Nonsteady Condensation and Evaporation Waves

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We study motion of a phase transition (PT) front at a constant temperature between stable and metastable states in fluids with the Van der Waals equation of state. We focus on a case of relatively large metastability and low viscosity, when no steadily moving PT front exists. Simulating the one-dimensional hydrodynamic equations, we find that the PT front generates acoustic shocks in forward and backward directions. Through this mechanism, the nonsteady PT front drops its velocity and eventually stops. The shock wave may shuttle between the PT front and the system’s edge, rarefaction waves appearing in the shuttle process. If the viscosity is below a certain threshold, an instability sets in, driving the system into a turbulent state.

Motion of phase transition (PT) fronts is the most important phenomenon in macroscopic physical kinetics \cite{1,2}. In most cases, it is described in the quasi-equilibrium approximation assuming a critical value of the temperature at the phase interface \cite{1}. A distinct class of phenomena are fast propagating phase transformations, such as detonation \cite{3}, and waves supported by mechanisms as different as relaxation in glassy solids \cite{4}, Belousov-Zhabotinsky reaction \cite{5}, bubble boiling \cite{6}, and the Marangoni flow coupled to a reaction on a fluid surface or chemical transformations coupled to mechanical stress \cite{7}. Coupling of the “chemistry” to the flow or elasticity is a necessary ingredient of the fast propagation of a PT wave.

A related problem is the propagation of condensation and evaporation waves in fluids. In this case, a consistent description is possible, based on the combination of the corresponding Navier-Stokes (NS) and heat-transport equations with the equation of state, e.g., the Van der Waals (VdW) one \cite{8}. Close to the critical point (CP), the VdW equation of a spatially inhomogeneous state takes the following form in terms of the normalized pressure \( p \equiv (P - P_{\text{CP}})/P_{\text{CP}} \), temperature \( \tau \equiv (T_{\text{CP}} - T)/T_{\text{CP}} \), and density \( \theta \equiv (\rho - \rho_{\text{CP}})/\sqrt{\tau}\rho_{\text{CP}} \) \cite{8}:

\[
p + 4\tau + 3\tau^{3/2} \left( 2\theta - \theta^3/2 \right) + G\sqrt{\tau}\Delta \theta = 0 ,
\]

where \( \Delta \) is the Laplacian, and \( G \) is an effective surface tension of the interface separating the vapor (\( \theta < 0 \)) and condensed (\( \theta > 0 \)) phases existing below CP (at \( \tau > 0 \)).

The hydrodynamic part of the problem is described by a system of the NS and continuity equations. In the simplest case when the PT front is one-dimensional (1D), in terms of the rescaled time \( t \equiv \tau \sqrt{P_c/\rho_c} \tilde{t} \) (\( \tilde{t} \) is the time proper), coordinate \( z \equiv \sqrt{\tau/G} x \), and flow velocity \( w \equiv \tau^{-1} \sqrt{\rho_c/P_c} v \), these equations are \cite{1}:

\[
w_t + \sqrt{\tau} w_w = 6\theta_z - (9/2)\theta^2 \theta_z + \theta_{zzz} + gw_{zzz} ,
\]

\[
\theta_z + \left[ (1 + \sqrt{\tau}\theta) w \right]_z = 0 ,
\]

where \( g \equiv [(4/3)\eta + \zeta] (GP_{\text{CP}}\rho_{\text{CP}})^{-1/2} \), \( \eta \) and \( \zeta \) being shear and bulk viscosities.

To produce a closed system, one should add the heat transfer equation to these equations. Analysis performed in Ref. \cite{8} demonstrates that a flat PT wave in a bulk medium is driven by the heat transfer giving rise to a slowly advancing front. This is drastically different in 1D case, corresponding, e.g., to the fluid inside a capillary, which allows to impose isothermal conditions, \( \tau = \text{const} \). However, it is not necessary to conduct the experiment in a capillary; instead, a PT wave may spontaneously propagate in a thin film sheathing an isothermal wire in a bulk medium. In fact, a fast PT front of this kind was already observed in experiment \cite{9}.

In the 1D situation, a solution for a PT front moving at a velocity \( -V \) can be sought for as \( w = w(\xi) \), \( \theta = \theta(\xi) \), with \( \xi = z + Vt \). Eliminating \( w \) and assuming \( \theta'(\pm \infty) = 0 \), one arrives at an equation

\[
\theta'' - gV \left[ 1 + \sqrt{\tau} (\theta_2 - 2\theta) \right] \theta' = (3/2) \left( \theta^3 - \theta_0^3 \right)
\]

\[- \left[ 6 + V^2 \left( 1 + 2\sqrt{\tau}\theta_2 \right) \right] (\theta - \theta_0) ,
\]

where \( \theta_0 \) is a critical value of the temperature.
where \( \theta_0 \equiv \theta(-\infty) < 0 \) is the density of the supercooled vapor invaded by the condensation front, and \( \theta_2 \equiv \theta(+\infty) > 0 \) is the density of the stable liquid phase behind it; recall that the metastable states have \( 2/\sqrt{3} < |\theta| < 2 \), while the regions \( |\theta| > 2 \) and \( |\theta| < 2 \) are absolutely stable and unstable, respectively.

An exact solution to Eq. (4) satisfying the boundary conditions \( \theta(\pm \infty) = \theta_{2,0} \) was found in \( \ddagger \), neglecting the terms \( \sim \sqrt{\tau} \). As is known \( \ddagger \), an equation of this type selects the velocity as an eigenvalue, \( V(\theta_0) \). A final result is that there is a pair of stable and unstable branches of \( V(\theta_0) \), which meet and disappear at a critical density \( \theta_* = -\sqrt{8/(3)}(9 - 2g^2)/(6 - g^2) \). At this point \( V(\theta_0) \) attains its maximum, \( V_{\text{max}} = 18g^2 [(9 - 2g^2)(6 - g^2)]^{-1} \). The density of the stable phase behind the front is also found as a part of the solution, \( \theta_2 = -\theta_0/2 + [(2/3)V^2 + 4 - (3/4)\theta_0^2]^{1/2} \). In particular, in the case \( g = 0 \) (inviscid fluid) \( \theta_* = -2 \), which is exactly the border between the stable and metastable states (binodal), hence a steadily moving PT front cannot exist in inviscid fluids.

Eq. (4) also gives rise to traveling-wave solutions of a different type, which are acoustic shock waves (ASW) without PT. Unlike the PT wave for which the density \( \theta_2 \) behind the front is determined by \( \theta_0 \), in the case of ASW the densities \( \theta_1 \) and \( \theta_f \) before and after the front may be arbitrary, the velocity being determined by the boundary conditions. Neglecting the \( \sqrt{\tau} \) terms, it is

\[
V_{\text{ASW}}^2 = (3/2) (\theta_f^2 + \theta_i^2 + \theta_i \theta_f - 4).
\]

In the limit \( \theta_f - \theta_i \to 0 \), this yields the sound velocity at a given density, \( c^2 = (9/2)\theta^2 - 6 \). The PT front may move faster than sound velocity in the metastable phase invaded by the front. In particular, the velocity \( V_{\text{max}} \) is transonic, provided that \( g > \sqrt{3} \). Thus, the PT wave is related to detonation, whose characteristic feature is transonic propagation \( \ddagger \).

The critical density \( \theta_* \) belongs to the metastable region if \( g < 2 \). In this case, there is a region of the metastable states, \( 2/\sqrt{3} < |\theta_0| < |\theta_*| \), which cannot be converted into an absolutely stable state by a steadily moving PT wave \( \ddagger \). The objective of the present work is to investigate the propagating PT front in this region by means of direct simulations of Eqs. (4) and (3) (analytical investigation of weakly nonsteady fronts is difficult, as the corresponding perturbative expansion contains terms secular in \( t \)).

Before that, we notice that, because of the term \( \sim \theta^2 \), Eq. (4) with \( \sqrt{\tau} \) terms kept in it does not belong to the standard type for which the velocity can be found exactly \( \ddagger \). Nevertheless, an ansatz similar to that solving the standard equation yields an exact result for Eq. (4) as well: \( V = -1/(3\sqrt{3}/2g)|\theta_1[(1 + \sqrt{\tau}\theta_2) (1 + \sqrt{\tau}(3\theta_1 + \theta_2))]^{-1/2} \), \( \theta_1 \neq \theta_{0,2} \) being another root of the r.h.s. of Eq. (4). As \( \sqrt{\tau} \ll 1 \), we look for lowest-order corrections to the final results. They contain a new effect, breaking the symmetry between the condensation (+) and evaporation (−) waves: the \( \sqrt{\tau} \)-corrected threshold value of the viscosity \( g \), below which there is a region of the nonexistence of steady PT waves, is \( 2 \pm (5/2)\sqrt{\tau}/3 \).

In systematic numerical simulations of Eqs. (2) and (3), the \( \sqrt{\tau} \)-corrections were omitted, and \( w \) was eliminated, differentiating Eq. (2) in \( z \) and substituting \( w_z \) by \( -\theta^2 \), as per Eq. (3) (for some typical cases, it was checked that the \( \sqrt{\tau} \) terms produce a small insignificant change of the numerical solution). The resulting equation of the second order in \( t \) and fourth order in \( z \) was numerically integrated with the initial conditions \( \theta_i(t = 0) = 0, \theta(t = 0, z) \) being a smoothed step between the values \( \theta_0 < 0 \) and \( \theta_2 > 0 \). For the boundary conditions (b.c.), it was always taken that \( \theta = \theta_0 \) at the left edge and \( \theta = 0 \) at both edges. Note that the natural b.c. for the flow, \( w(\infty) = 0 \), is compatible with these, as is seen from Eq. (3). The b.c. for the flow at the right edge is not fixed, because, as a matter of fact, we are dealing with an open system, with a possible influx of fluid from \( +\infty \).

In the case when the steady PT front exists, the fourth b.c. was naturally taken as \( \theta(+\infty) = \theta_0 \). Simulations have demonstrated that the steady front is always stable when it exists. When it does not exist, the density to be established past the PT wave is unknown, therefore initial \( \theta_2 \) was taken arbitrarily from the absolute stability region \( |\theta| > 2 \). In this case, the missing b.c. was taken as \( \theta_x = 0 \) (i.e., the density profile must be flat) at the right edge. The results displayed below clearly show that no artifacts are generated by b.c.

A representative picture of the nonsteady propagation of the condensation front, when the steady one does not exist, is shown in Fig. 1. Essential features revealed by many simulations are well seen in it: (i) the nonsteady PT wave immediately begins to generate two ASWs in forward and backward directions; (ii) the forward ASW (precursor) travels essentially faster than the PT front, so that a rapidly expanding trough with an increased value \( |\theta| > |\theta_0| \) is formed ahead of the front; (iii) the fast backward-propagating ASW hits the right edge, bounces from it, and then hits the PT front. Velocities of all the observed ASWs were checked to comply with Eq. (4).

Thus, the first finding is that the nonsteady PT wave does not self-accelerate, which could be natural to expect \( \ddagger \); instead, it generates a strong acoustic precursor. Fig. 2a demonstrates that in all the cases with \( g \leq \sqrt{3} \) the newly established value \( \bar{\theta} \) of the density ahead of the front originally turns out to be fairly close to \( \theta_* \), corresponding to the minimum of \( |\theta_0| \) at which the steady PT wave exists. Then, quasi-steady propagation of the PT wave with the density
\( \theta \approx \theta_* \) ahead of it becomes possible. Note that simulations of 2D hydrodynamic equations with the VdW equation of state, in the problem of transverse instability of shock waves, have also revealed strong emission of acoustic waves \( \theta \).

The PT front decelerates and eventually comes to halt, while the precursor keeps propagating at a nearly constant velocity until it hits the left edge of the integration domain (Fig. 2b). Moreover, simulations show that the PT front begins then to slowly move in the reverse direction. We do not consider the reverse motion in detail, as it is a manifestation of finiteness of the system, while in this work we focus on properties of a semiinfinite (to the left) system, although, of course, finiteness effects may be important for experiment. As concerns the value of \( |\theta| \) ahead of the PT front, at a later stage of the evolution it slowly increases from the originally established value \( \approx |\theta_*| \) to \( |\theta| = 2 \) at the halt stage. This can be easily understood, as \( |\theta| = 2 \) is the binodal (a minimum value of \( |\theta| \) at which the interface between the two phases may be quiescent). The halt of the front at \( \theta = -2 \) implies that the density behind it must take the conjugate value \( \theta = +2 \), which is indeed observed, see below.

An intriguing case is \( \sqrt{3} < g < 2 \), when the nonsteady situation is possible whilst the maximum velocity of the steadily moving PT exceeds the sound velocity at \( \theta = \theta_* \), suggesting that the PT front cannot send a sound wave ahead of itself. A typical picture for this case is displayed in Fig. 3, which shows that the acoustic precursor is nevertheless launched. The difference from the previous case is that the trough before the PT front quickly deepens, so that \( \theta \), rather than being stuck at the value \( \theta_* \), quickly drops to the binodal value \( \theta = -2 \), see Fig. 2a. This leads to PT coming to halt earlier than in the case \( g \leq \sqrt{3} \). Thus, an attempt to launch a “superfast” PT front into a deeply metastable phase produces an opposite result: the front generates strong acoustic waves and decelerates, seeing a less metastable state ahead of itself (physically, the metastability is relatively deep, as everything happens close to the critical point).

An altogether different result is found at very small \( g \), viz., onset of instability, which quickly switches the system into a fully turbulent state and destroys the interface. For instance, with the initial values \( \theta_0 = -1.2 \) before the interface and \( \theta = 2.7 \) behind it, the instability sets in at \( g \leq 0.3 \). However, systematic study the present system as a model of 1D turbulence is beyond the scope of this work.

The situation behind the PT front deserves special description. We observe that ASW which hits the PT front in the last configuration shown in the upper part of Fig. 1 bounces from the front, travels to the right edge, is reflected from it, and then again hits the PT front (Fig. 4). A nontrivial feature of ASW in this case, evident in Fig. 4, is that it is reflected by the PT front as an antishock, or rarefaction wave. The present model does not admit steady rarefaction waves; however, the wave in Fig. 4 is unsteady, as it propagates between variable densities. Taking instantaneous values of the densities, we conclude that the antishock’s velocity also obeys Eq. \( \theta \).

Analysis of the numerical results leads to the following inferences concerning the shuttling shock/antishock wave behind the PT front in Figs. 1 and 4: (i) bounces from both the right edge of the system and PT front do not change the absolute value of the velocity; (ii) bounces from the right edge are elastic without a change in the step height \( (\theta_f - \theta_i) \); (iii) bounces from the PT front are highly inelastic: the shock bounces as an antishock and vice versa, each reflection decreasing the step height by a factor \( \sim 5 \), which explains why the shuttling wave disappears after a few reflections.

Thus, we conclude that the system eventually drives itself into an equilibrium state with a quiescent interface between the liquid and vapor phases. A mechanism establishing the equilibrium is the generation of acoustic shocks, which bounce elastically from the system edge, but are muffled by strongly inelastic collisions with the interface.

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FIGURE CAPTIONS

Fig. 1. Propagation of the nonsteady condensation front with \( g = \sqrt{3} \). This and other figures display results for a typical case with the initial densities before and behind the front \( \theta_0 = -1.2 \) and \( \theta_2 = +2.7 \) (note that \( \theta_*(g = \sqrt{3}) = -1.63 \)). Profiles \( \theta(z) \) are shown through time intervals \( \Delta t \), different in the upper and lower portions. An interval \(-1 < \theta < 2.5\), where nothing happens, is dropped. The bold arrows in the upper portion (and in Fig. 4) show velocities of the shuttling acoustic shock behind the front.

Fig. 2. (a) The difference between the density \( \tilde{\theta} \), established ahead of the phase transition front after the passage of the acoustic precursor, and the critical density \( \theta_* \). (b) The velocities of the acoustic shock and condensation front for \( g^2 = 2.4, 3.0, \) and 3.6. A small jump at \( t \sim 200 \) is due to hitting the front by the acoustic shock reflected from the right edge.

Fig. 3. Evolution of the nonsteady condensation front at \( g^2 = 3.6 \).

Fig. 4. The propagation of the antishock at \( g = \sqrt{3} \) between two inelastic collisions with the condensation front: before (a) and after (b) elastic reflection from the right edge.
$g^2 = 3.0$

$\Delta t = 4$

$\Delta t = 8$

acoustic shock waves

$t = 0$

$t = 40$

$t = 144$
velosity-time

(b) acoustic shock wave

phase transition wave

\[ g^2 = 2.4 \]

\[ g^2 = 3.0 \]

\[ g^2 = 3.6 \]
(a) \[ g^2 = 3.0 \]
\[ \Delta t = 4 \]

(b) \[ t = 72 \]
\[ t = 128 \]