# A Fundamental Derivative in Gasdynamics

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# A Fundamental Derivative in Gasdynamics

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The quantity which is here called the fundamental derivative has been defined as the nondimensional form $\Gamma \equiv \frac{1}{2}\rho^3 c^4 (\partial^2 \mathcal{V}/\partial P^2)_s$. The relation of $\Gamma$ to other thermodynamic variables is discussed. It is already known that the existence of conventional compression shocks requires $\Gamma > 0$. It is shown that other dynamic behavior of compressible fluids is fixed by the sign of $\Gamma$. Particular emphasis is given to phenomena corresponding to negative $\Gamma$. These phenomena include the area variation of a transonic passage, the form of a Prandtl–Meyer wave, the behavior of adiabatic flow with friction, and nonlinear wave propagation. Formulas and numerical values are given for $\Gamma$ in various substances.

## I. INTRODUCTION

The curvature of an isentrope drawn in the pressure/specific-volume plane corresponds to the derivative $(\partial^2 \mathcal{V}/\partial P^2)_s$. It is the purpose of this paper to discuss the crucial effect of this thermodynamic property on the dynamic behavior of compressible fluids.

It has been known for some time that the existence of *compression* shockwaves (i.e., the normal kind) is associated with the condition

$$\left(\frac{\partial^2 \mathcal{V}}{\partial P^2}\right)_s > 0. \tag{1}$$

Conversely, the possibility of rarefaction shock waves is associated with its violation. The importance of this condition has been discussed by Duhem,[1] Bethe,[2] Weyl,[3] Courant and Friedrichs,[4] and others. The basic behavior of shock waves thus depends on the *sign* of $(\partial^2 \mathcal{V}/\partial P^2)_s$. This derivative also appears in other roles, however, as will be discussed in following sections.

Following Hayes[5,6] and Landau and Lifshitz,[7] it is quite useful to write the derivative in the nondimensional form

$$\Gamma \equiv \frac{c^4}{2\mathcal{V}^3}\left(\frac{\partial^2 \mathcal{V}}{\partial P^2}\right)_s, \tag{2}$$

where $c$ is the sound speed. The symbol $\Gamma$ is the one used by Hayes. To the author's knowledge, this form was first used (omitting the factor $\frac{1}{2}$) by Landau.[8] In acoustics this quantity appears in the form $2(\Gamma-1)$, as discussed in Sec. VII.

Conventional treatments of gasdynamics assume $\Gamma > 0$, either explicitly or implicitly: The consequent gasdynamical behavior is well known. In this paper some emphasis will be put on the bizarre behavior of fluids for which $\Gamma < 0$. Bethe[2] and Zel'dovich and Raizer[9] have speculated on the possible existence of such substances. In particular, the latter authors find that $\Gamma < 0$ for a van der Waals substance in the vapor phase near the saturation line, at pressures somewhat below the critical pressure. In addition, they point to the peculiar behavior of shocks at a solid–solid (polymorphic) phase transition where $(\partial \mathcal{V}/\partial P)_s$ is discontinuous in such a way that $(\partial^2 \mathcal{V}/\partial P^2)_s = -\infty$. Rarefaction shocks in iron and steel, corresponding to such a phase transition, were reported to have been experimentally observed by Ivanov and Novikov.[10] Bethe[2] also discussed the behavior of shocks at phase boundaries. In this paper, however, we will be concerned only with single-phase substances.

## II. THERMODYNAMICS OF $\Gamma$

The sound speed $c$ is defined by

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s = -\mathcal{V}^2\left(\frac{\partial P}{\partial \mathcal{V}}\right)_s > 0, \tag{3}$$

where $\rho$ is the density. This quantity is necessarily positive by the requirement for mechanical stability.

TABLE I. Behavior of fluid properties along an isentrope for various values of $\Gamma$.

| $\Gamma$ | Behavior |
|---|---|
| $\Gamma > 1$ | Soundspeed increases with $P$; behavior of usual substances. |
| $\Gamma = 1$ | Constant soundspeed; $P$ a linear function of $\rho = 1/\mathcal{V}$. |
| $0 < \Gamma < 1$ | Soundspeed decreases with $P$. |
| $\Gamma = 0$ | $P$ a linear function of $\mathcal{V}$. |
| $\Gamma < 0$ | Negative curvature of isentrope; behavior of unusual substances. |

Normal thermodynamic manipulations yield the following identities:

$$c^2 = -\mathcal{V}^2\left[\left(\frac{\partial P}{\partial \mathcal{V}}\right)_T - \frac{T}{c_\mathcal{V}}\left(\frac{\partial P}{\partial T}\right)_\mathcal{V}^2\right], \tag{4}$$

$$\Gamma \equiv \frac{c^4}{2\mathcal{V}^3}\left(\frac{\partial^2 \mathcal{V}}{\partial P^2}\right)_s = \frac{\mathcal{V}^3}{2c^2}\left(\frac{\partial^2 P}{\partial \mathcal{V}^2}\right)_s = c^{-1}\left(\frac{\partial \rho c}{\partial \rho}\right)_s, \tag{5}$$

$$\Gamma - 1 = \frac{c}{\mathcal{V}}\left(\frac{\partial c}{\partial P}\right)_s = \frac{c}{\mathcal{V}}\left(\frac{\partial c}{\partial P}\right)_T + \frac{cT}{\mathcal{V}c_P}\left(\frac{\partial \mathcal{V}}{\partial T}\right)_P\left(\frac{\partial c}{\partial T}\right)_P, \tag{6}$$

where symbols have the usual meanings. The last form of Eq. (5) was given by Hayes.[6] Equations (4) and (6) allow the calculation of $\Gamma$ from $P\mathcal{V}T$ and specific heat data.

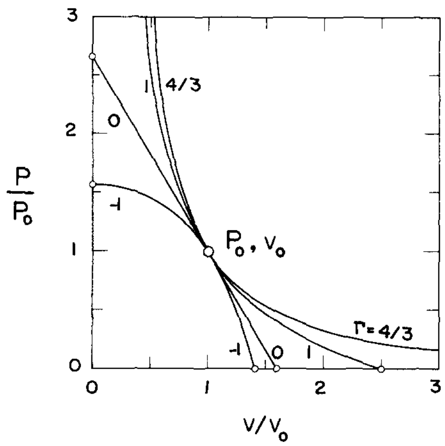



FIG. 1. Isentropes in the $P\mathcal{V}$ plane for various (constant) values of $\Gamma$, with a common value of the sound speed at some reference state $P_0$, $\mathcal{V}_0$.

For a perfect gas (i.e., an ideal gas with constant specific heats) the above formulas give a constant value

$$\Gamma=\tfrac{1}{2}(\gamma+1) \qquad \text{(perfect gas)}, \tag{7}$$

where $\gamma\equiv c_P/c_{\mathcal{V}}$ is the (constant) ratio of specific heats. Since $\frac{5}{3}\geq\gamma\geq1$, we necessarily have $\frac{4}{3}\geq\Gamma\geq1$ for this case. Thus we can describe a perfect gas as a fluid with constant $\Gamma>1$. For many fluids, the value $\Gamma\gtrsim1$ may be considered typical.

The behavior of $\Gamma$ as shown by the identities (3)-(6) is summarized in Table I and illustrated in Fig. 1.

## III. ROLE IN STEADY ISENTROPIC FLOW

Steady isentropic flow is the useful basic model in elementary gasdynamics. We consider, respectively, (i) the relation between velocity and Mach number, (ii) transition from subsonic to supersonic flow, (iii) the limiting Mach number for a fluid with constant $\Gamma<0$, and (iv) Prandtl–Meyer waves in two-dimensional supersonic flow.

The change of velocity $u$ along a streamline in inviscid flow is given by

$$u\,du+\mathcal{V}\,dP=0. \tag{8}$$

With $\mathcal{V}\,dP=c\,dc/(\Gamma-1)$ from Eq. (6), this becomes

$$u\,du+[c\,dc/(\Gamma-1)]=0.$$

With the Mach number $M=u/c$ this gives

$$\frac{du}{u}=\frac{dM/M}{1+(\Gamma-1)M^2}. \tag{9}$$

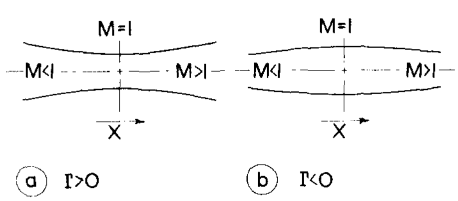



FIG. 2. Throat geometry for transition from subsonic to supersonic flow, or vice versa.

Thus, the Mach number increases monotonically with velocity for all Mach numbers only if $\Gamma>1$. This is, of course, the behavior of usual fluids. If $\Gamma<1$, the Mach number increases with velocity only for $M^2<1/(1-\Gamma)$.

For quasi-one-dimensional flow in a pipe or stream tube of cross-sectional area $A(x)$, where $x$ is the coordinate in the flow direction, the equations of momentum and continuity are

$$\rho u\frac{du}{dx}+\frac{dP}{dx}=0, \qquad \frac{d}{dx}(\rho uA)=0.$$

With $dP=c^2d\rho$, these may be combined to give

$$u^{-1}\frac{du}{dx}=(M^2-1)A^{-1}\frac{dA}{dx} \tag{10}$$

which is often used to describe the different behavior of subsonic ($M<1$) and supersonic ($M>1$) flows. With the substitution of Eq. (9) this yields

$$M^{-1}\frac{dM}{dx}=\frac{1+(\Gamma-1)M^2}{M^2-1}A^{-1}\frac{dA}{dx}. \tag{11}$$

Transition from subsonic to supersonic flow (or vice versa) through $M=1$ can only occur where $dA/dx=0$,

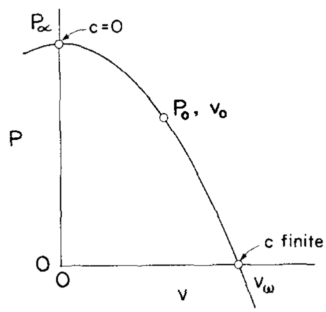



FIG. 3. Isentrope for a fluid with constant $\Gamma<0$.

i.e., the right side must be of the form 0/0. With l'Hospital's rule we obtain

$$\left(\frac{dM}{dx}\right)^2=\frac{\Gamma}{2A}\frac{d^2A}{dx^2}\geq0. \tag{12}$$

Depending on whether $\Gamma$ is positive or negative, this gives the types of area variation shown in Fig. 2. The conventional "throat" for $\Gamma>0$ shown is a well-known feature of supersonic nozzles, for example.

Consider a fluid accelerated from a state of rest, denoted by the stagnation state $P_0$, $\mathcal{V}_0$. For a perfect gas, the fluid Mach number $M$ is given in terms of the local (static) thermodynamic state by well-known formulas.[11] In the notation of this paper, such a relation is

$$M^2=(\Gamma-1)^{-1}[(\mathcal{V}/\mathcal{V}_0)^{2(\Gamma-1)}-1]. \tag{13}$$

Since such a gas will expand isentropically to infinite volume (at zero pressure), the maximum Mach number is infinite, $M_{\max}=\infty$. While the corresponding velocity $u_{\max}$ is finite, the sound speed is zero.

It is of interest to find the corresponding expression for a fluid with constant $\Gamma<0$. (It should be remarked, however, that a *constant* $\Gamma<0$ does not correspond to the expected physical behavior of fluids for which $\Gamma<0$.) The isentrope is shown in Fig. 3 and is given by the equation

$$P/P_\alpha = 1-(\mathcal{V}/\mathcal{V}_\omega)^{1-2\Gamma}. \tag{14}$$

Using this, integration of Eq. (8) yields

$$u^2 = -2\int_{P_0}^{P} \mathcal{V}\, dP = \frac{1-2\Gamma}{1-\Gamma} P_\alpha \mathcal{V}_\omega \times \left[\left(\frac{\mathcal{V}}{\mathcal{V}_\omega}\right)^{2(1-\Gamma)} - \left(\frac{\mathcal{V}_0}{\mathcal{V}_\omega}\right)^{2(1-\Gamma)}\right].$$

The local sound speed from Eq. (3) is

$$c^2 = (1-2\Gamma) P_\alpha \mathcal{V}_\omega (\mathcal{V}/\mathcal{V}_\omega)^{2(1-\Gamma)}.$$

These equations then give for $M^2 = u^2/c^2$

$$M^2 = (1-\Gamma)^{-1}[1-(\mathcal{V}_0/\mathcal{V})^{2(1-\Gamma)}] \tag{15}$$

which is formally identical to Eq. (13) for a perfect gas. The interpretation is different, however; since $\mathcal{V}_0/\mathcal{V}$ has a minimum value of zero (corresponding to $\mathcal{V}_0=0$ or $\mathcal{V}=\infty$, the latter condition achieved only at negative pressures), the maximum Mach number is finite,

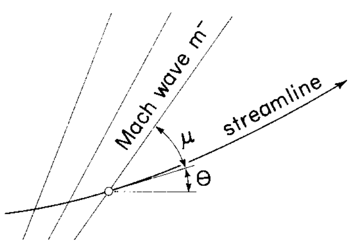



FIG. 4. Flow plane geometry for (simple) Prandtl–Meyer waves.

$M_{\max} = 1/(1-\Gamma)^{1/2}$. Thus, a fluid with constant $\Gamma<0$ cannot be continuously accelerated from rest to supersonic speed. Presumably, however, real processes exist which will allow the value $M_{\max}$ to be exceeded (e.g., unsteady flow, physical Galilean transformation).

The turning of a homentropic supersonic flow via Prandtl–Meyer waves is well-known.[12] We now examine the role of $\Gamma$ in such a process. Consider simple "left-running" or $m^-$ waves (Fig. 4): for such waves it follows from the theory of characteristics that

$$\theta+\omega = \text{const everywhere}, \tag{16}$$

where $\omega$ is the Prandtl–Meyer function defined by $d\omega \equiv (M^2-1)^{1/2} du/u$: with Eq. (9),

$$d\omega = \frac{(M^2-1)^{1/2}}{1+(\Gamma-1)M^2}\frac{dM}{M}. \tag{17}$$

Note that $M^2>1$ for supersonic flow. The $m^-$ waves are inclined to the horizontal at angle $\theta+\mu$, where $\theta$ is the local streamline angle and $\mu$ is the Mach angle, $\mu \equiv \sin^{-1} 1/M$. Now the condition for continuous isentropic turning to be maintained is that the waves diverge

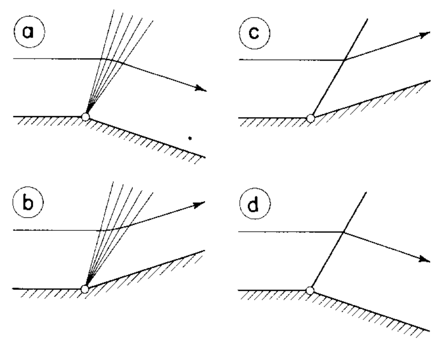



FIG. 5. Simple waves at a sharp corner. (a) Centered rarefaction, $\Gamma>0$ and $d\theta<0$. (b) Centered compression, $\Gamma<0$ and $d\theta>0$. (c) Oblique compression shock, $\Gamma>0$. (d) Oblique rarefaction shock, $\Gamma<0$.

(convergent waves result in shock formation). This condition can be written

$$d(\theta+\mu)<0 \tag{18}$$

along a streamline in the sense of the flow direction. With Eqs. (16) and (17) this becomes

$$d\theta+d\mu = [\Gamma M^2/(M^2-1)]d\theta<0 \tag{19}$$

which is satisfied if $\Gamma\, d\theta$ is negative. This leads to centered Prandtl–Meyer waves, for example, of the types shown in Figs. 5(a) and (b). For $\Gamma>0$, it is a conventional centered rarefaction wave; for $\Gamma<0$, it is a centered compression wave. (It has been assumed that $\Gamma$ does not change sign across the wave.) Violation of Eq. (19) leads to shocks as shown in Figs. 5(c) and (d); the behavior of such shocks is discussed in Sec. V.

## IV. ROLE IN STEADY DUCT FLOW WITH FRICTION

A very simple model for steady flow of a compressible fluid in a constant-area duct treats the duct walls as adiabatic and the flow as quasi-one-dimensional (that is, properties are uniform at any given cross section).[13] Such a flow is sketched in Fig. 6.

The energy equation for the flow is

$$h+\tfrac{1}{2}u^2 = h_0 = \text{const},$$

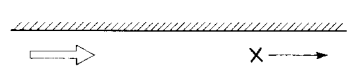
where $h$ is the specific enthalpy. With the mass flux $J=u/\mathcal{V}=\text{const}$, this is written

$$h+\tfrac{1}{2}J^2\mathcal{V}^2 = h_0 = \text{const}. \tag{20}$$

This defines a parabola (sometimes called a Fanno line) in the thermodynamic $h\mathcal{V}$ plane, as shown in Fig. 7(a). The second law of thermodynamics requires that entropy can only be created in any given region or

$$\frac{ds}{dx} \geq 0. \tag{21}$$

FIG. 6. Constant-area duct.



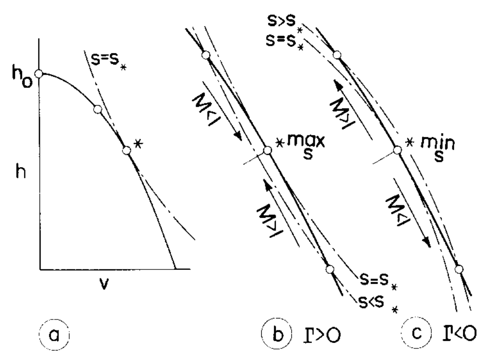



FIG. 7. (a) Fanno line in the $h\mathcal{V}$ plane. (b) Neighborhood of the sonic point, case $\Gamma>0$. (c) Neighborhood of the sonic point, case $\Gamma<0$.

Together with the properties of the particular fluid, this condition fixes the sense in which a point representing the local state of the fluid moves along the Fanno line given by Eq. (20); i.e., it must move in the sense of increasing entropy.

For any given values of the parameters $h$ and $J$ there will be some point on the Fanno line at which an isentrope is tangent; this point is marked with a star (*) in Fig. 7(a). At such a point

$$\left(\frac{dh}{d\mathcal{V}}\right)_F=\left(\frac{\partial h}{\partial\mathcal{V}}\right)_s.$$

With $(dh/d\mathcal{V})_F=-u^2/\mathcal{V}$ from Eq. (20) and $(\partial h/\partial\mathcal{V})_s=-c^2/\mathcal{V}$ from thermodynamics, this gives $u^*=c^*$. That is, the point (*) at which the entropy is stationary is a sonic point for the flow. The following arguments are confined to the neighborhood of this polnt.

It remains to determine whether point (*) is a point of maximum or minimum entropy. In the former case, a point representing the local state will move toward (*); in the latter case it will move away from (*). The magnitude of $(\partial^2h/\partial\mathcal{V}^2)_s$ determines the issue. Shown in Fig. 7(b) is the case

$$\left(\frac{\partial^2 h}{\partial\mathcal{V}^2}\right)_s>\left(\frac{d^2h}{dv^2}\right)_F$$

for which (*) is a point of maximum entropy. By differentiation of $(\partial h/\partial\mathcal{V})_s=-c^2/\mathcal{V}$ and Eq. (20), this condition reduces to simply $\Gamma>0$. Similarly, the case $(\partial^2h/\partial\mathcal{V}^2)_s<(d^2h/dv^2)_F$ shown in Fig. 7(c) corresponds to $\Gamma<0$ and (*) is a point of minimum entropy. Thus,

$\Gamma>0\leftrightarrow$ (*) is a point of maximum entropy,

$\Gamma<0\leftrightarrow$ (*) is a point of minimum entropy.

The local flow is subsonic if $u<c$ and supersonic if $u>c$. By the same reasoning as that which leads to finding (*) a sonic point, these conditions correspond to the relative slopes of the isentrope and the Fanno curve, as follows:

$$\left(\frac{\partial h}{\partial\mathcal{V}}\right)_s<\left(\frac{dh}{d\mathcal{V}}\right)_F\leftrightarrow u<c\ (M<1),$$

$$\left(\frac{\partial h}{\partial\mathcal{V}}\right)_s>\left(\frac{dh}{d\mathcal{V}}\right)_F\leftrightarrow u>c\ (M>1).$$

This correspondence leads to the labels shown in Figs. 7(b) and (c).

We can summarize the above results: If $\Gamma>0$, the effect of friction is to drive the Mach number toward unity; if $\Gamma<0$, the effect of friction is to drive the Mach number away from unity. The statement for $\Gamma>0$ is the one found in standard books about gasdynamics.[14]

In arriving at the above conclusions, we have assumed the crucial condition

$$\left(\frac{\partial s}{\partial h}\right)_{\mathcal{V}}>0. \tag{22}$$

It is of interest that this is precisely Hayes' condition II-strong which guarantees the uniqueness of shock waves.[15] [The appearance of this shock stability condition here is not too surprising, since the frictional Fanno equation (20) and entropy equation (21) correspond to shock conditions.] It is also of interest to note that Hayes' condition II-strong appears in the $h\mathcal{V}$ plane (Fig. 7) simply as

$$\left(\frac{\partial P}{\partial\mathcal{V}}\right)_h<0. \tag{23}$$

Making use of $(\partial P/\partial\mathcal{V})_s=-c^2/\mathcal{V}^2<0$ (i.e., the pressure increases upward along an isentrope), this condition guarantees that pressure increases upward along the Fanno curve. Thus, one finds that $dP/dx>0$ if $\Gamma$ and $M-1$ have the same sign and $dP/dx<0$ if $\Gamma$ and $M-1$ have different signs.

## V. ROLE IN WEAK SHOCK WAVES

Let the states upstream and downstream of a normal shock be denoted by (1) and (2), respectively, as shown in Fig. 8. Let the jump in any quantity $F$ across the shock be denoted by $[F]\equiv F_2-F_1$: in this notation the shock conditions for balance of mass, momentum, energy, and entropy are

$$[\rho w]=0, \tag{24}$$

$$[P+\rho w^2]=0, \tag{25}$$

$$[h+\tfrac{1}{2}w^2]=0, \tag{26}$$

$$[s]\geq 0, \tag{27}$$

where $w$ is the velocity relative to the shockfront.

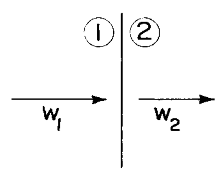



FIG. 8. Normal shock.

It is useful to define the shock strength $\Pi$ as

$$\Pi \equiv [P]/\rho_1 c_1^2 \tag{28}$$

If this value is small compared with unity, the shock is said to be weak; if large compared with unity, the shock is said to be strong. If $\Pi>0$, the shock is called a compression shock (the usual kind): if $\Pi<0$, the shock is called a rarefaction shock. From Eqs. (24) and (25) we find

$$\Pi = -M_1[w]/c_1 = -M_1^2[\mathcal{V}]/\mathcal{V}_1, \tag{29}$$

where $M_1 \equiv w_1/c_1$ is the shock Mach number.

Equations (24)–(26) can be combined to yield the Hugoniot equation,

$$[h] = \mathcal{V}_1[P] + \tfrac{1}{2}[\mathcal{V}][P]. \tag{30}$$

If we consider $h=h(s, P)$ and $\mathcal{V}=\mathcal{V}(s, P)$, in principle this yields a relation for the entropy jump in the form $[s]=f([P])$. Carrying out this operating by means of Taylor series yields

$$[s] = (12T_1)^{-1}\left(\frac{\partial^2\mathcal{V}}{\partial P^2}\right)_s [P]^3 - (24T_1)^{-1} \times \left[T_1^{-1}\left(\frac{\partial T}{\partial P}\right)_s\left(\frac{\partial^2\mathcal{V}}{\partial P^2}\right)_s - \left(\frac{\partial^3\mathcal{V}}{\partial P^3}\right)_s\right][P]^4\cdots,$$

where the coefficients are evaluated at the upstream state (1). A form of this equation was first found by Bethe.[2] Putting it into nondimensional form,

$$T_1[s]/c_1^2 = \tfrac{1}{6}\Gamma_1\Pi^3 + O(\Pi^4). \tag{31}$$

This embodies the well-known result that the entropy jump varies as the third power of the shock strength. Since $[s]\geq 0$, we have the immediate result, for weak shocks at least,

$$\Gamma>0 \leftrightarrow \Pi>0 \qquad \Gamma<0 \leftrightarrow \Pi<0,$$

i.e., only compression shocks are possible in a positive-$\Gamma$ fluid, only rarefaction shocks are possible in a negative-$\Gamma$ fluid.

Let $M_2 \equiv w_2/c_2$ be the downstream Mach number. The basic condition of shock stability is simply $M_1 \geq 1 \geq M_2$. This is satisfied for both positive-$\Gamma$ and negative-$\Gamma$ fluids: suitable Taylor series expansions yield

$$M_1 = 1 + \tfrac{1}{2}\Gamma_1\Pi + O(\Pi^2), \tag{32}$$

$$M = 1 - \tfrac{1}{2}\Gamma_1\Pi + O(\Pi^2) \tag{33}$$

which satisfy the basic condition.

We remark that the results given in this section were already known, in particular, by Zel'dovich and Raizer.[9] Here, only the algebraic forms are new. Note also that compression and rarefaction shocks correspond, respectively to the oblique shocks shown in Figs. 5(c) and (d).

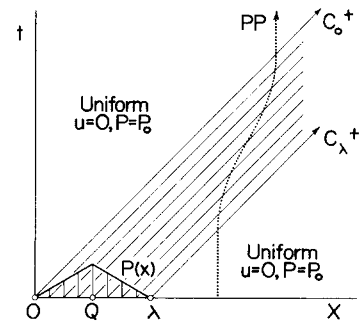



FIG. 9. Wave diagram showing initial pressure wave form.

## VI. ROLE IN SHOCK FORMATION BY PLANE WAVES IN UNSTEADY FLOW

This calculation is similar to that for Prandtl–Meyer waves. For an unsteady one-dimensional homentropic flow in the $x$ direction, the method of characteristics[16] in the space-time $(xt)$ plane gives

$$u - F = \text{constant everywhere} \tag{34}$$

for simple waves moving in the $+x$ direction, where $F \equiv \int dP/\rho c$ depends only on the local thermodynamic state.

Consider an initial pressure waveform moving in the $+x$ direction as shown in Fig. 9. The portion $Q\lambda$ is often called a compression wave and the portion $OQ$ a rarefaction wave (these terms derive from the respective increase or decrease in pressure experienced by a traversing fluid particle). According to simple-wave theory, the value of any property ($P, u, c$, etc.) is constant along a $C^+$ characteristic $dx/dt=u+c$. Where any two characteristics intersect, a shock will form: such intersection will tend to occur whenever $d(u+c)>0$, corresponding to the coalescence of infinitesimal waves, along any path traversing the $C^+$ characteristics from $C_\lambda$ to $C_0^+$ (e.g., the path PP of a fluid particle). From Eq. (34)

$$d(u+c) = du + dc = dF + dc.$$

With $dF = dP/\rho c$ and $dc = (\Gamma-1)dP/\rho c$ from Eq. (6), this becomes

$$d(u+c) = (\Gamma/\rho c)dP. \tag{35}$$

Since $\rho c>0$, characteristics will converge and tend to form shocks when $\Gamma dP>0$. This leads to the statements

$\Gamma>0 \leftrightarrow$ compression waves steepen, rarefaction waves spread out,

$\Gamma<0 \leftrightarrow$ rarefaction waves steepen, compression waves spread out,

$\Gamma=0 \leftrightarrow$ waves have fixed form.

The corresponding qualitative wave diagrams are shown in Fig. 10. We thus find that only compression shocks will form in a positive-$\Gamma$ fluid and only rarefaction shocks will form in a negative-$\Gamma$ fluid. Thus, shocks

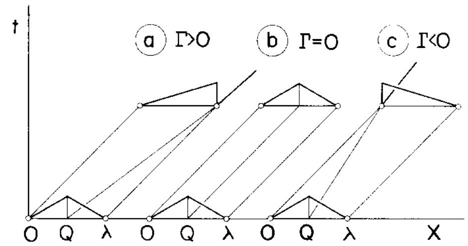



FIG. 10. Qualitative behavior of the wave for various values of the fundamental derivative.

form dynamically according to the same selection rule imposed by the second law of thermodynamics (Sec. V).

It can be verified from the theory of weak shocks that compression or rarefaction shocks formed in this way have the required supersonic/subsonic property.

## VII. VALUES OF Γ FOR COMMON SUBSTANCES

For a perfect gas, the result $\Gamma=\frac{1}{2}(\gamma+1)=$const has already been given. A slightly more general case is the Clausius gas with variable specific heats, defined by the $P\mathcal{V}T$ relation

$$P(\mathcal{V}-b)=RT. \tag{36}$$

This will include the ideal gas ($P\mathcal{V}=RT$, temperature-dependent $\gamma$) as a special case. In any substance for which the $P\mathcal{V}T$ relation is of the form $\mathcal{V}=\mathcal{V}(P/T)$, as above, it can be shown that the internal energy $e$ depends only on temperature. In consequence, one finds that the ratio of specific heats $\gamma$ for a Clausius gas depends only on temperature. Making use of the identity $\gamma(\partial\mathcal{V}/\partial P)_s=(\partial\mathcal{V}/\partial P)_T$ one finds by differentiation of Eq. (36)

$$\left(\frac{\partial\mathcal{V}}{\partial P}\right)_s=-\frac{\mathcal{V}-b}{\gamma P}$$

and with Eq. (3) the soundspeed is given by $c^2=\gamma P\mathcal{V}^2/(\mathcal{V}-b)$. Differentiating the above equation

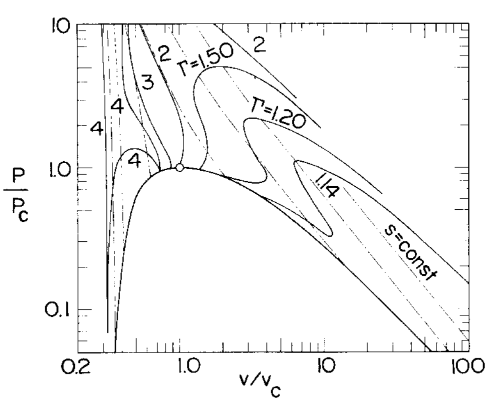



FIG. 11. Values of Γ and isentropes for water shown on a $P\mathcal{V}$ diagram. Pressure and specific volume are normalized by the critical-point values, $P_c=220.9$ bar and $\mathcal{V}_c=3.155$ cm³/g.

again and making use of the identity $(\partial T/\partial P)_s=(\gamma-1)\mathcal{V}^2(\partial T/\partial\mathcal{V})_P c^{-2}$ yields after some algebra

$$\Gamma=\tfrac{1}{2}(\gamma+1)\,\frac{\mathcal{V}}{\mathcal{V}-b}+\frac{\gamma-1}{2\gamma}\,\frac{P\mathcal{V}}{R}\,\frac{d\gamma}{dT}. \tag{37}$$

For an ideal gas this specializes to

$$\Gamma=\tfrac{1}{2}(\gamma+1)+\frac{\gamma-1}{2\gamma}\,T\,\frac{d\gamma}{dT}. \tag{38}$$

Now $d\gamma/dT$ is actually negative for common diatomic and triatomic gases (due to excitation of vibrational modes), and Γ is somewhat decreased from the perfect-gas value $\frac{1}{2}(\gamma+1)$. For $CO_2$ at $T=300$ K, for which $\gamma(T)$ varies rapidly, one finds $\Gamma\approx1.15-0.02=1.13$. There seems little hope of finding a negative-Γ ideal gas! More extensive speculation along these lines is given by Bethe,[2] who suggests the possibility of $\Gamma<0$ for an ionizing monatomic gas at $10^{-44}$ atm!

TABLE II. Values of Γ for liquids at 1 atm and 30°C.

| Substance | Reference | Γ |
|---|---|---|
| Water | 19 | 3.60 |
| Methanol | 20 | 5.81 |
| Ethanol | 20 | 6.28 |
| *l*-Propanol | 21 | 6.2 |
| *n*-Propanol | 20 | 6.36 |
| *n*-Butanol | 20 | 6.36 |
| Mercury | 22 | 4.94 |
| Acetone | 23 | 6.0 |
| Glycerine | 23 | 6.1 |

The behavior of compressed liquids is conveniently and approximately described by the Tait equation[17]

$$(P+B)/B=(\rho/\rho_0)^n \tag{39}$$

reminiscent of the isentrope for a perfect gas, where $B=B(s)$ is often treated as a constant, $n$ is a constant, and $\rho_0$ is a reference density. Straightforward differentiation yields

$$\Gamma=\tfrac{1}{2}(n+1) \tag{40}$$

which is exactly in the form of the expression for a perfect gas. The exponent $n$ is typically in the range 7–11.

Values of Γ for $H_2O$ have been investigated in some detail. The modern thermodynamic data tabulation of Keenan *et al.*[18] is based on the canonical equation of state

$$a=a(T,\mathcal{V}), \tag{41}$$

where $a\equiv e-Ts$ is the specific Helmholtz function. In the above tables, this function is given in a series form containing 83 empirical constants. All thermodynamic properties may be found in terms of the independent variables of a canonical equation of state by suitable differentiation. In the above case, differentiation yields the expression

$$\Gamma = \frac{\mathcal{V} a_{\mathcal{V}T}}{2(a_{\mathcal{V}\mathcal{V}} a_{TT} - a_{\mathcal{V}T}^2)} \frac{\partial}{\partial T}\left(a_{\mathcal{V}\mathcal{V}} - \frac{a_{\mathcal{V}T}^2}{a_{TT}}\right), \quad (42)$$

where the subscript notation has been used for partial derivatives. This function has been evaluated on a digital computer and the result is shown on a $P\mathcal{V}$ diagram in Fig. 11. The behavior at low pressures in the vapor region approximates that of a perfect gas, as expected. In the liquid region, curves of constant $\Gamma$ are roughly coincident to the isentropes, corresponding to the behavior of a Tait liquid. No region of negative $\Gamma$ was found, although the region to the right of the critical point near the phase boundary needs further investigation.

In nonlinear acoustics $\Gamma$ appears in the (constant entropy) Taylor expansion for $P(\rho, s)$ from the undisturbed state $P_0$, $\rho_0$

$$P - P_0 = \left(\frac{\partial P}{\partial \rho}\right)_s (\rho - \rho_0) + \frac{1}{2}\left(\frac{\partial^2 P}{\partial \rho^2}\right)_s (\rho - \rho_0)^2 \cdots$$
$$= A[(\rho-\rho_0)/\rho_0] + \tfrac{1}{2} B[(\rho-\rho_0)/\rho_0]^2 \cdots.$$

The quantity $B/A$ is referred to as the parameter of nonlinearity: in our notation,

$$B/A = 2(\Gamma - 1).$$

This quantity has been determined for many liquids[19–23] primarily by measuring the variation of sound speed with temperature and pressure and making use of Eq. (6). Resulting values for $\Gamma$ are given in Table II.

## VIII. CLOSURE

For fluids with $\Gamma < 0$, the classical results of ordinary gasdynamics are inverted. It may be noted that these results fit together; for example, the existence of rarefaction shocks is consistent with the tendency of rarefaction waves to steepen. Thus, if certain results are inverted, others necessarily follow.

The interest in such phenomena is quite academic, however, if no real fluids with negative $\Gamma$ exist. We believe that such fluids do exist, and will report more specifically in the near future.

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