



**Operational Equations of State.  
2. The Generalized Courant-Friedrichs Equation of State  
for Condensed Matter**

**by M. A. Grinfeld**

**ARL-TR-5745**

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**M. A. Grinfeld**

**Weapons and Materials Research Directorate, ARL**

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| 14. ABSTRACT<br>The equation of state (EOS) with separable internal energy played a big role in the analysis of dynamics of condensed matter and development of the mathematical basis of the shock-wave physics (Courant, R.; Friedrichs, K. O. <i>Supersonic Flow and Shock Waves</i> ; Interscience: New York, 1948). For such models, the internal energy density $E$ , as a function of the specific volume $V$ and entropy density $S$ , can be presented as $E(V, S) = \Delta(V) + X(S)$ , where functions $\Delta(V)$ and $X(S)$ should be determined from experiment. We call this model the Courant-Friedrichs (CF) EOS. We suggest a generalized Courant-Friedrichs (gCF) EOS based on three functional degrees of freedom. It includes the CF EOS as a special case. The additional degree of freedom allows us to consider additional physical phenomena. We discuss the interrelations between the newly introduced gCF EOS and several classical EOS, including the incomplete Mie-Grüneisen EOS and its complete extensions. We also discuss how the three functions can be recovered from experimental data. |                             |                              |                                                            |                                                               |                                                             |
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## 1. Introduction

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Fundamentals of thermodynamics were developed during two centuries. The primary notion of thermodynamics is the notion of the equation of state (EOS), which was originally associated with something later coined as the thermal EOS. Later, it was changed and replaced with the concept of one of the thermodynamic potentials referred to canonical variables. There are several reviews describing the evolution of the topic and its current state-of-the-art (1–5).

The role of the EOS can be played by (1) the internal energy density  $E(V, S)$ , referred to as its canonical variables—the specific volume  $V$  and entropy  $S$ ; (2) the free energy density  $F(V, T)$ , referred to as its canonical variables—specific volume  $V$  and absolute temperature  $T$ ; and (3) the entropy density  $S(V, E)$ , referred to its canonical variables—specific volume  $V$  and the internal energy  $E$ , etc.

Finding the appropriate EOS is very important for any discipline using continuum description of media. Phenomenological thermodynamics suggests some canonical experiments to determine the required thermodynamic potential. The recommended methodology guarantees thermodynamic consistency of the model. In other words, this methodology guarantees that the model obeys the First and Second laws of thermodynamics.

The idealized experiments, recommended by theoretical thermodynamics, are not easy or even impossible to realize practically (e.g., when dealing with planets or celestial bodies). Therefore, different theoretical and experimental techniques for establishing the EOS have been suggested.

A combination of different approaches and data can easily violate thermodynamic consistency of newly suggested models. For instance, the classical models of the ideal and van der Waals gases are thermodynamically consistent with the assumption of the heat capacity  $C_V$ , depending solely on the absolute temperature, and are incompatible with the more general models of heat capacity. As it was demonstrated in Davis (6), the classical models of the Mie-Grüneisen EOS are thermodynamically consistent with the assumption of the heat capacity  $C_V$ , depending solely on the entropy density  $S$ , and are incompatible with more general models of heat capacity.

Contrary to the essentially canonized basic principles of thermodynamics, the demand for novel EOS always remains strong. This happens because of the permanent appearing novel substances or because of the necessity of working within extended ranges of thermodynamic parameters.

Development of novel EOS is unthinkable without further progress of the phenomenological thermodynamics itself. No single EOS can work for all substances and all ranges of thermodynamic parameters. The progress and revision should take into account novel types of experiments, not just those idealized experiments considered in the classical textbooks.

Thermodynamics and theory of shocks contain strong mathematical cores which should also be further developed. The models appropriate for deep mathematical analysis are certain abstractions of the practically used EOS. By sacrificing some details, mathematical analysis allows a much deeper analysis. One such model was analyzed in Courant and Friedrichs (7). We suggest its generalization in the next section.

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## 2. The Suggested Model

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The generalized Courant-Friedrichs (gCF) EOS is defined by the following relationship:

$$E(V, S) = X(S)\Omega(V) + \Delta(V), \quad (1)$$

where  $V$  is the specific volume,  $S$  is the specific entropy,  $E$  is the specific internal energy, and  $X(S)$ ,  $\Omega(V)$ ,  $\Delta(V)$  are three functions. The functions  $X(S)$ ,  $\Omega(V)$ ,  $\Delta(V)$  should be specified based on available experimental data. Thus, we arrive at the EOS based on three functions of one variable each— $X(S)$ ,  $\Omega(V)$ , and  $\Delta(V)$ .

The gCF EOS satisfies the following differential equation:

$$\frac{\partial^2}{\partial V \partial S} \ln \frac{\partial E(V, S)}{\partial S} = 0. \quad (2)$$

The gCF EOS generalizes the Courant-Friedrichs (CF) EOS with the separable internal energy:

$$E(V, S) = X(S) + \Delta(V), \quad (3)$$

which is specified by two functions— $X(S)$  and  $\Delta(V)$  (7).

The CF EOS found various applications in modeling shocks in condensed liquid media. It is not only useful for practical needs but also permits deep mathematical analysis; this cannot be overestimated. As it was obvious from the very beginning, the CF EOS has limited applicability. For instance, the Grüneisen parameter associated with this model vanishes identically. Because of this, we think it makes sense to analyze the properties and practical applicability of the gCF EOS (equation 1).

Using equation 1, we arrive at the following formulas of the absolute temperature  $T(V, S)$  and pressure  $P(V, S)$  for the gCF EOS:

$$T(V, S) = \frac{dX(S)}{dS} \Omega(V), \quad P(V, S) = -X(S) \frac{d\Omega(V)}{dV} - \frac{d\Delta(V)}{dV}. \quad (4)$$



According to equation 4, the absolute temperature appears to be the product of the functions of  $S$  and  $V$ .

Also, using thermodynamic identities, we arrive at the following formulas of the heat capacity at constant volume  $C_V(V, S)$  and the Grüneisen parameter  $\Gamma(V, S)$ :

$$\frac{1}{C_V(V, S)} = \frac{d}{dS} \ln \frac{dX(S)}{dS}, \quad (5)$$

and

$$\Gamma(V, S) = -V \frac{d \ln \Omega(V)}{dV}. \quad (6)$$

Equations 5 and 6 show that for the gCF EOS, the heat capacity  $C_V$  appears to be the function of the entropy  $S$  only, whereas the Grüneisen assumption is satisfied automatically:

$$C_V(V, S) = C_V(S), \Gamma(V, S) \equiv \Gamma(V). \quad (7)$$

It was demonstrated in reference 6 that independence of  $\Gamma$  of  $S$  and independence of the heat capacity of  $C_V$  of  $V$  are mutually related facts because of the universal and elegant thermodynamic identity:

$$\frac{\partial}{\partial S} \frac{\Gamma(V, S)}{V} = -\frac{\partial}{\partial V} \frac{1}{C_V(V, S)}. \quad (8)$$

As any thermodynamic function of state, the Grüneisen function (parameter) can be expressed in different sets of thermodynamic parameters. It can, of course, look different depending on the choice of independent thermodynamic variables. Among the many presentations of the Grüneisen parameter are the following two (8):

$$\Gamma(V, E) \equiv V \frac{\partial P(V, E)}{\partial E}, \Gamma(V, S) \equiv -\frac{\partial \ln T(V, S)}{\partial \ln V}. \quad (9)$$

Per the terminology of reference 7, equations 1 and 3 should be treated as the complete EOS, whereas equations 5–7 can be treated only as the incomplete EOS.

In the case of constant heat capacity  $C_V$ , we get

$$X(S) = C_V e^{\frac{S-S^*}{C_V}}, \quad (10)$$

and the gCF EOS can be presented in the following form:

$$E(V, S) = C_V e^{\frac{S-S^*}{C_V}} \Omega(V) + \Delta(V). \quad (11)$$

Thus, in this case, the gCF has only two functional degrees of freedom.

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### 3. Recovery of the Functions $X(S)$ , $\Omega(V)$ , and $\Delta(V)$ From Experiment

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The completeness of the EOS is an important feature. On the other hand, the completeness of the EOS in no way guarantees its practical usefulness. It only guarantees its compatibility with the First and Second Laws of Thermodynamics. This compatibility is important but not sufficient for ultimate success. The EOS can be useful not being complete and can be complete not being useful.

Real usefulness of the EOS comes from comparing it with experimental data. Fortunately, the generalized gCF has three functional degrees of freedom— $X(S)$ ,  $\Omega(V)$ , and  $\Delta(V)$ , which matches various existing experimental data. If the data is reliable and the experiments are chosen wisely, there is a reasonable chance of obtaining useful EOS.

What is the useful set of experiments? It depends on the intended applications. For instance, measurements of the heat capacity at 0 K, however precise they are and however useful they are for the low-temperature physics, can be quite misleading if the intended application deals with modeling a supersonic projectile penetrating through a thick metallic or ceramic wall and vice versa.

For determining functions  $X(S)$ ,  $\Omega(V)$ , and  $\Delta(V)$ , each set of experiments requires its own formula of conversion. Next, we provide one example of the experiments, giving the flavor of the typical formulas of the conversion. These formulas are basically certain integral operators.

Let us first choose the reference configuration  $(V^*, S^*)$ . We will also use the superscript “\*” for all quantities relating to the referenced configuration. Naturally, in order to recover the three functions, we need three sets of measurements. We will consider the following set of canonical experimental measurements.

Let the first experiment be the isochoric heating at  $V = V^*$ . It determines the heat capacity  $C_V(S)$  at constant volume as a function of the entropy density. Let the second experiment be the static adiabatic loading corresponding to the reference value  $S = S^*$  of the entropy density. Let  $T_S^* = T_S^*(V)$  and  $P_S^* = P_S^*(V)$  be the values of the absolute temperature and pressure on that very adiabata.

Then, the measured functions  $C_V(S)$ ,  $T_S^* = T_S^*(V)$ , and  $P_S^* = P_S^*(V)$  determine the functions  $X(S)$ ,  $\Omega(V)$ , and  $\Delta(V)$  and recover the corresponding gCF EOS. The recovered equation reads as follows:

$$E(V, S) = T_S^*(V) \int_{S^*}^S d\xi e^{\int_{S^*}^{\xi} d\eta C_V^{-1}(\eta)} - \int_{V^*}^V d\varpi P_S^*(\varpi) + E^*, \quad (12)$$

where  $E^*$  is the internal energy density in the reference configuration.

In other words, the formulas of conversion for this set of experiments read

$$X(S) = \int_{S^*}^S d\xi e^{\int_{S^*}^{\xi} d\eta C_V^{-1}(\eta)}, \quad \Omega(V) = T_S^*(V), \quad \Delta(V) = \int_{V^*}^V d\varpi P_S^*(\varpi). \quad (13)$$

In the case of constant heat capacity, the EOS (equation 12) can be rewritten as follows:

$$E(V, S) = C_V T_S^*(V) e^{\frac{S-S^*}{C_V}} - \int_{V^*}^V d\varpi P_S^*(\varpi) + E^*. \quad (14)$$

When the Hugoniot adiabata data (9, 10) is used instead of the data relating to the static adiabata, the inversion formulas (equation 13) should be considerably modified. Additional important aspects should be considered when dealing with substances undergoing phase transformations (see references 9–11).

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## 4. Discussion and Conclusion

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Following the footprints of Courant and Friedrichs (7), we suggested a novel complete EOS called the gCF EOS. The gCF EOS depends on three functions of one variable.

For the case of two available experiments, isochoric and adiabatic loading, we established explicit formulas (equations 12 and 13), which converted the experimental data into the gCF EOS. The conversion was reduced to using certain integral operations. These integral operations are stable regarding small perturbations of experimental data.

The *thermodynamic Grüneisen parameter* should be clearly distinguished from *the Grüneisen assumption* and *the Mie-Grüneisen EOS*. The Grüneisen parameter for any two-parameter media is a thermodynamic function of state, i.e., function of any two chosen thermodynamic parameters. It is a meaningful notion applicable to any two-parameter media. The Grüneisen assumption is the hypothetical statement applicable to a limited set of substances. The

Grüneisen assumption claims that the Grüneisen parameter is a function of the specific volume only. The Mie-Grüneisen EOS is the incomplete EOS based on the Grüneisen assumption.

In fact, the Mie-Grüneisen EOS is the canonical example of the *operational* EOS. It can be presented in the following form:

$$P(V, E) = P_\gamma(V) + [E - E_\gamma(V)] \frac{\Gamma(V)}{V}, \quad (15)$$

where the functions  $P_\gamma(V)$ ,  $E_\gamma(V)$ , and  $\Gamma(V)$  are functions to be determined from experimental data. It is the example of the incomplete EOS for hydrocode. Indeed, as any EOS, it is a function of two variables— $V$  and  $E$ . At the same time, equation 15 defines an operator transforming experimentally measured functions  $P_\gamma(V)$  and  $E_\gamma(V)$  into an incomplete EOS.

For the gCF EOS, the Grüneisen assumption is automatically satisfied. In other words, the Grüneisen parameter appeared to be the function of the volume only, whereas the heat capacity appeared to be the function of the entropy density only. The gCF EOS is, in fact, the most general form of the complete EOS that is compatible with the Grüneisen assumption.

Other examples of complete EOS will be given in the forthcoming papers of this set of reports.

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1 US ARMY RESEARCH OFFICE  
RDRL ROI M  
J MYERS  
BLDG 4300  
DURHAM NC 27703

2 US ARMY RESEARCH OFFICE  
RDRL ROE M  
J PRATER  
D STEPP  
BLDG 4300  
DURHAM NC 27703

1 US ARMY RESEARCH OFFICE  
RDRL ROE N  
R ANTHINIEN  
BLDG 4300  
DURHAM NC 27703

3 US ARMY RESEARCH OFFICE  
J LAVERY  
D MANN  
S MATHAUDHU  
BLDG 4300  
DURHAM NC 27703

ABERDEEN PROVING GROUND

72 DIR USARL  
RDRL WM  
B FORCH  
J MCCAULEY  
S KARNA  
P PLOSTINS  
RDRL WMP B  
R BECKER  
S BILYK  
D CASEM  
J CLAYTON  
D DANDEKAR  
J FITZPATRICK  
M GRINFELD (20 CPS)  
C HOPPEL  
R KRAFT  
B LEAVY  
D POWELL  
M RAFTENBERG  
M SCHEIDLER



NO. OF  
COPIES ORGANIZATION

T WEERASOORIYA  
C WILLIAMS  
RDRL WMP C  
T BJERKE  
S SEGLETES  
W WALTERS  
RDRL WML B  
I BATYREV  
J BRENNAN  
S IZVEKOV  
B RICE  
RDRL CIH C  
P CHUNG  
J CAZAMIAS  
J KNAP  
RDRL WMM G  
I ANDZELM  
F BEYER  
J LENHART  
B RINDERSPACHER  
RDRL WMP E  
W GOOCH  
B LOVE  
C KRAUTHAUSER  
RDRL WMM E  
J ADAMS  
L KECSKES  
J LASALVIA  
P PATEL  
J SWAB  
M WILL-COLE  
RDRL WMM B  
B CHEESEMAN  
C FOUNTZOULAS  
G GAZONAS  
RDRL SER L  
W NOTHWANG  
RDRLWML H  
M FERMEN-COKER  
RDRL WMP  
B BURNS  
S SCHOENFELD  
RDRL WMP D  
H MEYER  
RDRL WMP G  
R BANTON  
S KUKUCK

NO. OF  
COPIES ORGANIZATION

- |   |                                                                                                                                       |
|---|---------------------------------------------------------------------------------------------------------------------------------------|
| 1 | CAVENDISH LAB<br>MOTT BLDG RM 316B<br>JJ THOMSON AVE<br>M CHAUDHRI<br>CAMBRIDGE CB3 0HE<br>UNITED KINGDOM                             |
| 1 | LOUGHBOROUGH UNIV<br>WOLFSON SCHOOL OF MECH &<br>MANUFACTURING ENGRG<br>LOUGHBOROUGH<br>V SILBERSCHMIDT<br>LE11 3TU<br>UNITED KINGDOM |
| 1 | UNIVERSITY OF LIVERPOOL<br>DEPT OF ENGRG<br>BROWNLOW HILL<br>LIVERPOOL<br>OUYANG<br>L69 3GH<br>UNITED KINGDOM                         |
| 4 | AWE ALDERMARSTON READING<br>BERKSHIRE RG7 4PR<br>N BOURNE<br>J C F MILLETT<br>G A COX<br>C M ROBINSON<br>UNITED KINGDOM               |
| 1 | DEFENCE SCI & TECHLGY<br>ORGANISATION<br>WEAPONS SYSTEMS DIVISION<br>A RESNYANSKY<br>EDINBURGH SA 5111<br>AUSTRALIA                   |
| 1 | CSIRO EXPLORATION & MINING<br>PO BOX 883<br>KENMORE QLD 4069<br>F D STACEY<br>AUSTRALIA                                               |
| 1 | MOSCOW STATE UNIV<br>INSTITUTE OF MECHANICS<br>MICHURINSKIE PR 1<br>S S GRIGORYAN<br>MOSCOW 117192<br>RUSSIA                          |

NO. OF  
COPIES ORGANIZATION

- |   |                                                                                                                                                                                       |
|---|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | STEKLOV MATHEMATICAL<br>INSTITUTE<br>GUBKINA AV 8<br>A G KULIKOVSKII<br>MOSCOW 117966<br>RUSSIA                                                                                       |
| 1 | LANDAU INSTITUTE FOR<br>THEORETICAL PHYSICS<br>N INOGAMOV<br>RAS CHERNOGOLOVKA 142432<br>RUSSIA                                                                                       |
| 5 | JOINT INSTITUTE FOR HIGH<br>TEMPERATURE PHYSICS<br>RUSSIAN ACADEMY OF SCIENCES<br>V FORTOV<br>V GRYAZNOV<br>G KANEL<br>M LOMONOSOV<br>S RAZORENOV<br>JIHT RAS MOSCOW 125412<br>RUSSIA |
| 1 | INSTITUTE OF CONTINUOUS MEDIA<br>MECHANICS<br>URAL BRANCH OF RAS<br>O B NAIMARK<br>1 ACAD KOROLEV STR<br>PERM 614013<br>RUSSIA                                                        |
| 1 | BEN GURION UNIVERSITY<br>DEPARTMENT OF MECHANICAL<br>ENGRG<br>E B ZARETSKY<br>PO BOX 653<br>BEER SHEVA 84105<br>ISRAEL                                                                |
| 1 | RAFAEL<br>PO BOX 2250<br>Y PARTOM<br>HAIFA 31021<br>ISRAEL                                                                                                                            |