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Negative nonlinearity in selected fluorocarbons

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The Martin-Hou equation has been employed to compute the fundamental derivative of gasdynamics for seven commercially available fluorocarbons. Each fluid was found to have a region of negative nonlinearity large enough to include the critical isotherm. Negative nonlinearity twice as strong as that found in previous investigations is reported. In addition, estimates for the fundamental derivative at saturation are given.

I. INTRODUCTION

The qualitative behavior of many compressible flows is determined by the fundamental derivative Γ defined by

$$\Gamma = \frac{1}{\rho} \left. \frac{\partial(\rho a)}{\partial p} \right|_s, \quad (1)$$

where ρ is the density, a is the thermodynamic sound speed, and s is the entropy. Other versions of the fundamental derivative have been summarized by Thompson.¹ We also note that Thompson and other authors reserve the symbol Γ for the nondimensional form of (1), viz., $\rho\Gamma/a$. In a simple wave Γ is just the rate of change of the convected sound speed with density. Thus disturbances steepen forward to form compression shocks when $\Gamma > 0$ and steepen backward to form expansion shocks when $\Gamma < 0$. In all that follows we refer to the case $\Gamma > 0$ as that of positive nonlinearity and that where $\Gamma < 0$ as negative nonlinearity. The nonclassical behavior of steady isentropic flows, nozzle flows, pipe flows with friction (Fanno flows), and shock formation with $\Gamma < 0$ have been described by Thompson.¹ When Γ changes sign within a given flow (mixed nonlinearity), new phenomena having no counterpart in the $\Gamma > 0$ theory may be observed. Examples include the partial disintegration of both compression and expansion shocks, sonic shocks, double sonic shocks, and shock splitting; detailed descriptions and further references may be found in Thompson and Lambrakis,² Cramer and Sen,³ and Cramer.^{4,5}

Bethe⁶ and Zel'dovich⁷ were the first to suggest that the fundamental derivative could become negative. The arguments are based on the version of (1) obtained by regarding the sound speed a as a function of temperature and specific volume $V \equiv \rho^{-1}$ rather than density and entropy; the resultant expression for Γ reads

$$\Gamma = \frac{V^4}{2a} \left\{ \frac{\partial^2 p}{\partial V^2} - \frac{3T}{c_v} \frac{\partial p}{\partial T} \frac{\partial^2 p}{\partial V \partial T} + \left(\frac{T}{c_v} \frac{\partial p}{\partial T} \right)^2 \right. \\ \left. \times \left[3 \frac{\partial^2 p}{\partial T^2} + \frac{1}{T} \frac{\partial p}{\partial T} \left(1 - \frac{T}{c_v} \frac{\partial c_v}{\partial T} \right) \right] \right\}, \quad (2)$$

where $c_v = c_v(V, T)$ is the specific heat at constant volume and $p = p(V, T)$ is the pressure. For fluids having a relatively large specific heat we may approximate (2) as

$$\Gamma \approx \frac{V^4}{2a} \frac{\partial^2 p}{\partial V^2}(V, T).$$

It is well known that the isotherms are necessarily concave down in the general neighborhood of the thermodynamic critical point. Thus $\partial^2 p / \partial V^2$ is always negative in this neighborhood. As a result, we expect that fluids with sufficiently large specific heat will have $\Gamma < 0$ in the dense gas region at pressures and temperatures on the order of the critical values. Bethe and Zel'dovich verified these claims with the van der Waals equation of state. The advantage of the van der Waals model is that it is the simplest equation having correct qualitative behavior in the dense gas region. Extensive calculations with realistic equations of state were performed by Lambrakis and Thompson⁸ and Thompson and Lambrakis.² Several examples of fluids in which $\Gamma < 0$ were provided. Furthermore, the general trend toward negative nonlinearity with increasing specific heats was firmly established. Because of the importance of the identification of fluids exhibiting strong negative nonlinearity for the design of experiments and the fact that much of the most interesting behavior, e.g., double sonic shocks and shock splitting, require a negative Γ region of the order of the largest predicted by Thompson and Lambrakis,² the present study seeks to extend the list of negative Γ fluids. The Martin-Hou⁹ equation of state is applied to seven commercially available fluorocarbons and it is shown that the region of negative nonlinearity of each fluid is large enough to include the critical isotherm. We note that only two of the fluids analyzed by Thompson and Lambrakis were found to have $\Gamma < 0$ at critical or supercritical temperatures, at least when the Martin-Hou equation was applied directly. Therefore we feel the present report is a significant addition to the evidence for negative nonlinearity in single-phase gases.

We follow previous investigators^{2,8} in that we restrict our attention to single-phase gases at temperatures and pressures such that near-critical effects can be ignored. In particular, the anomalous near-critical increase in the specific heats cannot be taken into account in the classical approach pursued here. However, we expect that such phenomena will have little direct effect on the present results. For example, the minimum values of $\rho\Gamma/a$ on the critical isotherm tend to occur at densities on the order of two-thirds of the critical value. This finding is also consistent with the conclusions of Thompson and Lambrakis.²

To the extent that the classical theory employed here may be carried over, it appears that both metastable condi-

TABLE I. Summary of calculations. The quantity $Z_c = p_c V_c / RT_c$ is the critical compressibility and $(\rho\Gamma/a)|_\sigma$ and $(\rho\Gamma/a)|_{T_c}$ are the minimum values of $\rho\Gamma/a$ on the saturated vapor line and the critical isotherm, respectively.

Fluid	T_c °K	p_c atm	Z_c	T_b °K	$c_{v\infty}$ (T_c)/ R	n	$\rho\Gamma/a _\sigma$	$\rho\Gamma/a _{T_c}$
C ₁₂ F ₂₇ N(FC-43) pf-tributylamine	567.2	11.2	0.260	447.2	93.0	0.5256	− 0.25	− 0.03
C ₁₅ F ₃₃ N(FC-70) pf-tripentylamine	608.2	10.2	0.270	488.2	118.7	0.4930	− 0.43	− 0.17
C ₁₈ F ₃₉ N(FC-71) pf-trihexylamine	646.2	9.3	0.275	526.2	145.0	0.4273	− 0.59	− 0.29
C ₁₃ F ₂₂ (PP10) pf-perhydrofluorene	632.2	16.0	0.283	463.2	78.4	0.5255	− 0.34	− 0.08
C ₁₄ F ₂₄ (PP11) pf-perhydrophenanthrene	650.2	14.4	0.269	488.2	97.3	0.5776	− 0.42	− 0.15
C ₁₆ F ₂₆ (PP24) pf-fluoranthene	701.2	15.1	0.289	517.2	112.0	0.5113	− 0.68	− 0.36
C ₁₇ F ₃₀ (PP25) pf-benzyltetralin	687.3	10.9	0.239	533.2	123.0	0.5080	− 0.48	− 0.22

tions and the anomalous increase in the specific heats only tend to increase the chances of observing negative nonlinearity. Metastable conditions occur at pressures above those corresponding to saturation. The dry isotherms in this region then have even stronger negative curvature than those in the single-phase region. Thus the first term on the right-hand side of (2) will be even smaller, i.e., more negative, than at pressures below saturation. The influence of the near-critical increase in the specific heat is seen by noting that Γ decreases with increasing specific heat. In fact, Borisov *et al.*¹⁰ have argued that $\Gamma \rightarrow -\infty$ as the critical pressure is approached from below along the critical isotherm. The strength of this effect can be illustrated by noting that Borisov and co-workers were able to demonstrate negative nonlinearity in Freon-13 even though classical theory, i.e., that employed here, predicts $\Gamma > 0$ at all p and T for Freon-13.

The fluids chosen are listed in Table I along with their trade and chemical names and properties. The FC series are manufactured and marketed by the 3M Corporation whereas the PP series are products of ISC Chemicals Limited. Each fluid is currently used in heat transfer applications and is known to be highly stable and inert under a wide variety of conditions.

II. THERMODYNAMIC MODEL

In the present study we compute Γ directly through use of (2). We therefore require an analytic equation of state $p = p(V, T)$ and the zero-pressure specific heat at constant volume defined by

$$c_{v\infty}(T) \equiv \lim_{V \rightarrow \infty} c_v(V, T). \quad (3)$$

The actual specific heat and sound speed in (2) are then given by

$$c_v(V, T) = c_{v\infty}(T) - T \int_V^\infty \frac{\partial^2 p}{\partial T^2} dV, \quad (4)$$

$$a(V, T) = V \left[\frac{T}{c_v} \left(\frac{\partial p}{\partial T} \right)^2 - \frac{\partial p}{\partial V} \right]^{1/2}. \quad (5)$$

The equation of state chosen is that of Martin and Hou⁹ with the high-density correction found in the footnote on p. 148 of that paper. The motivation for this choice is the accuracy and versatility of the Martin–Hou equation. Furthermore, Lambrakis and Thompson⁸ and Thompson and Lambrakis²

found that the Martin–Hou equation is the most conservative equation of those treated. By most conservative we mean it is the least likely to predict $\Gamma < 0$. Input data for the Martin–Hou equation are the normal boiling temperature T_b , and the critical specific volume V_c , temperature T_c , and pressure p_c . In the original article, the Boyle temperature T_B and quantity

$$M \equiv - \frac{T_c}{p_c} \frac{dp_\sigma}{dT}(T_c),$$

where $p_\sigma = p_\sigma(T)$ is the vapor pressure, must be obtained graphically. For the Boyle temperature we have employed the following curve fit, based on the data given by Martin and Hou:

$$T_B = 9.654\,291 - 2.505\,308T_c - 6.492\,324 \times 10^{-4}T_c^2,$$

where T_c and T_B are in degrees Kelvin. We have also noted that M is just the Riedel parameter α_c and have computed this using Riedel's formula¹¹

$$\alpha_c = (0.315\zeta - \ln \bar{p}_b) / (0.0838\zeta - \ln \bar{T}_b),$$

where $\bar{T}_b \equiv T_b/T_c$ and

$$\zeta \equiv -35 + 36/\bar{T}_b + 42 \ln \bar{T}_b - (\bar{T}_b)^6.$$

The quantity $\bar{p}_b = p_b/p_c$, where p_b is the pressure at the normal boiling point, i.e., one atmosphere.

The values of T_b , V_c , p_c , and T_c for PP10, PP11, PP24, and PP25 were provided by the manufacturer.¹² The values of T_b , p_c , and T_c for FC-43, 70, and 71 are listed in the manufacturer's product information.¹³ The critical volume was estimated by a modification of Lydersen's technique, which is due to Joback; details are outlined in Reid, Prausnitz, and Poling.¹⁴

The fluid description is complete once the zero pressure specific heat (3) is given. At $T = T_c$, $c_{v\infty}$ was computed by the group contribution method of Rihani and Doraiswamy.¹⁵ To simplify the computations, the temperature dependence in the neighborhood of T_c is approximated by the power law:

$$c_{v\infty}(T) = c_{v\infty}(T_c)(T/T_c)^n. \quad (6)$$

The constant n is computed from

$$n = \ln[c_{v\infty}(T_2)/c_{v\infty}(T_1)] / \ln(T_2/T_1),$$

where T_1, T_2 are any two convenient temperatures satisfying $T_1 < T_c < T_2$ and $c_{v\infty}(T_1), c_{v\infty}(T_2)$ are also computed by the

method of Rihani and Doraiswamy. Thus (6) gives exactly the same result as the method of Rihani and Doraiswamy at three temperatures. For the temperature ranges used here the difference between (6) and the method of Rihani and Doraiswamy is typically a fraction of a percent. This is seen to be considerably smaller than the error inherent in the method of Rihani and Doraiswamy (about 5%) and we conclude that the use of the power law will not significantly affect our results. Our calculations of $c_{v\infty}(T_c)$ appear to agree well with those of previous investigators. For example, Thompson and Lambrakis² give the critical temperature of perfluorodecane as 578 °K and $c_{v\infty}(T_c) = 76R$, where R is the gas constant. The method of Rihani and Doraiswamy yields a value of 74.77R, which differs by about 1.6%. We note that our calculation of $c_{v\infty}$ results in a value that is slightly smaller than that calculated by Thompson and Lambrakis.² Comparison with other fluids treated by Thompson and Lambrakis yields similar results and we conclude that our results for $c_{v\infty}$ and therefore Γ are likely to be slightly more conservative than those found by Thompson and Lambrakis.

We should also point out that the computations presented here may be unrealistically conservative. To illustrate this point we note that Thompson and Lambrakis² find that $\Gamma > 0$ for all $T > T_c$ for perfluoromethyldecalin when the Martin-Hou equation is used to compute Γ directly, i.e., with (2). This was checked and is in complete agreement with our calculations. However, when the Martin-Hou equation is used to interpolate the manufacturer's data, Lambrakis and Thompson⁸ found negative nonlinearity in the supercritical region. The region of negative nonlinearity is the region of downward curvature of the isentropes in their Fig. 1; this clearly extends into the $T > T_c$ region of the p - V plane. The reason for the discrepancy appears to be that the Martin-Hou equation underpredicts the downward curvature of the isotherms. A similar underprediction was also found for perfluorodecalin (PP5). The interpolation performed by Lambrakis and Thompson⁸ is expected to be a more accurate fit to the data and we conclude that the direct application, i.e., the method used here and in Thompson and Lambrakis,² is likely to be overly pessimistic for the purposes of finding $\Gamma < 0$.

We also expect the estimates for $\rho\Gamma/a$ for FC-43, FC-70, and FC-71 to be overly conservative because of the critical volume calculation. The reason for this claim is that the Joback-Lydersen technique used to estimate V_c was found to underestimate, by about 9%–10%, the value of V_c of PP10, PP11, PP24, and PP25 when compared to the values provided by ISC Chemicals Ltd. If a similar error carries over to the FC series, we would expect the estimates of V_c and therefore Z_c to be on the low side. Because the value of $\rho\Gamma/a$ tends to increase with decreasing Z_c , we conclude that the actual values of $\rho\Gamma/a$ for the FC fluids are likely to be even smaller, i.e., more negative, than those recorded in Table I.

III. RESULTS

A summary of our computations is found in Table I and an example of the variation of $\rho\Gamma/a$ on isotherms is given in

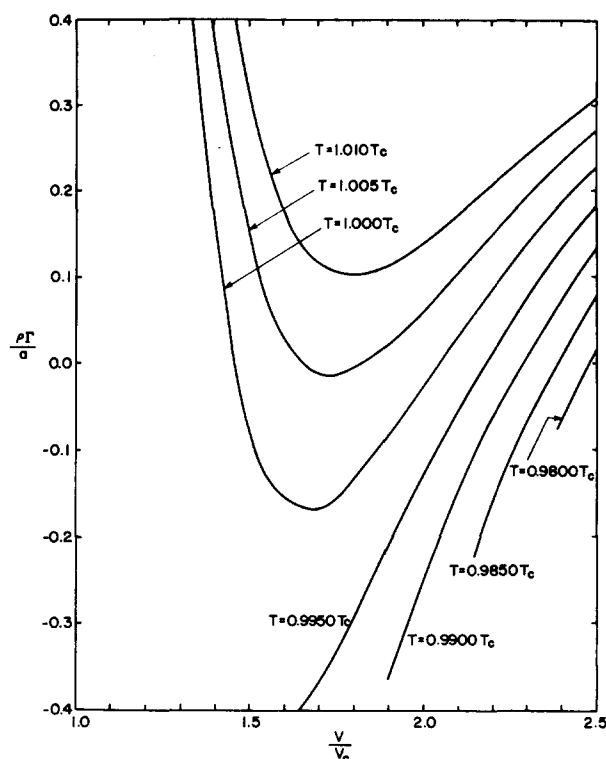


FIG. 1. Variation of $\rho\Gamma/a$ on various isotherms for FC-70. Lowest three subcritical isotherms have been terminated at the saturated vapor line as computed by Riedel's formula.¹¹

Fig. 1. All seven fluids are found to have $\Gamma < 0$ on the critical isotherm with the largest value of $|\rho\Gamma/a|_{\min}$ on $T = T_c$, being more than twice the corresponding value found by Thompson and Lambrakis for the fluorinated ether E-5. In Table I we have also recorded estimates of the minimum values of $\rho\Gamma/a$ on the saturated vapor line. The saturation curve was estimated by Riedel's vapor pressure equation.¹¹ The pressures obtained were found to be accurate to within 2% of the manufacturer's data (3M Corporation¹³ and ISC Chem. Ltd.^{16,17}) for FC-72 (perfluorohexane), PP5 (perfluorodecalin), and PP9 (perfluoromethyldecalin) over the range of reduced temperatures used here. As pointed out by Thompson and Lambrakis,² the values of $\rho\Gamma/a$ at saturation can be considerably smaller than at $T = T_c$. This relatively strong negative nonlinearity at subcritical temperatures is also illustrated in Fig. 1. Although the isotherms are terminated at saturation, it is clear that even smaller values of $\rho\Gamma/a$ will be attained at metastable conditions.

The errors inherent in the Martin-Hou equation and the various estimation procedures will, of course, lead to errors in the values of $\rho\Gamma/a$ listed in Table I. However, the general conclusions concerning the existence of negative nonlinearity in these fluids are likely to remain unchanged. For example, the most difficult estimate is that for V_c . If we assume a $\pm 10\%$ error in the value of V_c for FC-70 we find that the minimum value of $\rho\Gamma/a$ on $T = T_c$ lies in the range

$$-0.23 < \rho\Gamma/a|_{T_c} < -0.11.$$

Even a $\pm 10\%$ error in the $c_{v\infty}(T_c)$ for FC-70 yields a range of -0.24 to -0.10 for the minimum value of $\rho\Gamma/a$ on a critical isotherm.

IV. SUMMARY

The results described here represent compelling numerical evidence for strong negative nonlinearity in single-phase gases. The range of pressures and temperatures corresponding to $\Gamma < 0$ is sufficiently large to admit both shock-splitting and double sonic shocks. The only systematic errors identified suggest that our estimates are overly conservative and the actual regions of negative nonlinearity are likely to be somewhat larger than indicated here. The present extension of the list of fluids with strong negative nonlinearity should provide a solid basis for the design of experiments capable of detecting negative nonlinearity as well as numerical/experimental studies of the potential applications of the nonclassical dynamics of these fluids.

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