# Effect of spinodal singularities on the evaporation of a superheated liquid

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Possible manifestations of spinodal singularities in the course of surface evaporation of a liquid by intense electromagnetic radiation are investigated. It is shown that the increase of the specific heat and of the reciprocal thermal diffusivity near the spinodal lead to an essentially nonmonotonic character of the establishment of the steady-state evaporation. Experimental observation of such a behavior could serve as proof of the existence of the spinodal as a realistically observable line of singularities of the thermophysical parameters of a metastable liquid.

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**1.** The behavior of the thermophysical parameters of a liquid at the absolute-instability boundary (spinodal) has been investigated only near the critical point immediately adjacent to the thermodynamically stable region. The remaining spinodal points are separated from the stable state by a metastability region. At shallow penetrations into the metastable region, no singularities whatever have been observed in the superheated liquid.[1] At the same time, extrapolation of the experimental results on light scattering, from the stable to the metastable region, suggests that the thermal diffusivity $\chi = \varkappa/c\rho$ tends to zero near the spinodal.[2] It follows from the Van der Waals equation that the specific heat $c$ diverges on the spinodal, but it is known that this equation does not provide a correct description of the critical singularities because the fluctuations are not adequately accounted for.

Fluctuations assume a special role in the metastable phase, since the state of the system is not stable. As a result of the increase of the "transcritical" heterophase fluctuations, the time during which a superheated metastable liquid can exist as a homogeneous system is limited, and the liquid may decay even before the spinodal is reached. This raises the fundamental question whether it is possible at all to attain near the spinodal a region in which the possible singularities of the thermophysical parameters become actually observable.[3,4] There is at present no answer to this question.

It is obvious that the experimental methods used in the stable region will hardly work in studies of the behavior of a superheated metastable liquid, whose lifetime near the spinodal is very short. In such a situation one must use pulsed methods that yield information on the properties of the liquid in a time on the order of $t \lesssim 10^{-6}$ sec. We analyze in this paper the possible manifestations of spinodal singularities in the course of rapid heating and evaporation of an absorbing liquid acted upon by intense electromagnetic radiation.

**2.** The temperature $T$ of a superheated liquid exceeds the boiling point corresponding to the external pressure $p$ acting on the liquid, i.e., $p$ is less than the saturated vapor pressure $p_s(T)$. If the metastable liquid has a free surface, the value of $p$ is determined by the kinetics of the surface evaporation and is approximately one-half the saturated-vapor pressure, if the back-flow of the evaporated particles is small and the sticking coefficient is close to unity.[5] Thus, the behavior of the surface temperature $T_0$ can be assessed from the time dependence of the recoil pressure $p \approx 0.5 p_s(T_0)$. The closest approach to the spinodal is reached in this case not on the very surface of the superheated liquid, but at a certain distance from it, in the region where the temperature distribution has a maximum. In the one-dimensional case, which we shall consider, this region is a plane parallel to the interface.

To determine the influence of the spinodal singularities on the behavior of the surface temperature $T_0(t)$ it is necessary to find the temperature profile in the metastable liquid with allowance for the volume absorption of the radiation and the boundary condition on the evaporation surface, which moves relative to the immobile surface at a velocity $v(T_0)$. In a coordinate frame with origin on the evaporation surface, the corresponding boundary-value problem for the heat-conduction equation takes the form

$$c\rho\left(\frac{\partial T}{\partial t} - v\frac{\rho_0}{\rho}\frac{\partial T}{\partial x}\right) - \frac{\partial}{\partial x}\left(\varkappa\frac{\partial T}{\partial x}\right) - c\rho\left(\frac{\partial T}{\partial p}\right)_s \frac{\partial p}{\partial t} = \alpha I \exp\left(-\int_0 \alpha\, dx\right), \tag{1}$$

$$\varkappa \partial T_0/\partial x = \varepsilon\rho_0 v, \quad T(x, 0) = T(\infty, t) \equiv T_\infty, \tag{2}$$

where $\alpha$, $\varkappa$, $\varepsilon$, and $c$ denote the absorption and heat-conduction coefficients, the heat of evaporation, and the specific heat at constant pressure. In the case of free evaporation in vacuum, the velocity $v$ is given by[5]

$$v = (p_s\rho'/\rho_0\rho_{id}')(m/2\pi k T_0)^{0.5}, \tag{3}$$

where $\rho_0$ is the density of the liquid on the interface, $m$ is the mass of the evaporated particles, and the ratio $\rho'/\rho_{id}'$ takes into account the difference between the vapor density $\rho'$ and the density $\rho_{id}'$ of an ideal gas at a temperature $T_0$ and a pressure $p_s(T_0)$. The last term in the left-hand side of (1) takes into account the adiabatic changes of the temperature with changing pressure $p$.

**3.** Owing to the nonlinear dependence of the evaporation rate $v(T_0)$ on the temperature, the problem (1), (2) is nonlinear even at constant values of the thermophysical parameters, and it has no known analytic solution in

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the general case. The stationary distribution of the temperature at constant $\alpha$, $c$, and $\chi$ is given by[6]

$$T=[T_0-T_\infty+\varepsilon/c](1-y)^{-1}[\exp(-\alpha x)-\exp(-vx/\chi)] + (T_0-T_\infty)\exp(-vx/\chi)+T_\infty, \tag{4}$$

and the following relation

$$\varepsilon+(T_0-T_\infty)c=I/\rho_0 v \tag{5}$$

is valid and determines, given the function $v(T_0)$, the dependence of the surface temperature $T_0$ on the absorbed intensity $I$.

The excess of the maximum of the temperature profile over the surface temperature is small: $T_m - T_0 \approx \varepsilon/cy$, if the dimensionless parameter $y=\alpha\chi/v>1$ and the distance from the maximum to the interface, $x_m \approx \alpha^{-1}$, coincides with the characteristic absorption length of the electromagnetic radiation. This situation is typical of liquid metals.

In the opposite case of interest to us, $y<1$. The quantities $T_m - T_0 = \varepsilon/c$ and $x_m = \chi/v$ do not depend on the absorption coefficient. Since the ratio $\varepsilon/c$ is of the same order as the critical temperature $T_c$, the stationary evaporation regime described by (4) and (5) is in fact never reached. The maximum of the temperature profile exceeds the limiting superheat temperature $T_L$ even before the stationary regime is established, and explosive decay of the metastable phase sets in. Thus, at $y<1$ the stationary regime can be reached only if the specific heat $c$ increases appreciably near the limiting superheat temperature $T_L$. This evaporation regime, however, can no longer be described by formulas (4) and (5).

If account is taken of the temperature dependences of $c$ and $\varkappa$, the relation between $T_m$ and $T_0$ can be obtained in the following manner: After integrating (1) with respect to the spatial coordinate from $x=0$ to $x=x_m$ we have in the stationary regime

$$v\rho_0\left(\varepsilon-\int_{T_0}^{T_m} c\,dT\right)=I[1-\exp(-\alpha x_m)]. \tag{6}$$

Since $\alpha x_m \approx y \ll 1$ and

$$I=v\rho_0\left(\varepsilon+\int_{T_\infty}^{T_0} c\,dT\right), \tag{7}$$

we can neglect the right-hand side of (6). The result is the equation

$$\varepsilon=\int_{T_0}^{T_m} c\,dT, \tag{8}$$

which determines the connection between $T_0$ and $T_m$ in the stationary evaporation regime. The physical meaning of (8) is obvious: the energy consumed in surface evaporation corresponds to the enthalpy change on the section from the interface to the position of the maximum of the temperature profile, since the role of the absorbed radiation as a volume heat source is negligibly small over the length $x_m$.

To determine $x_m$ explicitly we need more detailed information on the behavior of the temperature profile. A simple analytic expression for $x_m$ is obtained when the thermophysical parameters $c=c_0[(T_L-T)/(T_L-T_0)]^{-k}\equiv c_0\Delta^{-k}$ and $\varkappa=\varkappa_0\Delta^{-n}$ have integrable power-law singularities $0\leqslant n<k<1$, and the maximum of the temperature profile coincides with the temperature of the limiting superheat: $T_L=T_m$. Expressing at $x\leqslant x_m$ the temperature profile in the form $\Delta=b\alpha^q(x_m-x)^q$, we obtain from (1) in the considered approximation

$$b=[\alpha\chi_0(q-1-qn)/v]^{-q}, \quad q=(k-n)^{-1}. \tag{9}$$

We obtain ultimately for $x_m$ and $T_m-T_0$ the expressions:

$$x_m=\chi_0(1-k)/v(k-n), \tag{10}$$

$$T_m-T_0=\varepsilon(1-k)/c_0, \tag{11}$$

which differ from the analogous quantities at constant values of the thermophysical parameter by the factors $(1-k)/(k-n)$ and $1-k$, respectively. Formula (11) agrees, of course, with Eq. (8) (the expressions for $T_m-T_0$ and $x_m$ in[7] are of the correct form only if $n^2 \ll 1-k$). Formula (10) no longer holds at $k=n$, but in this case the expression for the temperature profile is obtained directly from (1), which after an obvious substitution for the function reduces to a linear first-order differential equation.

**4.** We consider now the establishment of a stationary evaporation regime. To determine the dependence of the recoil pressure $p[T_0(t)]$ on the time we must solve the boundary-value problem (1), (2). This can be done only by numerical means. Since our purpose is to investigate the qualitative singularities of the nonstationary evaporation regime, we shall henceforth regard the absorption coefficient $\alpha$ as constant and neglect in the convective term the difference between the ratio $\rho_0/\rho$ and unity.

Using the dimensionless quantities

$$u=T/T_c, \quad \sigma=p/p_c, \quad \tau=\alpha^2\chi_1 t, \quad z=\alpha x,$$

$$D=I/\alpha\varkappa_1 T_c, \quad y=\alpha\chi_1/v=\alpha\chi_1(2\pi kT_c u/m)^{0.5}\rho_0\rho_{id}'/p_c\rho'\equiv f_3\rho_{id}'\rho_0/\rho'\rho_1,$$

we write down the boundary-value problem (1), (2) in the form

$$\frac{\partial u}{\partial\tau}-\frac{1}{y}\frac{\partial u}{\partial z}-f\frac{\partial}{\partial z}\left(\frac{1}{f_2}\frac{\partial u}{\partial z}\right)-\left(\frac{\partial u}{\partial\sigma}\right)_s\frac{\partial\sigma}{\partial\tau}=f_1De^{-z}, \tag{12}$$

$$\frac{\partial u_0}{\partial t}=\frac{f_2}{f_3}\frac{\varepsilon}{c_1T_c}\frac{\rho'}{\rho_{id}'}, \quad u(z,0)=u(z_R,\tau)=u_\infty. \tag{13}$$

The singular behavior of the specific heat and of the thermal conductivity will be described by the functions $f_1=c_1\rho_1/c\rho$ and $f_2=\varkappa_1/\varkappa$:

$$f_1=f^{1.2}, \quad f_2=f^{0.66}, \quad f=\{1-\exp[-10^4(u_L-u)^4]\}^{0.25}. \tag{14}$$

At $u_L-u>0.1$, the functions $f_1$ and $f_2$ differ little from unity, and when the difference decreases to $u_L-u<0.1$ these functions tend to zero in power-law fashion, with respective exponents 1.2 and 0.66. Since the limiting superheat temperature $u_L=0.9+0.1\sigma$ depends on the pressure,[1] the specific heat and the thermal conductivity turn out to be functions not only of the temperature but also of the pressure.

Far from $u_L$, the term with the adiabatic derivative in Eq. (12) has little influence on the dynamics of the liquid heating, but as $u$ approaches $u_L$ the derivative $(\partial u/\partial\sigma)_s$ increases and reaches at $u=u_L$ the value 0.1 which is obtained in the approximation under consideration from the relation $(\partial u/\partial\sigma)_s^{sp}=du_L/d\sigma$. This relation expresses the fact that in the plane of the thermodynamic variables $\sigma$ and $u$ the spinodal is the envelope for the adiabats and the isochores.[1] In the present paper the adiabatic derivative was approximated by the expressions $0.1(1-f_1)^4$ and $0.1\exp[10(u-u_L)]$, which differ, in particular, in the rate of fall-off at $u_L-u\gtrsim 0.1$.

The nonlinear boundary-value problem (12), (13) was solved numerically with the BÉSM-6 computer, using an implicit finite-difference scheme. Without dwelling on the details of the numerical algorithm, we note the following features of the computation. Equation (12), which in our problem preserves its parabolicity together with its difference analog, was approximated by an assembly of four-point, implicit in time, nonlinear difference equations of the divergent type. In each time step the aggregate of nonlinear algebraic equations approximating the problem (12), (13) was solved by successive approximations, with the iterations stopped when the condition $|u_i^{(s)}-u_i^{(s-1)}|\leq\varepsilon_1$, and with given $\varepsilon_1>0$, was satisfied at each node $i$ in $z$. In view of the scale differences in the behavior of the temperature profile, we used in the calculations a non-uniform $z$-grid with intervals $h_z$ between $10^{-4}$ and $8\times10^{-2}$ on the segment $z\leq z_R\approx 3.12$. The sizes of the steps $h_z$, $h_\tau$, and $\varepsilon_1$ were chosen such that when the stationary regime was reached the functional of the numerical solution was within 10% of its theoretical value (7).

With a concrete physical situation in mind for the sake of argument—rapid heating of water by intense infrared radiation—we used in the numerical calculation the following values of the absorption coefficient and of the thermophysical parameters of the liquid:

$$\alpha=10^3\,\text{cm}^{-1},\quad \chi_1=1.62\cdot10^{-3}\,\text{cm}^2/\text{sec},\quad c_1=4.2\ \text{J/g-deg},$$

$$\rho_1=1\,\text{g/cm}^3,\quad u_\infty=0.45,\quad p_s=2p=p_c\exp[7.4(1-u^{-1})],$$

$$f_3=10^{-3}u^{0.5}\exp[7.4(u^{-1}-1)],\quad p_c=22.1\ \text{J/cm}^3,\quad T_c=647\ \text{K},$$

$$\varepsilon\rho'/c_1T_c\rho_{id}'=0.81,\quad \rho_{id}'\rho_0/\rho'\rho_1=\exp(-1.3u^5).$$

The behavior of the recoil pressure $\sigma(\tau)$ at various values of $D$ and $(\partial u/\partial\sigma)_s=0.1(1-f_1)^4$ is shown in Fig. 1 (the coefficients for the conversion from $\tau$ and $D$ to the dimensional quantities $t$ and $I$ are respectively $(\alpha^2\chi_1)^{-1}=1.47\cdot10^{-4}$ sec and $\alpha\varkappa_1T_c=4.4\cdot10^3$ W/cm²). The initial sections of the $\sigma(\tau)$ curves hardly differ from the case of the constant thermophysical parameters $f_1=f_2=1$, when the pressure increases monotonically until the maximum temperature profile $u_m$ reaches the value $u_L\approx 0.9$, after which explosive decay of the superheated liquid should set in. The recoil pressure at the instant of the explosive decay is much smaller than the stationary value determined from Eq. (7) using the surface temperature. At $D$ equal to 100, 250, and 500 the ratio $\sigma/\sigma_{st}$ is respectively 0.11, 0.074, and 0.052, and the instant when the limiting superheat temperature is reached turns out to be approximately inversely proportional to

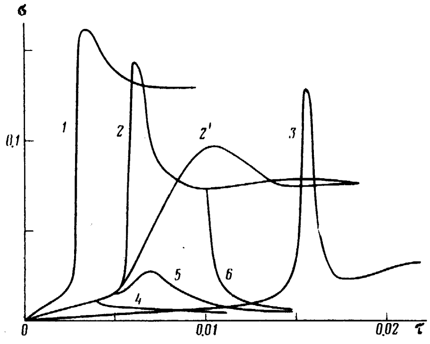


FIG. 1. Plots of the recoil pressure at various intensities $D$: 500 (1), 250 (2.2′), 100 (3) and durations $\tau$: $4\cdot10^{-3}$ (4), $5\cdot10^{-3}$ (5), $10^{-2}$ (6) of the action of the radiation.

$D$: the corresponding values of $\tau$ are $5.5\times10^{-3}$, $2\times10^{-3}$, and $10^{-3}$.

The increase of the specific heat near the spinodal is the necessary condition for the establishment of a stationary evaporation regime at $y<1$. As seen from the figure, this regime is reached in an essentially nonmonotonic manner. The $\sigma(\tau)$ curve has a sharp peak whose amplitude exceeds the stationary pressure level and depends little on the radiation intensity. The principal growth of the pressure on the leading front of this peak takes place within a time $\tau_f\approx4\times10^{-1}$ ($t_f\approx6\times10^{-8}$ sec). This behavior of $\sigma(\tau)$ is due to the adiabatic variations of the temperature when the external pressure is changed, and also to the fact that in our problem the heat source and sink are separated in space, a situation aided by the decrease of the thermal diffusivity near the spinodal.

During the transient process, the energy accumulated as a result of the volume absorption of the radiation in the liquid exceeds the value needed to maintain the stationary evaporation regime at a given value of $D$. This excess energy is then "dumped" via an abrupt increase of the surface temperature and an increase in the loss to evaporation, and these take place at the instant when the moving evaporation boundary reaches the excessively heated region. The dynamics of the transient process depends little on the actual form of the term with the adiabatic derivative in (12). If we use the expression $(\partial u/\partial\sigma)_s=0.1\exp[10(u-u_L)]$ for the adiabatic derivative, then the behavior of the pressure curve changes little in comparison with the case described above, and the general picture of the heating remains the same as before. The nonmonotonic character of the transient process is conserved to a certain degree even if the term with $(\partial u/\partial\sigma)_s$ is not taken into account in (12), but then the sharp peak disappears, as seen from the figure (curve 2′).

The excessive superheating manifests itself, in particular, in the behavior of $\sigma(\tau)$ after the radiation is turned off. For sufficiently short rectangular radiation pulses, the pressure begins to fall off immediately after the end of the pulse (curve 4), but if the excessive energy accumulation has already started prior to the instant of termination of the pulse, then the growth of the surface temperature and of the recoil pressure continues also after the radiation is turned off (curve 5). For pulses long enough for dumping of the excess superheat to take place, the recoil pressure decreases abruptly on the trailing edge of the radiation pulse (curve 6). We note that in all these cases the difference $\delta = u_L - u_m$ begins to increase immediately after the end of the pulse, i.e., there is no relative approach of the limiting-superheat temperature to the maximum of the temperature profile. In this situation the direct cause of the "induced" decay, which is observed on the trailing edge of the radiation pulse,[8] may be the fact that the expansion of the superheated metastable liquid is not quasistatic when the pressure is rapidly decreased.[9]

A characteristic feature of the transient process of evaporation is also the nonmonotonic time dependence of $\delta$. The minimal value $\delta_m$ is reached not in the stationary regime, but at the instant $\tau_m$ that corresponds approximately to the start of the rapid growth of the recoil pressure. The dependence of $\tau_m$ on the intensity is almost that of inverse proportionality, with $\delta_m(\tau_m)$ equal to $7.8\cdot10^{-4}$ $(1.5\cdot10^{-2})$, $7.2\cdot10^{-4}$ $(5.7\cdot10^{-3})$ and $7\cdot10^{-4}$ $(2.8\cdot10^{-3})$ respectively for $D$ equal to 100, 250, and 500. At these values of $\delta_m$ the ratio $c/c_1$ increases to $c/c_1 \approx (10\delta_m)^{-1.2} \approx 400$, which is approximately four times larger than $c/c_1$ in the stationary regime. The time interval within which such an increase of $c/c_1$ over the stationary value is realized is relativel small compared with the duration $\Delta\tau$ of the entire transient process. For $D=250$, for example, the condition $c/c_1 \gtrsim 200$ is satisfied on the interval $\Delta\tau_1 \approx 10^{-3}$ at $\Delta\tau \approx 10^{-2}$. If the functions $c/c_1$ and $\varkappa/\varkappa_1 = (c/c_1)^{0.55}$ are bounded from above by the condition $c/c_1 \leq 200$, then the behavior of the pressure curve $\sigma(\tau)$ remains practically unchanged. Of course, the value $\delta_m = 5.1\times10^{-4}$ is then decreased. The more stringent condition $c/c_1 \leq 100$ causes the maximum of the temperature to be no longer bounded from above by the limiting-superheat temperature, i.e., $\delta$ passes through zero and becomes negative for some time. A similar situation arises also in the case of the integrable singularity $c/c_1 = f^{-k}$, $k<1$, but then the quantity $-\delta$ continues to grow after passing through zero. This behavior of $\delta$ is already outside the framework of the assumed physical model, in which the region of absolute instability is not considered and $\delta$ can not be negative.

**5.** Our results show thus that the singular behavior of the thermophysical parameters near the spinodal leads to an essentially nonmonotonic character of the transient process in the evaporation of a liquid by electromagnetic radiation. An actual manifestation of singularities of the nonstationary behavior of the recoil motion is possible, however, only if the explosive decay of the superheated metastable liquid does not start before the above-described pressure peak occurs. In other words, the necessary condition for attaining the stationary evaporation regime is a sufficient "strength" of the metastable phase relative to the excessive superheating that occurs during the transient process. The specific heat of the metastable phase should increase, in particular, not more slowly than the correlation length. If the limiting superheating temperature is reached without being accompanied by a sufficiently singular behavior of the thermophysical parameter, then the explosive decay will be initiated on the gently sloping section of the recoil-pressure curve, which precedes the pressure peak. This result can be used for an experimental investigation of the question whether the spinodal actually exists as an observable line of singularities of the thermophysical parameters of a metastable liquid.


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