \rho) = S_{\text{vW}}(T, V, N)/V$.

To this point, $V$ is not necessarily equal to $V_*$. Then, for the steady state value $V_*$, we express $T^G_m$ and $T^L_m$, as

$$T^G_m = T_c(p^{ex}) + \frac{\Delta N^G}{2N}, \quad (S36)$$

$$T^L_m = T_c(p^{ex}) - \frac{\Delta N^L}{2N}. \quad (S37)$$

See Sec. [13] for the derivation of (S36) and (S37). We then obtain

$$\mu^L_* - \mu^G_* = \frac{s(T^L_m, \rho(T^L_m, p^{ex}))}{\rho^L}(N^L_* - \frac{\Delta}{2N}) + \frac{s(T^G_m, \rho(T^G_m, p^{ex}))}{\rho^G}(N^G_* - \frac{\Delta}{2N}), \quad (S38)$$

where we have used $\rho(T^L/G, p^{ex}) = \rho^L_* = N^L_/V^L_*$. By substituting this result into (S30), we obtain

$$\mathcal{G}(V_* + \delta V; \tilde{T}, p^{ex}, \Delta, N) - \mathcal{G}(V_*; \tilde{T}, p^{ex}, \Delta, N) = O(\epsilon^2). \quad (S39)$$

This leads to [S2].
A. Proof of (S4)

In this section, we prove the equivalence relation (S4).

We start with preliminaries. We take an interval \( I = [x_1, x_2] \) in which there is no singularity of \( \rho(x; V) \). For a smooth function \( b(x) \), we consider the integral

\[
B \equiv \frac{1}{|I|} \int_{x_1}^{x_2} dx \ b(x),
\]  

(S40)

where \( |I| = x_2 - x_1 \). Since \( dT(x; V)/dx > 0 \), we transform the integration variable from \( x \) to \( y = T(x; V) \). The function \( x(y) \), which gives \( x \) for \( y \), satisfies \( y = T(x(y); V) \). We also introduce a function \( J(y) \) by

\[
\frac{dT(x; V)}{dx} \bigg|_{x=x(y)} = \frac{T(x_2) - T(x_1)}{|I|} \ J(y).
\]  

(S41)

We then have

\[
B = \frac{1}{T(x_2) - T(x_1)} \int_{T(x_1)}^{T(x_2)} dy \ \psi(y)
\]  

(S42)

with

\[
\psi(y) \equiv \frac{b(x(y))}{J(y)}.
\]  

(S43)

Here, we expand \( \psi(y) \) as

\[
\psi(y) = \psi(T_I^m) + (y - T_I^m) \ \frac{d\psi}{dy} \bigg|_{y=T_I^m} + O(\epsilon^2).
\]  

(S44)

Substituting it into (S42), we obtain

\[
B = \frac{b(x(T_I^m))}{J(T_I^m)} + O(\epsilon^2).
\]  

(S45)

This is nothing but the trapezoidal rule of the integral. For later convenience, we also define

\[
R(y) \equiv \rho(x(y); V)
\]  

(S46)

for \( y \) satisfying \( y = T(x(y); V) \).

We here take \( b(x) = p(T(x), \rho(x)) \) and apply the above argument to the identity for the pressure as

\[
p^{ex} = p(T(x), \rho(x))
\]  

\[
= \frac{1}{|I|} \int_{x_1}^{x_2} dx \ p(T(x), \rho(x))
\]  

\[
= \frac{p(T_I^m, R(T_I^m))}{J(T_I^m)} + O(\epsilon^2),
\]  

(S47)

Since \( p(T_I^m, \rho(x(T_I^m); V)) = p^{ex} \), we obtain

\[
J(T_I^m) = 1 + O(\epsilon^2),
\]  

(S48)

and therefore (S48) is simplified as

\[
B = b(x(T_I^m)) + O(\epsilon^2)
\]  

(S49)

for any local thermodynamic quantities \( b(x) \). By setting \( b(x) = \rho(x; V) \) in (S49) and recalling (S46), we have

\[
\bar{p}^I = \frac{1}{|I|} \int_{x_1}^{x_2} dx \ \rho(x; V)
\]  

\[
= R(T_I^m) + O(\epsilon^2).
\]  

(S50)
Finally, by applying (S49) to $b(x) = \phi(T(x; V), \rho(x; V))$, we obtain
\begin{align*}
\Phi_I &= V \left| T \right| \int_{x_1}^{x_2} dx \phi(T(x; V), \rho(x; V)) \\
&= V \phi(T^I_m, R(T^I_m)) + O(\epsilon^2) \\
&= V \phi(T^I_m, \beta^I) + O(\epsilon^2).
\end{align*}
For the last transformation we have used (S50).

**B. Derivation of (S36) and (S37)**

We derive (S36) and (S37) from the basic assumptions on the steady state with an interface. We express the steady state with an interface by $(p^e, N^L_*, \Delta, N)$. As examples, we write
\begin{align*}
T^L_{m*} &= T^L_m(p^e, N^L_*, \Delta, N), \\
T^G_{m*} &= T^G_m(p^e, N^L_*, \Delta, N).
\end{align*}
From the homogeneity in direction to perpendicular to $x$, $T^L_{m*}$ and $T^G_{m*}$ are invariant for $(p^e, N^L_*, \Delta, N) \rightarrow (p^e, \lambda N^L_*, \Delta, \lambda N)$. We thus write
\begin{align*}
T^L_{m*} &= T^L_m(p^e, r_*, \Delta), \\
T^G_{m*} &= T^G_m(p^e, r_*, \Delta),
\end{align*}
where
\begin{equation}
\lambda_0 = \frac{N^L}{N}.
\end{equation}
By noting $T^G_{m*} - T^L_{m*} = \Delta/2$, we express $T^L_{m*}$ and $T^G_{m*}$ as
\begin{align*}
T^L_{m*} &= T_c(p^e) - \tau(p^e, r_* \Delta/2) + O(\Delta^2), \\
T^G_{m*} &= T_c(p^e) + (1 - \tau(p^e, r_* \Delta/2) + O(\Delta^2)
\end{align*}
for small $\Delta \geq 0$. Now, we attempt to extend the gas region while keeping the thermodynamic state in the liquid region. See Fig. 5. First, we increase $\Delta$ as $\Delta \rightarrow \lambda \Delta$ with $T^L_{m*}$ fixed, where we take $\lambda \ll \epsilon^{-1}$ such that the system is still in the linear response regime. We estimate the $\lambda$ dependence of quantities in this asymptotic regime. First, the heat flux is proportional to $\lambda$ as a common value to the liquid and the gas region. Since $T^L_{m*}$ is fixed, it is plausible that the temperature difference in the liquid region remains to be $O(\lambda^0)$, and then this leads that the horizontal length of the liquid region is proportional to $1/\lambda$. On the other hand, in the gas region, the temperature difference is proportional to $\lambda$ and the horizontal length is $L$ in the leading order estimate. Thus, the total volume saturates at the finite value

![FIG. 5:](image-url)
with which the whole system is occupied by the gas with the temperature less than $T_c(p^{ex}) + \lambda \Delta$. From these, we find that the volume of the liquid region is proportional to $1/\lambda$. Although its proportional coefficient is not determined in the asymptotic region, we assume the scaling relation that the volume of the liquid is $V_L^L/\lambda$ as it is consistent with the case $\lambda = 1$. Since $p^{ex}$ and $T_m^{L*}$ is fixed in this operation, the density of the liquid is also fixed. Thus, the particle number of the liquid becomes $N_L^L$. Next, we increase $N$ as $N \to \lambda N$, then we have

$N_L^L/\lambda \to N_L^L$ and $V_L^L/\lambda \to V_L^L$. That is, for a series of processes

$$(p^{ex}, N^L, \Delta, N) \to (p^{ex}, N^L, \lambda \Delta, \lambda N),$$

we have

$$T_m^L(p^{ex}, N^L, \lambda \Delta, \lambda N) = T_m^L(p^{ex}, N^L, \Delta, N).$$

Since this condition cannot be concluded from the local equilibrium thermodynamics, we impose (S60) as a requirement for the steady state.

By using (S57) for (S60), we have

$$\tau(p^{ex}, r^* \lambda) \lambda = \tau(p^{ex}, r^*)$$

for $1 \ll \lambda \ll \epsilon^{-1}$. Expanding

$$\tau(p^{ex}, r) = a_0 + a_1 r + a_2 r^2 + O(r^3),$$

and substituting it to (S61), we obtain

$$(\lambda - 1) a_0 + a_2 r^2 (\lambda^{-1} - 1) + \cdots = 0$$

for $1 \ll \lambda \ll \epsilon^{-1}$. This gives $a_0 = a_2 = a_n = 0$ for $n \geq 3$. Thus,

$$\tau(p^{ex}, r^*) = a_1 r^*,$$

which restricts the $r^*$ dependence of $\tau$.

Next, we extend the liquid region while keeping the gas region. In this case, we consider the transformation $(\Delta, N) \to (\lambda \Delta, \lambda N)$, while fixing $(T_m^G, N_G^G)^*$. From (S58), we have

$$\left[1 - \tau\left(p^{ex}, 1 - \frac{N_G^G}{\lambda N}\right)\right] \lambda = 1 - \tau\left(p^{ex}, 1 - \frac{N_G^G}{N}\right)$$

Expanding

$$\tau(p^{ex}, 1 - u) = b_0 + b_1 u + O(u^2)$$

in the limit $u \to 0$, we obtain $b_0 = 1$ and $b_n = 0$ for $n \geq 2$. This leads to

$$b_1 (1 - r^*) = 1 - \tau(p^{ex}, r^*).$$

By combining (S64) and (S67), we obtain

$$b_1 (1 - r^*) = 1 - a_1 r^*.$$

Since this holds for any $r^*$, we obtain $b_1 = a_1 = 1$. By substituting (S64) with $a_1 = 1$ into (S57) and (S58), we have arrived at (S36) and (S37).

**II. A THEORY OF PRESSURE IN THE LIQUID-GAS INTERFACE**

In steady heat conduction states under constant pressure $p^{ex}$, the temperature field $T(x)$ and the density field $\rho(x)$ satisfy

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

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

(S69) (S70)
where the heat flux $J$ is independent of $x$. When $T_1 < T_c (p^{\text{ex}}) < T_2$, $T(x)$ and $\rho(x)$ for these equations are not uniquely determined and they are characterized by the interface position $X$. Since the volume is determined from

$$V \int_0^L dx \rho(x) = N,$$

we parametrize the solutions satisfying (S70) and (S71) by $V$. In order to express this dependence explicitly, in the main text, we use the notation $T(x;V)$ and $\rho(x;V)$. They are characterized by

$$-\kappa(T(x;V),\rho(x;V)) \partial_x T(x;V) = J,$$

$$p(T(x;V),\rho(x;V)) = p^{\text{ex}},$$

$$\frac{V}{L} \int_0^L dx \rho(x;V) = N.$$  \hspace{1cm} (S72) \hspace{1cm} (S73) \hspace{1cm} (S74)

These equations are equivalent to stationary solutions of the standard hydrodynamic equation. As the position of the interface is not determined in the framework of standard hydrodynamics, it is reasonable to take the account of the higher-order derivative terms in the hydrodynamic equation. In this section, we consider the pressure associated with the density gradient in the interface, which gives higher order terms in the hydrodynamic equation. We show that the steady-state value of $V$, which is denoted by $V_*$ in the main text, becomes accessible by adopting this extension.

In the standard hydrodynamics, the interface is treated as the discontinuous surface of density field. Here, we treat the interface as a transition layer of the width $\xi$ and consider the density profile in the layer. Since the density gradient in the transition layer is much larger than that in the bulk, we expect that its contribution to the pressure is uniquely determined and they are characterized by the interface position $X$.

Now, we proceed to nonequilibrium cases. We show that there is the unique solution (S72), (S74), and (S75) with $J = 0$. Then, following the argument by van der Waals, we derive the relation

$$d_1(\rho) = \frac{2}{p} d_2(\rho) - d_2(\rho),$$

where $d_1$, $d_2$, and $d_3$ are some functions of $p$ which are assumed to be independent of $\xi$. More precisely, $d_1$ and $d_2$ are functions of $(T,\rho)$ whose functional forms are specific to the type of material, while the functional form of $d_3$ may be influenced by the system condition ($p^{\text{ex}}, T_1, T_2$). The terms proportional to $d_1$ and $d_2$ were proposed by van der Waals and adopted in generalized hydrodynamic equations referred in the main text as [9,10].

The term proportional to $d_3$ does not appear in these approaches. The density gradient terms are relevant only in the transition layer where $|\xi \partial_x \rho| \approx |p^L - p^G|$, whereas $|\xi \partial_x \rho| \simeq \rho \xi / L \ll \rho / L$ for its outside, $d_2(\rho) > 0$ for the stability of the density profile. Furthermore, since the temperature $T$ is continuous at $x = X$ and $\xi$ is sufficiently small, the temperature $T(x)$ does not vary so much in the transition layer. Therefore, temperatures inside the transition layer may be evaluated as $T(X)$ for thermodynamic quantities.

Equilibrium cases are described by (S72), (S74), and (S75) with $J = 0$. Then, following the argument by van der Waals, we derive the relation

$$d_1(\rho) = \frac{2}{p} d_2(\rho) - d_2(\rho),$$

where the prime represents the derivative with respect to $\rho$. See Sec. [113] for the derivation. We assume that this relation also holds in the linear response regime.

Now, we proceed to nonequilibrium cases. We show that there is the unique solution $\rho(x;V_*)$ that satisfies (S72), (S74), and (S75). This solution also determines the value of $X_*$. Concretely, we define $\mu(T,\rho)$ as

$$\mu(T,\rho) \equiv \frac{f(T,\rho) + p(T,\rho)}{\rho},$$

where $f(T,\rho) = F_{\text{W}}(T,V,N) / V$ with $\rho = N / V$. We then find that $X_*$ satisfies

$$\lim_{\xi / L \to 0} [\mu(T(X_*;V_*),\rho(X_* + K \xi;V_*)) - \mu(T(X_*;V_*),\rho(X_* - K \xi;V_*))] = J \Delta_{\text{gap}},$$

which is derived in Sec. [114] where a numerical constant $K \gg 1$ is fixed. Here, $\Delta_{\text{gap}}$ takes a finite value in the limit $\xi / L \to 0$. In equilibrium cases $J = 0$, (S78) means the continuity of $\mu(T(x;V_*),\rho(x;V_*))$ at $x = X_*$. This balance relation determines the value of $V_*$, which is consistent with the variational principle in equilibrium thermodynamics. However, in heat conduction states, $\mu(T(x;V_*),\rho(x;V_*))$ is discontinuous at $x = X_*$. This implies that super-cooled gas or super-heated liquid becomes stable as a local equilibrium state in the heat conduction. This is consistent with the prediction in the main text.
A. Proof of (S78)

We first define
\[ \mathcal{M}(T, \rho; p^{ex}) = \frac{f(T, \rho) + p^{ex}}{\rho}. \] (S79)

Using the relation
\[ p(T, \rho) = -\frac{\partial (f(T, \rho)\rho^{-1})}{\partial \rho^{-1}}, \] (S80)
we express \( p - p^{ex} \) as
\[ p(T, \rho) - p^{ex} = \rho^2 \frac{\partial \mathcal{M}}{\partial \rho}. \] (S81)

Then, we express
\[ p^2 \frac{\partial \mathcal{M}}{\partial \rho} + \frac{d_1(\rho)}{\rho^2} \xi^2 (\partial_x \rho)^2 - d_2(\rho) \xi^2 \partial_x^2 \rho + d_3(\rho) J_\xi \partial_x \rho = 0. \] (S82)

We further note
\[ \frac{\partial}{\partial x} \left( \frac{d_2(\rho)}{\rho^2} (\partial_x \rho)^2 \right) = -\frac{2 \partial_x \rho}{\rho^2} \left[ \frac{d_1(\rho)}{2} (\partial_x \rho)^2 - d_2(\rho) \partial_x^2 \rho \right], \] (S83)
where we have used (S76) in order to remove \( d_2^2(\rho) \). Since (S82) is transformed into
\[ \frac{\partial \mathcal{M}}{\partial \rho} + \frac{d_3(\rho)}{\rho^2} J_\xi \partial_x \rho = -\frac{\xi^2}{\rho^2} \left[ \frac{d_1(\rho)}{2} (\partial_x \rho)^2 - d_2(\rho) \partial_x^2 \rho \right], \] (S84)
(S83) and (S84) lead to
\[ \frac{\partial}{\partial x} \left( \mathcal{M} - \frac{d_2(\rho)}{2 \rho^2} \xi^2 (\partial_x \rho)^2 \right) = -\frac{d_3(\rho)}{\rho^2} J_\xi (\partial_x \rho)^2, \] (S85)
where it should be noted that \( \partial_x \mathcal{M} = (\partial_\rho \mathcal{M})(\partial_x \rho) \).

Now, we integrate (S85) over the transition layer at \( x = X_* \). (S85) leads to
\[ \left. \left[ \mathcal{M} - \frac{d_2(\rho)}{2} \xi^2 \left( \frac{\partial_x \rho}{\rho} \right)^2 \right] \right|_{X_*} = -J \int_{X_*}^{X_* + K \xi} dx \; d_3(\rho)(\xi) \left( \frac{\partial_x \rho}{\rho} \right)^2, \] (S86)
where \( K \) is a large constant. Since \( \partial_x \log \rho = O(1/L) \) and \( \mathcal{M} = \mu \) at \( x = X_* \pm K \xi \), which is outside of the transition layer, (S86) is simplified as
\[ \mu(T(X_*; V_\star), \rho(X_* + K \xi; V_\star)) - \mu(T(X_*; V_\star), \rho(X_* - K \xi; V_\star)) = -J \int_{X_* - K \xi}^{X_* + K \xi} dx \; d_3(\rho)(\xi) \left( \frac{\partial_x \rho}{\rho} \right)^2 + O \left( \frac{\xi^2}{L^2} \right), \] (S87)
where we have used the continuity of temperature in the transition layer. By setting \( \rho(x) = \rho(X_* + \xi t) \) as a function of \( t \), we write
\[ \int_{X_* - K \xi}^{X_* + K \xi} dx \; d_3(\rho)(\xi) \left( \frac{\partial_x \rho}{\rho} \right)^2 = \int_{-\infty}^{K} dt \; d_3(\rho)(\partial_t \log \rho)^2. \] (S88)

Thus, we reach (S78), where
\[ \Delta_\text{gap} = -\int_{-\infty}^{\infty} dt \; d_3(\rho)(\partial_t \log \rho)^2, \] (S89)
which is independent of \( \xi \). (S89) indicates that \( \Delta_\text{gap} \) is finite in general.
B. Proof of (S76)

We consider equilibrium states at which liquid and gas coexist in a container with constant volume. For simplicity, we assume that the density depends only on $x$. We determine the density profile for this system by assuming the free energy

$$F(|\rho|) = \frac{V}{L} \int_0^L dx \left[ f(T, \rho(x)) + \frac{c(\rho(x))}{2} \xi^2 (\partial_x \rho)^2 \right],$$  \hspace{1cm} (S90)

where the term $c(\rho)\xi^2(\partial_x \rho)^2/2$ represents the effective energy density associated with the density gradient. This term may be relevant at the interface where the density is discontinuous in the thermodynamic description. We apply the variational principle for $F(|\rho|)$ under the condition

$$\frac{V}{L} \int_0^L dx \rho(x) = 1.$$  \hspace{1cm} (S91)

Noting that

$$\mu(T, \rho) = \frac{\partial f}{\partial \rho},$$  \hspace{1cm} (S92)

we obtain the variational equation for (S90) as

$$\mu(T, \rho) + \frac{c'(\rho)}{2} \xi^2 (\partial_x \rho)^2 - \xi^2 \partial_x (c(\rho) \partial_x \rho) + \lambda = 0,$$  \hspace{1cm} (S93)

where $\lambda$ is the Lagrange multiplier whose value is determined by (S91).

Next, we derive the pressure balance equation, which provides the equation of state for the system with the interface. By substituting

$$\mu(T, \rho) = f(T, \rho) + p(T, \rho)$$  \hspace{1cm} (S94)

into (S93) and taking the differentiation in $x$, we obtain

$$\partial_x \left( \frac{f + p}{\rho} \right) + \xi^2 \partial_x \left[ \frac{c'(\rho)}{2} (\partial_x \rho)^2 \right] - \xi^2 \partial_x^2 (c(\rho) \partial_x \rho) = 0.$$  \hspace{1cm} (S95)

Since $\partial_x f = \partial^2 f \partial_x \rho$, we have an equality

$$\partial_x \left( \frac{f + p}{\rho} \right) = \rho^{-1} \left( \partial_x^2 f \partial_x \rho + \partial_x p - \frac{f + p}{\rho} \partial_x \rho \right) = \partial_x p \rho.$$  \hspace{1cm} (S96)

From (S95) and (S96), we obtain

$$\partial_x p + \rho \partial_x \left[ \frac{c'(\rho)}{2} \xi^2 (\partial_x \rho)^2 \right] - \rho \xi^2 \partial_x^2 (c(\rho) \partial_x \rho) = 0.$$  \hspace{1cm} (S97)

Here, from the elementary calculation, we can show

$$\partial_x p + \partial_x \left[ \frac{1}{2} (c(\rho) - \rho c'(\rho)) \xi^2 (\partial_x \rho)^2 - c(\rho) \rho \xi^2 \partial_x^2 \rho \right] = 0,$$  \hspace{1cm} (S98)

which leads to

$$p(T, \rho) + \left[ \frac{1}{2} d_1(\rho) \xi^2 (\partial_x \rho)^2 - d_2(\rho) \xi^2 \partial_x^2 \rho \right] = \rho \rho^x,$$  \hspace{1cm} (S99)

where

$$d_1(\rho) = c(\rho) - \rho c'(\rho),$$  \hspace{1cm} (S100)

$$d_2(\rho) = c(\rho).$$  \hspace{1cm} (S101)

From these, we obtain (S76).