Unified theoretical framework for temperature regulation via phase transition

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Phase transition usually consumes or releases energy to produce cooling or heating within different materials, providing a generalized framework for temperature regulation in practical applications. Because of the strong coupling between the enthalpy change in thermodynamics and heat-mass transfer kinetics, unveiling the mechanism of temperature regulation via the phase transition remains a great challenge. Here, we develop a new theoretical method by establishing a connection of enthalpy change from thermodynamics to phase transition dynamics to study evaporation-induced cooling as an example. Our new approach can spontaneously generate evaporative cooling at interfaces, and the predicted results are consistent with recent experiments. The evaporation-induced steady vapor is dictated by an anomalous cold-to-hot mass transfer through temperaturedependent chemical potentials, which enables temperature regulation inside liquids via a thermodynamic-kinetic interplay. Moreover, we show that a simple prohibition of heat exchange between liquids and reservoir can greatly enhance the cooling magnitude by a factor of $2 \sim 4$, which is highly dependent on the thermodynamics and kinetic coefficients of liquids. Our new method paves the way for exploration of cooling or heating induced by different phase transitions, such as evaporation, sublimation, or condensation, in a unified framework, which can significantly promote the development of temperature regulation by phase transitions.

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I. INTRODUCTION

Phase transition of materials between different states, such as solids to liquids, liquids to vapor, or vapor to solids, requires the absorption or emission of a large amount of energies that results in the cooling or heating of distinct materials, providing a generalized framework for temperature regulation in practical applications [1–3]. Evaporation-induced liquid cooling is a typical phase transition-induced cooling phenomenon that can be easily observed in our daily life. This evaporative cooling is usually accompanied by a phase transition across the liquid-vapor interfaces [4-16] and has led to many applications of temperature control in different fields recently [17-24], ranging from conventional air conditioning [17–19] to the cooling of microelectronic devices [20], and even the generation of extremely low temperatures up to 21 nanokelvin by evaporation of microwave-shielded polar molecules [21]. Generally speaking, phase transitioninduced cooling or heating is mainly dictated by the enthalpy change to convert one thermodynamic state to another, such as the liquid-vapor phase transition; therefore, the regulation of cooling or heating highly depends on the thermodynamics of phase transition. Furthermore, unlike energy transfer in solids, where heat transfer is dictated primarily by photons [25], energy or heat transfer in liquid and vapor phases is dictated by heat conduction coupled with mass transportation. Consequently, temperature regulation by phase transition also relies on coupled heat-mass transfer dynamics [26-29]. For

example, recent experiments confirmed that the evaporative cooling of soap films strongly depended on the evaporative kinetics controlled by relative humidity in environments [30]. However, because of the complex interplay between thermodynamics and heat-mass transfer kinetics in both the liquid and the vapor phases, controlling the temperatures induced by phase transition *i.e.*, evaporation, remains a great challenge.

Unveiling the mechanisms that govern temperature regulations through the dynamics of phase transition, *i.e.*, evaporation, faces difficulties in the following thermodynamic and kinetic aspects. First, latent heat or enthalpy change during phase transition dictates temperature variations during phase transition, which should be explicitly considered for temperature regulations, such as evaporative cooling [31]. Preliminary attempts have been made to handle the enthalpy change of the liquid-vapor transition by treating it as an input parameter extracted from experiments to predict the drying dynamics of natural porous materials such as wood [26-29]. This treatment of the enthalpy change limits its validity in specific conditions, *i.e.*, water under ambient conditions [26–29], whereas extensions to other thermodynamic states, such as high pressures [20] or low temperatures [21], and even for different species, require additional input parameters, which limit its applications in different phase transitions. Second, capturing temperature regulation by phase transition requires not only heat transfer but also mass transport kinetics [26–45]. This heat-mass transfer kinetics can be described by the Hertz-Knudson-Schrage equation [39,40] or the Boltzmann kinetic equation [43-45] for evaporation. These equations require an assumption of a lower liquid temperature in prior and therefore do not explain why liquids are cooled during

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evaporation [41–45]. Furthermore, the coupled heat-mass transfer equations for wood drying dynamics attribute mass diffusion to water concentration gradients rather than chemical potentials [26–29], which are valid for water diffusion, but cannot describe the phase transition dynamics of evaporation [6]. Therefore, a suitable description of heat-mass transfer kinetics during phase transition is necessary for temperature regulation. Consequently, capturing the mechanism of temperature control via phase transition requires a complete description of thermodynamics in producing enthalpy change of the phase transition, as well as heat-mass transfer within the corresponding phase transition dynamics. To the best of our knowledge, such a thermodynamic-kinetic interplay to describe phase transition–induced temperature control is still lacking.

In this article, we propose a new theoretical method by extracting the enthalpy change from the free energy into heat transfer kinetics and coupling it to model B dynamics of the phase transition to systematically study evaporation-induced cooling as an example. This new approach can spontaneously generate a liquid cooling at the interface during evaporation, and the calculated results are consistent with recent experiments [30]. The evaporative flux inside the nonequilibrium vapor phase is compensated by a temperature-driven flux until it approaches a steady state. This is dictated by an anomalous cold-to-hot mass transfer through temperature-dependent chemical potentials, enabling temperature regulations inside liquids via a thermodynamic-kinetic interplay. Furthermore, we show that a simple prevention of heat exchange between liquids and reservoir can significantly improve the magnitude of cooling by a factor of $2 \sim 4$, which is highly dependent on the thermodynamics and kinetic coefficient of the liquids. Our findings reveal that even for the simplest single-component liquids, the inclusion of thermodynamic-kinetic interplay can produce abundant temperature regulations by evaporation, which may facilitate its practical applications in different fields, such as evaporation-induced self-assembly [4,5,46] and crystallization [9,10]. The new theoretical method outlined enables the exploration of cooling or heating induced by different phase transitions, such as sublimation, condensation, or crystallization, in a unified framework, which may greatly advance the progress in the field of temperature regulation by phase transition.

II. METHODS

In this section, we develop a new theoretical framework to describe temperature variations induced by phase transitions, which can be simplified into three steps. First, construct a free energy to describe the temperature-dependent phase behavior of a given thermodynamic system. Second, extract the enthalpy change of the phase transition from free energy to heat transfer kinetics via local energy conservation. Subsequently, we coupled this heat transfer equation to the model B dynamics of mass diffusion within phase transition through local mass conservation. Third, solve the coupled mass and heat transport equations under suitable boundary conditions, which are basically dictated by experimental applications, to obtain time evolutions of temperature and density distributions during the phase transition.

Here, we note that both mass and heat diffusion equations are derived from the free energy of thermodynamic system via chemical potential and enthalpy change during phase transition, and therefore the obtained temperature and density evolutions solely characterize dynamic features of selected thermodynamic system. In this sense, the construction of free energies to describe different species, such as simple liquids, binary mixtures [47], polymers [48], and other soft materials, enables the exploration of evaporative cooling in a variety of thermodynamic systems. Furthermore, the theoretical framework outlined can be generalized to explore evaporative cooling in different thermodynamic states, such as high pressures [20] or low temperatures [21], given that reasonable free energies are applicable. In the following, we describe this new theoretical framework by choosing a liquidvapor phase transition, *i.e.*, evaporation, of a simple liquid as an example.

A. Thermodynamics of a simple liquid

The thermodynamics of a simple liquid can be characterized by a free energy density as a function of the normalized density ϕ and the reduced temperature T [47,48]:

$$f_{\rm hom} = \phi T (\ln \phi - 1) + \frac{\upsilon}{2} \phi^2 + \frac{wT}{3} \phi^3.$$
 (1)

The first term represents the entropic contribution. The coefficient v describes the pair-wise interaction between molecules, and w in front of third-order term characterizes multibody interactions.

The chemical potential of the bulk homogeneous liquid μ_0 can be expressed as

$$\mu_0[\phi, T] = T \ln \phi + \upsilon \phi + T w \phi^2, \qquad (2)$$

and the equation of state of this simple liquid now takes the form

$$p_0[\phi, T] = \phi T + \frac{\upsilon}{2} \phi^2 + \frac{2wT}{3} \phi^3.$$
(3)

Here, p_0 is the bulk pressure, which can be considered as a virial expansion of the equation of state up to third orders. This equation of state can describe the thermodynamic properties of one-component van der Waals fluids [47]. Given the condition that pressure and chemical potential are equal in the coexistence of liquid and vapor phases, we can calculate the thermodynamic phase diagram of a simple liquid.

B. Enthalpy of vaporization with heat transfer kinetics

Exploring the temperature variations during phase transition requires thermal conduction in both the liquid and the vapor phases. Here, we ignore thermal radiation from the liquid or vapor phases during evaporation [49], and local energy conservation produces the following heat transfer equation [50]:

$$c_q \phi \frac{\partial T}{\partial t} = \nabla \cdot [k_T \phi \nabla T] - \frac{\mathrm{d}m}{\mathrm{d}t} \Delta h_{\mathrm{ev}}.$$
 (4)

Here, c_q represents the heat capacity of liquids. k_T shows the specific thermal conductivity coefficient, and a simple relation to liquid density is proposed by Bridgman $k_T = k_{T0}\phi^{2/3}$ [51],

where k_{T0} characterizes the thermal conductivity coefficient at a reference density. $\Delta h_{ev} = dh_{ev}(\mathbf{r})/dm$ denotes the enthalpy change of evaporation, also known as latent heat, which characterizes the consumption of enthalpy to convert liquids of mass dm to their coexistent vapor phases.

To link the enthalpy change of evaporation with the thermodynamic states of a simple liquid, *i.e.*, the free energy density in Eq. (1), we express the variation of the local enthalpy density as $dh_{ev}(\mathbf{r}) = [dU(\mathbf{r}) + pdV + Vdp]/V =$ $de(\mathbf{r}) - pd\phi/\phi + dp$. Here, $U(\mathbf{r})$ is the internal energy, $de(\mathbf{r})$ represents the variation of the internal energy density, and *p* is the coexistent pressure. Therefore, the local enthalpy change of the last term in Eq. (4) is

$$\frac{\mathrm{d}m}{\mathrm{d}t}\Delta h_{\mathrm{ev}} = \left(\frac{\partial e(\mathbf{r})}{\partial \phi} - \frac{p}{\phi} + \frac{\partial p}{\partial \phi}\right)\frac{\partial \phi}{\partial t}.$$
(5)

This relation links the enthalpy variation to the thermodynamics of a liquid, *i.e.*, internal energy, coexistence pressure, and their derivatives with respect to density. Unlike the treatment of enthalpy change as input parameters from experiments in wood drying dynamics [26–29], our approach outlined previously has linked the enthalpy change of the phase transition to the free energy of liquids; therefore, temperature variations are binding to selected thermodynamic systems, which can be easily extended to high pressures [20] or low temperatures [21], and also for other species without additional input parameters. This treatment of enthalpy change provides a unified framework for handling temperature variations induced by the phase transition.

C. Model B dynamics of phase transition

Phase transition dynamics with conserved order parameters can be well described by model B dynamics [52]. The bulk free energy density, Eq. (1), can be generalized to a free energy functional to describe liquid-vapor phase transition [53]:

$$\mathcal{F}[\phi, T] = \int \mathrm{d}\mathbf{r} \left(f_{\text{hom}} + \frac{\gamma T}{2} |\nabla \phi|^2 \right). \tag{6}$$

where the second term characterizes the free energy contribution induced by liquid-vapor interfaces and $\gamma = 0.01$ relates to the interfacial width.

Based on the local mass conservation, the phase transition dynamics can be described by the model B dynamics, which can be derived using the following continuity equations [52]:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}),\tag{7}$$

where the velocity of liquids depends on the gradients of both chemical potentials and temperatures [33-35] and

$$\mathbf{v} = -D\nabla\mu - D_T\nabla T. \tag{8}$$

Here, $\mu = \delta \mathcal{F}/(\delta \phi)$ denotes the chemical potential of liquid in the inhomogeneous system. *D* is the diffusion coefficient, which generally depends on temperature *T* and density ϕ in a simple form, $D = MT/\phi$ [54]. D_T is the thermal diffusion coefficient characterizing the diffusion of molecules in response to a temperature gradient $D_T(T, \phi) = M_T/(T\phi)$ [33]. Here, *M* and M_T are the diffusive and thermal mobilities at



FIG. 1. (a) Pressure-temperature (p - T) phase diagram of a simple liquid. The filled circle and blue square represent the critical point and initial state used in our calculation, respectively. (b) Pressure-density $(P - \phi)$ and (c) temperature-density $(T - \phi)$ phase diagram of the simple liquid. The black and green lines indicate the coexistent liquid and vapor phases, respectively. The blue arrow in panel (b) indicates the coexistent liquid and vapor densities of the initial state, and that in panel (c) depicts the enthalpy of vaporization h_{ev} from the liquid to vapor phase. (d) Variation of h_{ev} as a function of temperature calculated from panel (a).

a reference density $\phi_r = 1.0$ and temperature $T_r = 1.0$. Thus, the mass-diffusion equation takes the following form:

$$\frac{\partial \phi}{\partial t} = M[\nabla \cdot (T\nabla \mu) + S_T \nabla \cdot (\nabla \ln T)]. \tag{9}$$

 $S_T = M_T/M$ is the Soret coefficient, which characterizes the ratio between the diffusion coefficients driven by temperature and chemical potential gradients [33–35].

The heat and mass transfer Eqs. (4) and (9) can be solved numerically under suitable boundary conditions to obtain the mass and temperature evolutions during evaporation. In the following, we show how evaporation regulates liquid temperature at different conditions, and explore the relation between temperature regulation and thermodynamic-kinetic interplay during evaporation.

III. RESULTS AND DISCUSSION

A. Liquid-vapor coexistence and evaporation setup

The phase diagram of liquid-vapor coexistence of a simple liquid at v = -4.19 and w = 2.00 can be calculated by the equivalence of pressures and chemical potentials in both liquid and vapor phases; see Fig. 1(a). It is clearly shown that the pressure increases as the temperature increases until it approaches a critical point, above which there is no liquidvapor coexistence. This phase diagram qualitatively describes the phase behavior of single-component liquids, such as water, methane, and ethanol [55]. The relations of pressure and temperature with respect to densities form two coexisting lines; see Figs. 1(b) and 1(c). The vaporization enthalpy can be calculated from the densities of coexisting liquid and vapor, ϕ_l and ϕ_v , as $h_{ev} = (\phi_l e_v / \phi_v - e_l) + p(\phi_l / \phi_v - 1)$, where p is the coexisting pressure, and e_v and e_l are the internal energy densities of vapor and liquid phases. One can see in Fig. 1(d)



FIG. 2. (a), (b) Distributions of liquid-vapor density $\phi(z)$ (a) and temperature T(z) (b) along the z axis during evaporation at different times $t = 0\tau$, 50τ , 200τ , 400τ , and 900τ . The quench density at vapor boundary is set to be $\delta\phi = 0.063$. The blue arrow points to the minimum temperature during evaporation. (c) Distributions of density during evaporation without temperature variations in space at different times. (d) Time evolutions of the minimum temperature T_{\min} across the liquid-vapor phase during evaporation at different quench densities $\delta\phi = 0.043$, 0.063, 0.083.

that the vaporization enthalpy $h_{\rm ev}$ decreases to 0 as the temperature increases toward the critical point. In the following, we discuss the cooling induced by evaporation from an initial state at $T_0 = 0.9$ and $p_0 = 0.089$, where the coexisting liquid and vapor densities are $\phi_l = 1.150$ and $\phi_v = 0.143$.

The initial state of liquid-vapor coexistence in space can be obtained by solving dynamic Eqs. (4) and (9) together in one dimension along the z axis within a box of length $L_z = 216w$. Here, w is the width of the interface, and the time unit is defined as $\tau = 100w^2/M$. The boundary conditions to obtain the initial state are chosen as $\phi(0) = \phi_v$, $\phi(L_z) = \phi_l$, and $T(0) = T(L_z) = 0.9$, respectively. The coexistent liquid and vapor phases separated by a sharp interface and a homogeneously distributed temperature throughout the system are observed in Figs. 2(a) and 2(b) of $t = 0\tau$.

Evaporation can be achieved by changing the boundary density at z = 0 from coexistent ϕ_v to a lower density ϕ_1 , where the density difference $\delta \phi = \phi_v - \phi_1$ dictates the evaporation rate. In experiments, the value ϕ_1 can be easily controlled, for example, by the relative humidity in the evaporation of water [30]. The boundary temperature at z = 0 is fixed to the reservoir temperature T_0 during evaporation.

The boundary at $z = L_z$ represents the container to store liquids during evaporation, where mass exchange is prohibited, but energy or heat transfer could be possible. Therefore, we apply an absorbing boundary condition to the densities at $z = L_z$. For temperatures, we consider two boundary conditions. In case I, liquids can exchange heat with a reservoir, of which the temperature is set $T(L_z) = T_0$. In case II, the liquid does not change heat with reservoir, and an absorbing boundary condition is applied to temperatures at $z = L_z$. Other parameters in the numerical calculations of evaporation are set to $c_q = 10$ for the heat capacity and $k_{T0} = 40$ for the thermal conductivity coefficient. In the following, we discuss in detail how the temperature is regulated by phase transition dynamics under these conditions.

B. Regulation of evaporative cooling with heat exchange

We first consider case I where the liquids exchange heat with reservoir at $z = L_z$. Evaporation is obtained by performing a density quench of $\delta \phi = 0.063$ at z = 0. The density distributions in Fig. 2(a) show a recession of the liquid-vapor interface and an increase in the density of the interfacial liquid as evaporation proceeds. The increase in liquid density near the interface produces a skin layer, which is similar to that observed in solutions by experiments [56-60], simulations [10,61-64], and theoretical calculations [6,65-70]. Here, we emphasize that the mechanism controlling the skin layer for a one-component system in Fig. 2(a) is different from that in solutions. The skin layer in solutions is dictated by a Peclet number (Pe = $v_{ev}/v_s > 1$), where v_{ev} and v_s characterize the different velocities of the interfacial recession and the diffusive current of solutes [10,71]. In our case, the evaporation of one-component liquids couples the interface movement and liquid diffusion together, and therefore does not generate a skin layer. This can be verified by controlled evaporation of purely diffusive molecules where the enthalpy variation is set $\Delta h_{\rm ev} = 0$. In this case, the temperature does not change and the densities in Fig. 2(c) clearly show no skin layer during evaporation. This controlled calculation implies that the skin layer in a one-component liquid is dictated by the density-temperature interplay between thermodynamics and the corresponding heat-mass transfer kinetics, which is different from the velocity difference-induced skin layer in solutions.

The transition from the liquid to vapor phase across interfaces requires energy consumption due to the enthalpy difference between the liquid and vapor phases, resulting in liquid cooling at the interfaces during evaporation; see the black arrow in Fig. 2(b). The calculated liquid cooling is consistent with recent experimental measurements of evaporative cooling in soap films [30]. The coupling of the increase in density and the decrease in temperature inside the liquid phase is consistent with the trend in the liquid line on the $T - \phi$ phase diagram of Fig. 1(c), where the coexisting liquids become larger as the temperature decreases. These results indicate that the evaporation-induced cooling is highly dependent on the thermodynamics of liquids, where density and temperature are strongly coupled.

Due to the heat exchange of liquids with the reservoir, evaporative cooling can be compensated for by heat transfer from the reservoir to liquids, which prevents temperature regulation and eventually drives the liquid back to the reservoir temperature T_0 . As shown in Fig. 2(b), evaporative cooling weakens after $t = 50\tau$. The time evolution of the minimum temperature induced by evaporation throughout the system, T_{min} , marked by the blue arrow in Fig. 2(b), at different times is represented in Fig. 2(d). We can clearly see that T_{min} decreases first as the evaporation proceeds. However, after passing through a minimum at around $t = 50\tau$, T_{min} increases again until it approaches the reservoir temperature T_0 . We also show that the magnitude of evaporative cooling can be regulated by the quench density $\delta\phi$. The time evolutions of T_{min} in



FIG. 3. (a), (b) Distributions of liquid-vapor density $\phi(z)$ (a) and temperature T(z) (b) along z axis during evaporation. The parameters are the same as that in panels (a) and (b) of Fig. 2, except that the temperature at L_z is changed to be absorbing boundary condition, *i.e.*, the liquid has no heat exchange with reservoir or environments. (c) Distributions of the total flux J_{tot} , temperature-driven flux J_T , and chemical potential-driven flux J_{μ} along the z axis at $t = 1000\tau$ during evaporation. (d) Variation of coefficient $k = \partial \mu_0 / \partial T$ as a function of vapor density ϕ .

different $\delta \phi = 0.043$, 0.063, and 0.083 are shown in Fig. 2(d), where one can see that the cooling magnitude increases as $\delta \phi$. This is consistent with experimental observations that the cooling induced by evaporation of liquids strongly depends on humidity [30].

C. Evaporative cooling regulation without heat exchange

Now we consider case II, where the liquids do not exchange heat with reservoir at $z = L_z$. The other conditions are the same as those in case I. One can see a similar recession of interfaces and liquid cooling during evaporation in Fig. 3(a) and 3(b). Unlike case I in which the liquid temperature will eventually return to the reservoir temperature T_0 , in case II, evaporation will drive the liquids to a steady state with lower temperature and higher density; see Figs. 3(a) and 3(b). Because there is no heat exchange with reservoir from the boundary at $z = L_z$, this steady state is dictated solely by the evaporation process within the vapor phase. Therefore, the cooling magnitude is stronger than in case I; see the comparisons between Figs. 2(b) and 3(b). The cooling magnitude in case II can be considered as the theoretical limit induced by evaporation at a given density quench $\delta \phi$, providing a convenient approach to regulate temperatures by phase transition.

The steady state of the final liquid-vapor coexistence induced by evaporation can be further verified by flux distributions inside the vapor and liquid phases; see the fluxes driven by temperature gradients, J_T , and chemical potentials, J_{μ} , and their combinations J_{tot} at $t = 1000\tau$ in Fig. 3(c). The total flux J_{tot} is almost equal to 0 throughout the system, indicating a steady state within both liquid and vapor phases. However, the evaporation-induced temperature gradient from reservoir to liquid-vapor interface in Fig. 3(b) always yields a nonzero flux of $J_T = -M_T \nabla \ln T$ in the vapor phase, which has to be compensated for by another flux generated by the chemical





FIG. 4. (a), (b) Stable distributions of liquid-vapor density $\phi(z)$ (a) and temperature T(z) (b) along the z axis during evaporation at $t = 1000\tau$. The other conditions are the same as that in Fig. 3(c). Plot of temperature-density relations of stable liquid on the $T - \phi$ phase diagram. The green line represents the coexistent liquid line. (d) Plot of $T(\phi)$ within the stable vapor phase on the $T - \phi$ phase diagram. The black line and orange square are the coexistent vapor line and initial vapor state. The blue arrow shows the quench magnitude $\delta\phi$ at z = 0.

potential gradient $J_{\mu} = -MT\nabla\mu$. Fig. 3(c) indeed shows a negative J_{μ} , which indicates a cold-to-hot mass transfer driven by chemical potential gradients inside nonequilibrium vapor phases.

The cold-to-hot mass transfer induced by chemical potential gradients is interesting in the sense that the molecules have higher chemical potentials at lower temperatures. This can be attributed to the complex thermodynamics of chemical potentials with respect to temperature. From the expression of $\mu_0(\phi, T)$, we can calculate the following coefficient $k = \partial \mu_0 / \partial T = \ln \phi + w \phi^2$, which is always negative inside the vapor region; see Fig. 3(d). This ensures the decrease of chemical potentials inside the nonequilibrium vapor phase by increasing temperature, which yields a coldto-hot mass transfer to compensate for the flux driven by the temperature gradient. The findings imply that the steady state of a nonequilibrium vapor phase as well as the stable liquids during evaporation can be regulated by its complex thermodynamics coupled with heat-mass transport kinetics.

D. Regulation of evaporative cooling with thermodynamics

We have already shown in Figs. 3(c) and 3(d) that the thermodynamics of simple liquids dictate the cold-to-hot mass transfer inside the vapor region because of the temperature-dependent chemical potentials. These findings confirm that thermodynamics plays a central role in the evaporative cooling of single-component liquids. Here, we show further how the stable liquid and vapor phases are linked to the thermodynamics, *i.e.*, phase diagram, of simple liquids.

Three different quench densities $\delta \phi = 0.043$, 0.063, and 0.083 are performed in case II to generate stable density and temperature distributions; see Figs. 4(a) and 4(b). It is clearly shown that as $\delta \phi$ increases, the evaporative cooling becomes



FIG. 5. (a) Stable distributions of temperature T(z) along the z axis during evaporation at the same quench magnitude $\delta \phi = 0.01$ from different initial states at $T_0 = 0.90$, 0.85, 0.80, and 0.75. The blue arrow depicts the evaporative cooling magnitude ΔT . (b) Variation of cooling magnitude ΔT as a function of the enthalpy of vaporization $h_{\rm ev}$ at T_0 .

stronger and the liquid density increases. Such phenomena are quite similar to the temperature-density relations in the coexistent liquid line on the $T - \phi$ phase diagram of Fig. 1(c). Here, we plot these densities and temperatures of stable liquids on a $T - \phi$ phase diagram; see Fig. 4(c). It is surprising to see that the stable liquids induced by evaporation are located in the coexisting liquid line. We also plot the temperature and density distributions in the stable vapor phase in the phase diagram $T - \phi$ of Fig. 4(d). Because the temperature at the vapor boundary z = 0 is fixed to T_0 , the density quench $\delta \phi$ will locate horizontally to the left of the initial state; see the blue arrow in Fig. 4(d). The vapor state near the interface coexists with the liquid phase and therefore is located on the vapor line. Consequently, the density and temperature distributions inside the nonequilibrium vapor phase will form a line on the T - pphase diagram; see Fig. 4(d). The locations of stable liquids on the coexisting liquid line in Fig. 4(c) indicate that the magnitude of evaporative cooling can be regulated by varying the positions of stable liquids on the phase diagram, *i.e.*, changing the thermodynamics to different phase diagrams, or varying the kinetics in steady vapor via different kinetic coefficients.

Furthermore, as the vaporization enthalpy h_{ev} in Fig. 1(d) decreases with increasing temperature toward the critical point, it can be expected that the magnitude of evaporative cooling may change at different temperatures even at the same $\delta \phi$. Here, we perform a series of evaporation from different initial temperatures T_0 at the same $\delta \phi = 0.01$. In Fig. 5(a), one can see that the cooling magnitude ΔT decreases as T_0 increases from 0.75 to 0.90. Taking into account the variation of $h_{\rm ev}$ in different T_0 , we plot the relation of $\Delta T \sim h_{\rm ev}$ in Fig. 5(b), where it is clearly shown that the magnitude of evaporative cooling is dictated by the enthalpy of vaporization h_{ev} . This implies that the temperature variations induced by the phase transition can be regulated by changing the initial thermodynamic states of the materials, where a thermodynamic state far from the critical point can generate large temperature variations.

To this end, we demonstrate that the evaporation of simple liquids will drive the system toward a steady state where the non-equilibrium vapor phase coexists with a stable liquid in the co-existent liquid line on $T - \phi$ phase diagram. These findings demonstrate that the magnitude of evaporative



FIG. 6. (a), (b) Time evolutions of the minimum temperature T_{\min} during evaporation with and without heat exchange to the reservoir at the same quench magnitude $\delta \phi = 0.063$ and different Soret coefficients $S_T = 0.5$ (a) and $S_T = 2.0$ (b). The blue arrow depicts the evaporative cooling magnitude ΔT . (c) Variation of ΔT as a function of S_T for liquids with or without heat exchange with the reservoir. (d) Variation of cooling enhancement factor β as a function of S_T .

cooling induced by the liquid-vapor phase transition can be regulated by the thermodynamics of liquids.

E. Cooling enhancement and effect of soret coefficient

Evaporative cooling shown in Figs. 2(b) and 3(b) indicates that simple prevention of heat exchange between liquids and the surrounding reservoir can significantly improve the magnitude of cooling. The time evolutions of T_{\min} (labeled in Fig. 2(b)) for cases I and II at $S_T = 0.5$ are shown in Fig. 6(a), where a recovery of T_{\min} to T_0 is seen in case I and a stable value of T_{\min} in case II. These findings are interesting in the following aspects. First, the magnitude of evaporative cooling can be significantly enhanced by simply preventing the heat exchange between liquids and the reservoir, providing an easy approach to enhance evaporative cooling without additional treatments of evaporative kinetics or thermodynamics. Second, experimentally measured evaporative cooling with heat exchange between liquids and environments may not reach the theoretical limit induced by evaporation at given rates and thermodynamic conditions [30]. Therefore, our theoretical predictions may stimulate further experiments to explore the theoretical limit of evaporation-induced cooling.

As shown in Fig. 3(c), the total fluxes within the nonequilibrium vapor phase during evaporation are dictated by two fluxes driven by temperature and chemical potential, which are highly dependent on the Soret coefficient S_T . To clarify the role of this kinetic coefficient, S_T , in evaporative cooling, we calculate the evaporation process by changing S_T from 0.3 to 2.5, and the time evolutions of T_{\min} in 2.0 are shown in Fig. 6(b). We define the magnitude of evaporative cooling as $\Delta T = T_0 - T_{\min}(t^*)$, where $T_{\min}(t^*)$ is the minimum temperature at t^* during evaporation. For case I, t^* is located around $t \simeq 50\tau$, where in case II, t^* indicates the time to approach the final stable state. The variations of ΔT as a function of S_T for cases I and II are shown in Fig. 6(c). It can be seen that the cooling magnitude in case II obviously decreases as S_T increases. This is in general due to the larger fluxes driven by gradients of temperature compared to those of chemical potentials. However, the decrease is much smaller in case I than in case II, which can be attributed to suppression of evaporative cooling by heat exchange between liquids and the reservoir.

The ratio of ΔT between case II and case I can be taken as a cooling enhancement factor: $\beta = \Delta T_{\text{II}}/\Delta T_{\text{I}}$. This cooling enhancement factor β can vary from 2 to 4 by decreasing S_T from 2.5 to 0.3, see Fig. 6(d), which implies that the enhancement of evaporative cooling by a factor of 2 ~ 4 can be obtained simply by preventing heat exchange between liquids and environments. These findings might stimulate further experiments to better regulate temperatures induced by liquidvapor phase transitions in practical applications.

F. Discussion

Phase transition between different thermodynamic states, such as liquid and vapor, or vapor and solid, usually absorbs or emits energies to generate cooling or heating within different materials, providing a basic framework to regulate temperatures in different applications [1–3]. As a typical phase transition–induced cooling phenomenon, evaporation-induced cooling has been widely used in many applications recently, such as the cooling of microelectronic devices [19] and the generation of extremely low temperatures in nanokelvin [21]. Because of the strong coupling between the enthalpy change in thermodynamics and heat-mass transfer in phase transition dynamics, regulating the temperatures induced by the phase transition remains a great challenge.

In this article, we propose a unified theoretical framework by establishing a connection of enthalpy change during phase transition from free energy to heat transfer kinetics, and coupling it to model B dynamics to explore how to control temperatures via liquid-vapor phase transition, *i.e.*, evaporation, in simple liquids. The consistency between our theoretical predictions and recent experiments [30] validates the feasibility of this new method in exploring temperature regulation via phase transitions. As our approach is outlined for a simple liquid, its extension to other conditions may be applicable, *i.e.*, including hydrodynamic effects during evaporation or thermal radiation to capture the influence of solar energy on the liquid-vapor transition. Next, we briefly summarize these possibilities.

(I) The first is extension of model B to other phase transition dynamics. As the evaporation process is very slow in most cases, the hydrodynamic effects can be negligible. However, if the liquid-vapor phase transitions are carried out by a large pressure or temperature quench, where the liquids become unstable or boiling, the hydrodynamic effects should be included. In this scenario, the Peclet number is usually Pe \gg 1, indicating a fast evaporation that the convective flux is much stronger than the diffusive flux [5,10]. The dynamics of model B could be replaced by model H [52], where the Navier-Stokes equation can be included and solved with the mass-heat transfer equations to capture temperature variations during the phase transition.

(II) The heat transfer mechanism described in this article only considers thermal conduction [49], which is applicable in most evaporation processes where thermal radiation is negligible [72]. An additional heat transfer mechanism includes thermal radiation, which carries heat by electromagnetic waves or photons [49]. This thermal radiation may be included in heat transfer Eq. (4) employing a source term that can emit heat toward environments or absorb heat from external sources such as solar energy. Such an extension enables exploration of physical mechanisms governing thermal radiation and phase transition dynamics, such as solar-driven interfacial evaporation of seawater [73].

(III) The finite size effects will affect the temperature regulations within the phase transitions in small droplets or thin films in nanometers. How the temperature regulations induced by phase transition are affected by the finite size effects may also be considered within the framework of our model by converting the free energies into the Fourier spaces, as proposed by Brézin and Zinn-Justin [74]. This will stimulate further explorations of temperature regulations via phase transitions in small systems.

IV. CONCLUSION

In summary, we developed a unified theoretical framework by explicitly incorporating enthalpy change of the phase transition from thermodynamics into heat transfer kinetics and coupling it with model B dynamics of phase transition to study evaporation-induced cooling as an example. This new theoretical method can spontaneously generate a liquid cooling at interfaces, and the calculated results are in good agreement with recent experiments. In addition, we demonstrate that simple prevention of heat exchange between liquids and their surrounding environments can significantly enhance the magnitude of cooling by a factor of $2 \sim 4$, depending on the thermodynamic states and kinetic coefficients of the liquids. Our study reveals that the complex thermodynamickinetic interplay governs evaporation-induced cooling, which may promote its practical applications in different fields, such as evaporation-induced self-assembly [4,5,46] and crystallization [9,10]. The newly developed method enables the exploration of cooling or heating induced by different phase transitions in a unified framework, which may facilitate the development of temperature regulations via different phase transitions, such as sublimation, condensation, or crystallization.

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