FINITE AMPLITUDE SOUND NEAR THE CRITICAL POINT

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The problem is considered of sound propagation near the lamination curve of a liquid-vapor system. It is shown that the problem becomes nonlinear as the critical point is approached for small amplitudes. The shape and propagation velocity of the shock waves produced are found.

THE problem of sound propagation in matter in a state close to a phase transition is one of the fundamental problems in the theory of phase transitions. Inasmuch as anomalies appear in thermodynamic quantities near transitions in such systems, one can expect that sound propagation in them will possess a number of singularities. An appreciable number of works have been devoted to its study; however, sound of small amplitude is generally considered. In the case of finite amplitudes near phase transitions, specific singularities appear in the sound propagation. In particular, these phenomena exist for first-order phase transitions of the liquid-vapor type. We shall consider a one-component system near the lamination curve for two phases. Let the wavelength be large in comparison with the dimensions of the inhomogeneities (vapor bubbles) of the two-phase system. Because of the great difference in the specific volumes of the phases, the compressibility of such a system, and consequently its sound velocity, can be greatly different from the compressibility in any single phase.[1,2]

It was shown by Landau and Lifshitz[1] that the sound velocity in a liquid with a small number of vapor bubbles is determined by the following expression:

$$\frac{1}{c^2}=\frac{1}{V_1^2}\left[-\left(\frac{\partial V_1}{\partial P}\right)_T-\frac{2T}{r}\left(\frac{\partial V_1}{\partial T}\right)_P(V_2-V_1)+\frac{c_{P1}T}{r^2}(V_2-V_1)^2\right] \tag{1}$$

(here V is the specific volume, r the heat of vaporization, c_{P_1} the specific heat, and the indices 1 and 2 refer respectively to the liquid and the vapor), and falls off sharply in comparison with the velocity of sound in a liquid without the vapor. The dependence of the sound velocity of the density is shown in Fig. 1, where c_1 and c_2 are the sound velocities in the liquid and mixture, respectively. The value of the jump in the velocity is usually rather large: $c_2/c_1 \sim 10^{-2}$–10^{-4}; however, it can be expected that for some liquids with weak interaction between the molecules, the difference of c_1 and c_2 will not be very large. The proximity to the critical point of the material has a significant effect on the size of the velocity jump. The difference in the thermodynamic properties of the phases, and consequently of the sound velocities in approach to the discontinuity is diminished. It should be noted, however, that in a sufficiently small circle around the critical point, when the essential fluctuations of the thermodynamic quantities are established, Eq. (1) is not applicable. Comparison of the value of c_2 computed from Eq. (1) with the help of experimental data,[3] and the value of c_1[4] for methyl and ethyl alcohols at $(T_c - T)/T_c \approx (2$–$4) \times 10^{-2}$ gives $c_2/c_1 \approx 0.25$–0.5, and for heptane and hexane, $c_2/c_1 \approx 0.1$–0.3. The velocity of sound undergoes jumps also in the formation of liquid droplets in the vapor.

The difference in the sound velocities leads to the result that the linear theory of sound becomes inapplicable even at rather small amplitudes of the sound waves. Actually, the density oscillations can lead to a transition of the single phase system into a two-phase one, and the speed of sound will thus not be a constant. Investigation of the propagation of sound of finite amplitude in a system with an initial state close to the lamination curve is carried out in this research. It is assumed that the liquid is inviscid.

Let the system be a liquid of density ρ_0, inclosed in a tube bounded on one side by a piston capable of carrying out oscillatory motion, and unbounded on the other.

At the initial instant of time, the liquid is at rest and is homogeneous, so that the entropy is a constant throughout the liquid. If the sound frequency is sufficiently small, i.e., if the period of the sound wave is much larger than the time within which the phase transition takes place, then the system will be in virtual thermodynamic equilibrium, and the entropy will be a constant at lead up to the formation of a surface of discontinuity. We find the order of the frequency necessary for satisfying this condition. As Zel'dovich has shown,[5] the time of establishment of an equilibrium distribution of vapor bubbles of critical size can be roughly estimated from the formula $t = R_{cr}^4 n_0^2/\alpha$, where R_{cr} is the radius of a bubble of critical size, n_0 the concentration of the vapor in it and α the mean number of molecules of liquid vaporized per second per square centimeter of bubble surface. In the normal state, the time t is rather large; however, as one approaches the critical point, it decreases appreciably. In the case $(T_c - T)/T_c \sim 10^{-2}$ and $\delta P/P \sim 10^{-2}$ (here δP is the departure of the pressure in the metastable phase from the pressure for which the temperature of the system is a phase transition point) for methyl alcohol and hexane, for example, estimate gives the criterion $\omega \ll 10^5$ Hz for the possible frequencies. In reality, there factors that guarantee boiling (impurities, dissolved gas, etc) are always present in a liquid.

On the other hand, the period of acoustic oscillations should be small in comparison with the time of lamination of the phases. It is easy to show that there exists a region of frequencies which satisfies this condition.

We assume that the piston moves according to the law $X = A \cos \omega t$ and its velocity of motion is $|v|$

$\ll c_2, c_1$. In this case the amplitudes of the waves formed in the system will be small and therefore the values of the discontinuities which can be formed in the system will also be small. Inasmuch as we shall consider weak shock waves in what follows, we can assume that the entropy and the related Riemann invariant do not change; [6] therefore, the relation

$$v - l = v_0 - l_0, \text{ where } l = \int_{\rho_1}^{\rho} \frac{c(\rho)}{\rho} d\rho, \tag{2}$$

and the index 0 pertains to the initial state of the system, is satisfied for the velocity of motion of the medium. Here the index zero refers to the initial state of the system.

At the beginning of the motion, the liquid was at rest, i.e., $v_0 = 0$ for $\rho = \rho_0$; therefore,

$$v = l - l_0 = \int_{\rho_1}^{\rho} \frac{c(\rho)}{\rho} d\rho - \int_{\rho_1}^{\rho_0} \frac{c(\rho)}{\rho} d\rho = \int_{\rho_0}^{\rho} \frac{c(\rho)}{\rho} d\rho. \tag{3}$$

Taking for $c(\rho)$ the dependence sketched in Fig. 1 and assuming $\rho' = \rho - \rho_0 \ll \rho_0$, we get the following expression for the velocity of motion of the medium:

$$\begin{aligned} v &= c_1\rho'/\rho_0 \quad \text{for} \quad \rho > \rho_b \\ v &= c_2\rho'/\rho_0 + (c_2 - c_1)\Delta/\rho_0 \quad \text{for} \quad \rho < \rho_b \end{aligned} \tag{4}$$

Here $\Delta = \rho_b - \rho_0$ characterizes the closeness of the initial state to the lamination curve. Using (4), we express ρ' as a function of the velocity of motion of the medium

$$\begin{aligned} \rho' &= \rho_0 v/c_1 \quad \text{for} \quad v > v_b = -c_1\Delta/\rho_0, \\ \rho' &= v\rho_0/c_2 + (c_1 - c_2)\Delta/c_2 \quad \text{for} \quad v < v_b. \end{aligned} \tag{5}$$

The velocity of the piston $v = -A\omega \sin \omega t$; hence the dependence of ρ' on the time at the piston will have the form shown in Fig. 2.

We consider the propagation of a wave corresponding to motion of the piston from $t = 0$ to $t = 2\pi/\omega + \tau_0$, where $\tau_0 = (1/\omega)\sin^{-1}(v_b/A\omega)$. Excitations $\rho > \rho_b$ will be propagated with velocity c_1 inasmuch as for this case the medium is a liquid, and excitations $\rho < \rho_b$ will propagate with velocity c_2, since this is a two-phase medium. A rarefaction wave W_1 having the shape corresponding to a change of t from zero to τ_0 (Fig. 2) will be propagated in the system with velocity c_1; it will be followed by a rarefaction wave W_2 corresponding to $\tau_0 < t < \pi/\omega - \tau_0$ with velocity c_2, and in turn by a wave W_3 with velocity c_1 and corresponding to

$$\frac{\pi}{\omega} - \tau_0 < t < \frac{2\pi}{\omega} + \tau_0.$$

It is obvious that the wave W_2 will fall behind W_1 and a region is formed between them with constant density ρ_b and velocity of motion v_b. The wave W_3 will overtake

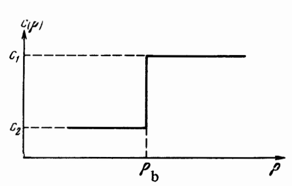

FIG. 1. Dependence of sound velocity $c(\rho) = [(\partial P/\partial \rho)_S]^{1/2}$ on the density of the medium. The lamination curve corresponds to $\rho = \rho_b$.

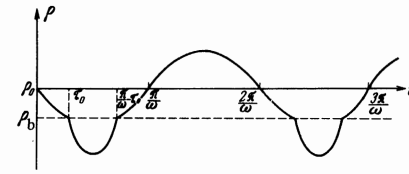

FIG. 2. Density on the piston as a function of the time.

the wave W_2, as a result of which a shock wave is formed.

In view of the smallness of the amplitude, we ascribe constant entropy and a constant Riemann invariant to the flow before and after the shock wave. Flow with constant entropy and Riemann invariant is a simple wave, [7] and in this approximation, the shock wave does not influence the simple wave; therefore, we shall disregard reflection from the shock front.

The equation of motion of the simple wave created by the piston (which moves according to the law $X(t) = A \cos \omega t$) is

$$x = A \cos \omega\tau + (t - \tau)[c(\rho) + v(\tau)], \tag{6}$$

where τ is the time of formation of the density ρ at the piston. Inasmuch as the velocity of motion of the medium is $|v| \ll c_2, c_1$, we shall neglect it in what follows in comparison with the speed of sound.

The upper and lower boundaries of the density jump in the shock wave at the point x should belong simultaneously to the corresponding simple waves which exist to the right and left of the jump. Moreover, it is necessary to satisfy the condition of continuity of matter flow through the discontinuity moving with velocity U relative to a fixed system of coordinates:

$$\rho_1(v_1 - U) = \rho_2(v_2 - U). \tag{7}$$

Here and below we shall denote by the indices 1 and 2 quantities corresponding to the waves W_3 and W_2.

Inasmuch as the boundaries of the jump $\rho_1 = \rho_0 + \rho_1'$ and $\rho_2 = \rho_0 + \rho_2'$ will change according to the motion of the shock front, the parameters τ corresponding to them will also depend on the time. Using (5), (6), and (7), we write down the equations for the motion and the magnitude of the jump:

$$\begin{gathered} x = A \cos \omega\tau_1(t) + [t - \tau_1(t)]c_1, \\ x = A \cos \omega\tau_2(t) + [t - \tau_2(t)]c_2, \\ dx/dt = U, \\ \left(1 + \frac{v_1}{c_1}\right)(v_1 - U) = \left(1 + \frac{v_2}{c_2} + \frac{c_1 - c_2}{c_2}\frac{\Delta}{\rho_0}\right)(v_2 - U), \end{gathered} \tag{8}$$

where x is the coordinate of the discontinuity. One can write down two equations corresponding to the conservation of momentum flow and energy flow, whence the jumps in pressure and temperature are determined. However, inasmuch as we are interested only in the shape and velocity of motion of the shock wave, the system (8) is sufficient. Differentiating the first and second equations of the system with respect to time and omitting in the third equation terms of the next order of smallness in the ratio v/c, we get

$$\begin{gathered} U = -A\omega\tau_1' \sin \omega\tau_1 + (1 - \tau_1')c_1, \\ U = -A\omega\tau_2' \sin \omega\tau_2 + (1 - \tau_2')c_2, \\ \left(1 - \frac{U}{c_1}\right)\sin \omega\tau_1 = \left(1 - \frac{U}{c_2}\right)\sin \omega\tau_2 + U\frac{c_1 - c_2}{c_1 c_2}\sin \omega\tau_0. \end{gathered} \tag{8'}$$

By solving this set of equations relative to $\tau_1(t)$, $\tau_2(t)$, and U, we determine the shape, velocity of motion, and place of the discontinuity at any instant of time. One can show that terms of the form $A\omega\tau' \sin\omega\tau$ in the first and second equations of the system (8′) give small corrections of the order of v/c to the solution; therefore, they can be neglected in first approximation. As a result, the system (8′) is written in the form

$$U = (1-\tau_1')c_1, \quad U = (1-\tau_2')c_2,$$
$$\left(1-\frac{U}{c_1}\right)\sin\omega\tau_1 = \left(1-\frac{U}{c_2}\right)\sin\omega\tau_2 + U\frac{c_1-c_2}{c_1c_2}\sin\omega\tau_0. \tag{9}$$

Solving the set of equations (9) with account of the initial conditions at the discontinuity ($\tau_1 = \tau_2 = t$), we get the following expressions for τ_1 and τ_2:

$$\tau_1 = c_2\tau_2/c_1 + (c_1-c_2)t/c_1, \tag{10}$$

$$\sin(\omega\tau_2 + z)\sin z = z\sin\omega\tau_0, \tag{11}$$

where $z = (\omega/2c_1)(c_1 - c_2)(t - \tau_2)$.

At first we consider the special case of the system (9) in which $\sin\omega\tau_0 \approx 0$. This corresponds to amplitudes of oscillation of the density that are large in comparison with $\Delta = \rho_b - \rho_0$, or $\Delta = 0$. The discontinuity arises for $\tau_1 = \tau_2 = \pi/\omega$. We represent τ_1 and τ_2 in the form

$$\tau_1 = \pi/\omega + \tilde{\tau}_1, \quad \tau_2 = \pi/\omega - \tilde{\tau}_2,$$

and we obtain the following from (9) and (3), taking the initial conditions at the discontinuity into account:

$$\tilde{\tau}_1 = \tilde{\tau}_2 = \frac{c_1-c_2}{c_1+c_2}\left(t-\frac{\pi}{\omega}\right),$$
$$U = \frac{2c_1c_2}{c_1+c_2},$$
$$\rho_1' = \frac{A\omega\rho_0}{c_1}\sin\left[\frac{c_1-c_2}{c_1+c_2}(\omega t-\pi)\right], \tag{12}$$
$$\rho_2' = -\frac{A\omega\rho_0}{c_2}\sin\left[\frac{c_1-c_2}{c_1+c_2}(\omega t-\pi)\right],$$
$$x = \frac{2c_1c_2}{c_1+c_2}\left(t-\frac{\pi}{\omega}\right).$$

It is seen from (12) that the shock wave will propagate with constant velocity, while the magnitude of the jump at first increases, reaching a maximum $\rho_1 - \rho_2 = A\omega\rho_0(c_1 + c_2)/c_1c_2$ at the instant of time

$$t_1 = \frac{\pi}{2\omega}\,\frac{3c_1-c_2}{c_1-c_2}$$

and then decreases to zero at the time

$$t_2 = \frac{2\pi}{\omega}\,\frac{c_1}{c_1-c_2}.$$

Thus, at the time t_2 at a distance

$$x_0 = \frac{2c_1c_2}{c_1+c_2}\left(t_2-\frac{\pi}{\omega}\right) = \frac{2\pi}{\omega}\,\frac{c_1c_2}{c_1-c_2}$$

the waves W_2 and W_3 completely cancel each other and there are no waves when $x > x_0$. Depending on the relation of the quantities c_1 and c_2 in the system for oscillations of the piston, several shock waves can exist at the distance $0 \le x \le x_0$. The value of the n-th discontinuity and its position will be determined by Eqs. (12), with the replacement of t by $t - (n-1)\pi/\omega$.

In the case $\sin\omega\tau_0 \sim 1$, i.e., when the deviations of the density from the initial value are of the order of the distance Δ from the lamination curve, Eq. (11) can be solved graphically. The form of this solution is shown in Fig. 3. For $\tau_2 = \pi/\omega - \tau_0$, we have $z = 0$, i.e., $t = \pi/\omega - \tau_0$. With decrease of τ_2, the value of z increases. However, it is evident from the definition of the parameters τ that τ_2, which corresponds to $\rho < \rho_b$, cannot be less than τ_0 and at the instant of the disappearance of the wave W_2, the equality $\tau_2 = \tau_0$ should be satisfied. Using Eq. (11), we determine this instant:

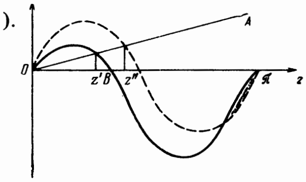

FIG. 3. Graphic solution of Eq. (11). The line OA corresponds to the right side of the equation, and the curves to the left. The dashed curve corresponds to the smaller value of τ_2; z′ and z″—solution of equation for various τ_2; the segment OB equals $\pi-\omega\tau_2$.

$$t_0 = \frac{2z_0}{\omega}\,\frac{c_1}{c_1-c_2} + \tau_0, \tag{13}$$

where z_0 is the solution of Eq. (11), which corresponds to $\tau_2 = \tau_0$. The parameter τ_{10}, which corresponds to the upper boundary of the discontinuity at the time t_0, is determined from (10) and (13):

$$\tau_{10} = \frac{2z_0}{\omega} + \tau_0. \tag{14}$$

For $\tau \neq 0$, $\tau_{10} < 2\pi/\omega$, inasmuch as the solution of Eq. (11) gives $z < \pi - \omega\tau_2$, as is seen from Fig. 3.

Thus, at the time t_0, the two-phase region disappears and the remaining wave is determined by Eq. (4) with

$$\frac{2z_0}{\omega} + \tau_0 \leqslant \tau_1 \leqslant \frac{2\pi}{\omega} + \tau_0$$

and propagates in the medium with density $\rho = \rho_b$. The speed of the front of this wave U at the time t_0 is easily determined from the third equation of the set (9). It turns out that $U = c_1$; this means that for further motion the shape of the wave will be unchanged, inasmuch as the simple wave following the discontinuity will be propagated with the same velocity. Of course, this is a consequence of our approximation. If we do not neglect v_1 in Eq. (4) in comparison with c_1, then ordinary spreading of the shock wave appears.

The process considered above will be repeated periodically; therefore, in the final analysis, the picture will be the following: When

$$x < \frac{2z_0}{\omega}\,\frac{c_1c_2}{c_1-c_2}$$

shock waves will exist of the type described by Eqs. (10) and (11). Their number is determined by the value of t_0 and is equal to the integral part of $\omega(t_0 - \tau_0)/2\pi$. When

$$x > \frac{2z_0}{\omega}\,\frac{c_1c_2}{c_1-c_2}$$

the two-phase state does not exist and we have periodically repeated shock waves of constant shape, which are propagated with the speed c_1 (Fig. 4).

We now consider the question of energy balance in more detail. In the case of sound of large amplitude

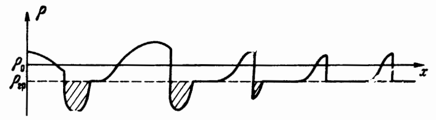

FIG. 4. Schematic representation of waves propagating in a system at a certain instant of time. The regions of phase-mixture existence are shown shaded.

$A\omega\rho_0/c_1 \gg \Delta$, the established waves have amplitudes much smaller than $A\omega\rho_0/c_1$ (the maximal amplitude on the piston). This means that the work done by the piston on the system in one period is very small. We shall not consider here the growth of entropy at the discontinuity, inasmuch as it has a value of third order of smallness in the amplitude and lies outside the limits of our accuracy.

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