fractal and fractional

Brief Report

Application of Fractional Calculus to Establish Equations of State for Solid Metals

Vladimir Kulish, Navid Aslfattahi * and Michal Schmirler

Department of Thermodynamics & Fluid Mechanics, Faculty of Mechanical Engineering, Czech Technical University in Prague, 166 07 Prague, Czech Republic; vladimir.kulish@fs.cvut.cz (V.K.); michal.schmirler@fs.cvut.cz (M.S.)

* Correspondence: navid.aslfattahi@fs.cvut.cz

Abstract: Fractional differ-integral operators are used to obtain the equation of state for a substance that can be seen as fractal. Two equations of state have been obtained, the first of which depends on two parameters that characterize the fractal dimension of the material and the thermal energy of the particles, respectively. The second equation involves three parameters, and expressions for the Helmholtz free energy and the bulk modulus have also been obtained for this equation. The model presented in this study has been validated using experimental data available in literature, and fractional exponent have been determined for various metals.

Keywords: equation of state; fractional calculus; thermodynamics; fractal materials

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1. Introduction

Many solid materials have a fractal structure, including porous substances (silicon, metals, rocks, etc.), polymers, carbon nano-materials and nano-composites. At present, a significant number of classical and quantum-mechanical methods have been proposed to obtain the equations of state of continuous media [1–4]. However, in order to derive the equations of state of substances that can be interpreted as having fractal geometry, it is required to involve, along with the methods of statistical physics, new mathematical methods, particularly fractional calculus [5–7]. It should be noted that for solids with a fractal structure, there have been very few attempts to establish the equation of state [8,9]. Modern wide-range equations of state can contain dozens of free parameters and experimentally found constants. In this regard, the problem of obtaining the equation of state with a small number of parameters remains relevant.

Using fractional integro-differentiation, the equation of state of R134 freon was obtained, which contains only four parameters [10]. A fundamentally new class of equations of state for bodies interpreted as physical systems with a fractal structure was proposed (inspired by the example of freon R134) [8]. In the same work, the mathematical apparatus of fractional differ-integration was applied in thermodynamics to calculate the surface energy and Gibbs adsorption. The equation of state for solids containing explicitly the fractal dimension was obtained using the Debye theory [9]. In addition, in the same work, fractional expressions for the density of states, average energy, free energy and the Grüneisen parameter have been derived as well.

In this paper, the Riemann-Liouville fractional differ-integral operators are used to establish the equation of state for a substance, which can be seen as fractal.

2. Two-Parameter Equation of State

By definition, pressure in terms of the Helmholtz free energy can be expressed by the following formula:

$$P = -\left(\frac{\partial F}{\partial V}\right) |_{T,N} = -\frac{1}{V_0}\left(\frac{\partial F}{\partial \varphi}\right) |_{T,N} \tag{1}$$

where F is the Helmholtz free energy, V_0 is the volume occupied by one particle, $\varphi = V/V_0$ is the dimensionless volume, with the temperature T and the number of particles N assumed constant. In a previous work [9], it was proposed to use the law of composition of fractional derivatives [5] to introduce a thermodynamic function–surface energy. Using a similar technique, for the Helmholtz free energy, we have:

$$\frac{dF(\varphi)}{d\varphi} = \mathfrak{D}^{\nu}\mathfrak{D}^{1-\nu}F(\varphi) \tag{2}$$

where $\mathfrak{D}^{-\nu}g(t) = \frac{1}{\Gamma(\nu)}\int_0^t \frac{g(\tau)d\tau}{(t-\tau)^{1-\nu}}$ is the Riemann–Liouville fractional differ-integral operator [5] of order ν. A similar technique was used for the specific surface energy [9]. In the said work, it has been shown that the density of states can be expressed as $z(\omega) \sim \omega^{\nu-1}$, where ν is the spectral fractal dimension, if a solid is modeled by a fractal filled with a phonon gas. Thus, from Equations (1) and (2),

$$P = \frac{1}{V_0}\mathfrak{D}^{\nu}f(\varphi), f(\varphi) = \mathfrak{D}^{1-\nu}F(\varphi) \tag{3}$$

Suppose that the function $f(\varphi)$ has the following form:

$$f(\varphi) = C\frac{(1-\varphi)^{\nu}}{\Gamma(1+\nu)}E(\nu, 1, 1+\nu, 1-\varphi) \tag{4}$$

where $E(\alpha, \beta, \gamma, z)$ is the Gauss hypergeometric function [5,6] and C is a nonzero parameter.

It is worth noting here that, as can be seen from the following treatment, the choice of the Gauss hypergeometric function leads to a physically meaningful result. To substantiate the choice even further, it can be noted that mathematical solutions of quite many second-order ordinary and fractional differential equations can be expressed in terms of the Gauss hypergeometric function [5]. Moreover, the hypergeometric function has allowed the development of many solvable models in physics and engineering [5–7]. In particular, the said function proved to be very useful for general parametrization of the effective potentials of interaction between atoms [11], which is a strong indication that the hypergeometric function may be a suitable choice when deriving equations of state.

Considering that $f(1) = 0$ from Equation (4), due to the equalities:

$$\mathfrak{D}^{\nu}f(\varphi) = \partial^{\nu}f(\varphi) + \frac{f(1)}{\Gamma(1-\nu)}(\varphi-1)^{-\nu} \tag{5}$$

and [5]:

$$\mathfrak{D}^{\nu}f(\varphi) = \partial^{\nu}f(\varphi) = \mathfrak{D}^{\nu-1}f'(\varphi) \tag{6}$$

where $\partial^{\nu}g(t) = \frac{1}{\Gamma(1-\nu)}\int_{\tau}^{t} \frac{g'(t-\zeta)d\zeta}{(\zeta-\tau)^{\nu}}$ denotes the Caputo derivative [6], it follows:

$$P = -\frac{1}{V_0}\mathfrak{D}^{\nu-1}f'(\varphi) \tag{7}$$

By virtue of equality [5]:

$$\frac{d}{dz}\left[z^{\gamma-1}E(\alpha, \beta, \gamma, z)\right] = (\gamma-1)z^{\gamma-2}E(\alpha, \beta, \gamma-1, z), E(\alpha, \beta, \gamma, z) = (1-z)^{-\beta} \tag{8}$$

the following expression is true:

$$f'(\varphi) = -\frac{C}{\Gamma(1+\nu)}\nu(1-\varphi)^{\nu-1}E(\nu, 1, \nu, 1-\varphi) = -\frac{C}{\Gamma(\nu)}(1-\varphi)^{\nu-1}\varphi^{-1} \tag{9}$$

From Equations (7) and (9):

$$P = \frac{1}{V_0} \frac{C}{\Gamma(\nu)} \mathfrak{D}^{\nu-1} (1-\varphi)^{\nu-1} \varphi^{-1} \tag{10}$$

The fractional differ-integral in Equation (10) can be calculated using the change of variable $t = 1 - (1-\varphi)\zeta$. Hence:

$$\begin{aligned} \mathfrak{D}^{\nu-1}(1-\varphi)^{\nu-1}\varphi^{-1} &= \tfrac{1}{\Gamma(1-\nu)} \int_{\varphi}^{1} (1-t)^{\nu-1} (t-\varphi)^{-\nu} t^{-1} dt \\ &= \tfrac{1}{\Gamma(1-\nu)} \int_{0}^{1} \zeta^{\nu-1} (1-\zeta)^{-\nu} [1-(1-\varphi)\zeta]^{-1} d\zeta = \\ &= \tfrac{B(\nu,1-\nu)}{\Gamma(1-\nu)} E(1,\nu,1,1-\varphi) = \Gamma(\nu)\varphi^{-\nu} \end{aligned} \tag{11}$$

where the Beta function, also known as the Euler integral of the first kind, is defined as $B(x,y) = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)} = \int_0^1 \zeta^{x-1}(1-\zeta)^{y-1} d\zeta$.

Substituting (11) into (10), we obtain the equation:

$$P = \frac{C}{V_0} \varphi^{-\nu} \tag{12}$$

where $C(T)$ is a constant–with respect to P and V–that characterizes the thermal energy of particles. Notice that, at $\nu = 1$, the fractional derivative turns into a first-order ordinary derivative because $d/dt = \mathfrak{D}^1 = \mathfrak{D}^2\mathfrak{D}^{-1}$ (also see Equation (2)), and the equation of state (12) reduces to the equation of state for an ideal gas $PV = RT$ (recall that $\varphi^{-1} = V_0/V$).

It is important to note at this point that, although the present study limits itself to the equation of state for solid metals, the fact that the resulting fractional equation of state has the equation of state for an ideal gas as its limiting case is a strong indication in favor of the model's physicality.

Thus, in this Section, the equation of state is obtained using the Riemann-Liouville fractional differ-integrals. The equation of state involves two parameters ν and $C(T)$, which characterize the fractal dimension of the object and the thermal energy of particles, respectively. The equation is supposed to be used to predict the thermodynamic properties of substances, which can be seen as fractals.

3. Three-Parameter Equation of State

Assume now that the function $f(\varphi)$ can be represented as a power series:

$$f(\varphi) = \sum_{n=0}^{\infty} a_n \varphi^n \tag{13}$$

where a_n denote the coefficients, the values of which are obtained by processing the experimental values of the phase diagrams by the least squares method.

The description of the shock wave experiment and the derivation of the equation of state consists of specifying a "cold curve" analytically with several adjustable parameters. To find the corresponding coefficients, experimental compressibility data and a number of other fitting parameters are involved. In the interpolation equations of state, the upper summation limit ∞ is replaced by a natural number N (for instance, in an earlier study [2], $N = 7$).

Applying the approach described above (see Equations (1)–(4)), and substituting $f(\varphi) = \sum\limits_{n=0}^{\infty} a_n \varphi^n$ into Equation (3), the equation of state is as follows:

$$P = \frac{1}{V_0} \sum_{n=0}^{N} a_n \frac{\Gamma(n+1)}{\Gamma(n+1-\nu)} \varphi^{n-\nu} \tag{14}$$

and the expression for the Helmholtz free energy becomes:

$$F = \frac{1}{V_0} \sum_{n=0}^{N} a_n \frac{\Gamma(n+1)}{\Gamma(n+2-\nu)} \varphi^{n+1-\nu} \tag{15}$$

For $N = 1$, the function $f(\varphi)$ depends linearly on φ, and Equation (14) takes the following form:

$$P = \frac{1}{V_0} \left[\frac{a_0}{\Gamma(1-\nu)} \varphi^{-\nu} + \frac{a_1}{\Gamma(2-\nu)} \varphi^{1-\nu} \right] \tag{16}$$

and:

$$F = \frac{a_0}{\Gamma(2-\nu)} \varphi^{1-\nu} + \frac{a_1}{\Gamma(3-\nu)} \varphi^{2-\nu} \tag{17}$$

At $\nu = 1$, the fractional differ-integral reduces to the ordinary first-order derivative, and the equation of state (14) transforms into the equation of state for an ideal gas $P = a_1/V_0$.

If by φ the dimensionless density is understood, i.e., $\varphi = \rho/\rho_0$, then Equation (16) can be written in the following form:

$$P = \frac{\rho_0 \varphi^2}{M_A} \left[\frac{a_0}{\Gamma(1-\nu)} \varphi^{-\nu} + \frac{a_1}{\Gamma(2-\nu)} \varphi^{1-\nu} \right] \tag{18}$$

where ρ_0 is the initial density and M_A is the volume of one mole of the substance.

The formula for the isothermal modulus of volumetric compression can be obtained in a similar way, namely:

$$K = \frac{\varphi}{V_0} \sum_{n=0}^{N} a_n \frac{\Gamma(n+1)}{\Gamma(n+1-\nu)} \varphi^{n-\nu} \tag{19}$$

For $N = 1$, Equation (19) reduces to:

$$K = \frac{\varphi}{V_0} \left[\frac{a_0}{\Gamma(1-\nu)} \varphi^{-\nu} + \frac{a_1}{\Gamma(2-\nu)} \varphi^{1-\nu} \right] \tag{20}$$

Thus, in this Section, the equation of state is obtained using the Riemann-Liouville fractional differ-integrals. Again, the equation of state thus obtained is low-parametric, that is, it does not involve a large number of adjustable parameters. It includes three parameters ν, which characterizes the fractal dimension of the object, as well as $a_0(T)$ and $a_1(T)$, which characterize the thermal energy of particles.

To conclude this section, an important note must be made. As has been shown earlier [9], generalizing the equation of state to fractal structures at ν = const does not change the form of the Grüneisen law [12]. According to this law, $\alpha = \gamma C_V/(3K)$, where α is the linear coefficient of thermal expansion, C_V is the isochoric heat capacity per unit volume, and the Grüneisen parameter $\gamma = -\partial(\ln\theta)/\partial(\ln V)$, which is defined through the Debye temperature θ. Hence, fractional expressions for $C_V = (\alpha K)/(\gamma\rho)$ are easily recovered from Equations (19) and (20).

4. Model Validation

To validate the model, the equation of state (12) was written in the following form:

$$P(\varphi) = P_0 \varphi^{-\nu} \tag{21}$$

and experimental data [13–20] were used to calculate the values of the fractional exponent, ν, for several metals. In Equation (21), P_0 is the reference pressure in the corresponding experiments, $1 < P_0 < 10$ GPa. All experiments were conducted at $T = 300$ K.

The values of the fractional exponent, ν, were calculated using the least square method to fit experimental data [13–20] by Equation (21).

The values of the fractional exponent calculated are shown in Table 1.

Table 1. Calculated values of the fractional exponent, ν, for several metals.

Metal	Be	Na	Mg	Al	K	Fe	Cu	W	Pb
ν	4.39	4.50	4.43	3.71	3.39	3.87	4.95	5.00	5.64

As can be seen, the values of the fractional exponent vary within the range $3.3 < \nu < 5.7$. No correlation with the values of atomic weight is observed.

For the sake of illustration, Figure 1 shows the calculation results for the phase diagram of iron. The curve has been calculated by Equation (21), where φ is the dimensionless volume of the substance and P is pressure measured in gigapascal (GPa).

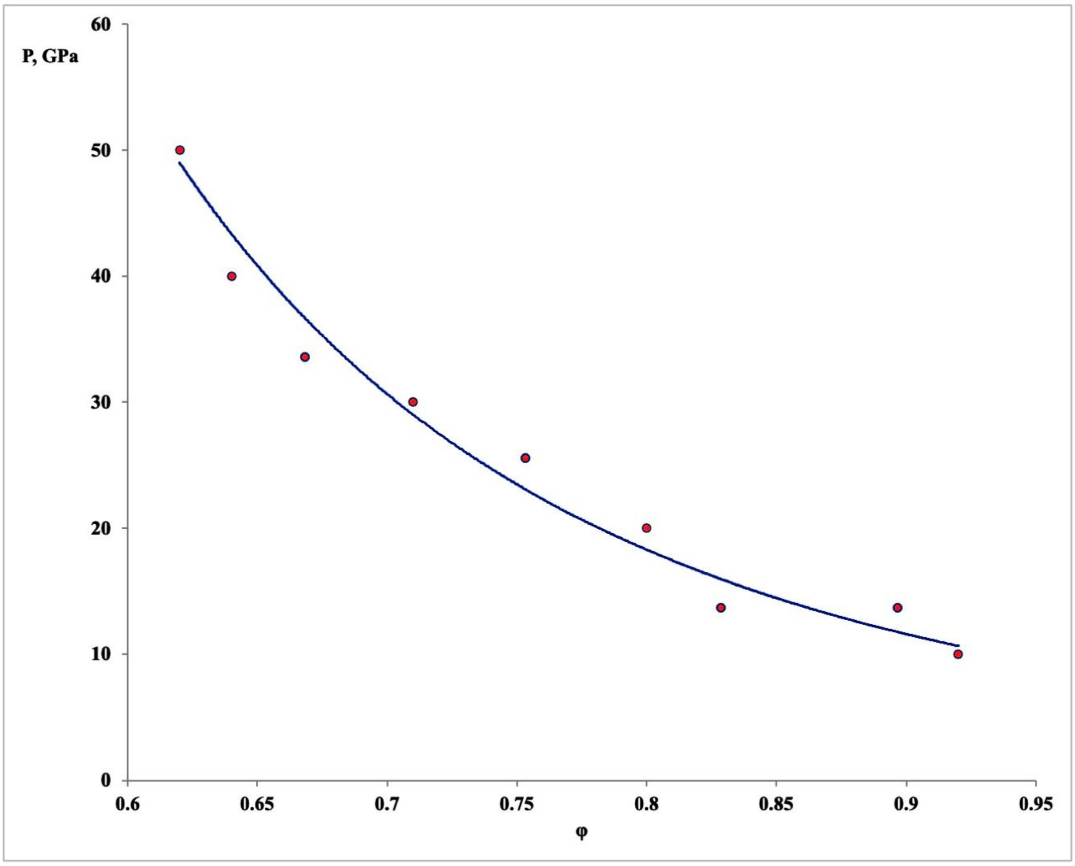

Figure 1. Calculation results for the phase diagram of iron.

As can be seen from Figure 1, the fractional state Equation (21) fits experimental data quite well.

One very important remark is to be made before concluding this section. From the model presented in this study, it follows that, for solid metals, the unit compressibility factor (Zeno-Line) [21], defined as $Z = P/(\rho T)$, is not a straight line. Indeed, from Equation (12), it follows that:

$$Z = \frac{C(T)}{\rho_0 V_0 T}\varphi^{1-\nu} = \frac{C(T)}{\rho_0 V_0 T}(1+\varepsilon)^{\nu-1} \tag{22}$$

where $0 < \varepsilon < 1$ because $0 < \varphi \leq 1$ and $\nu > 1$ (see Table 1). Hence, the Zeno-Line slightly deviates from a straight line. This is in accord with the findings reported recently [22].

5. General Discussion

In the present work, two equations of state are obtained using the Riemann-Liouville fractional differ-integral operators. Both equations are low-parameter equations, meaning that they do not involve a large number of adjustable parameters. The first equation depends on two parameters, which characterize the fractal dimension of the material and the thermal energy of the particles, respectively. The second equation of state includes three parameters, and expressions for the Helmholtz free energy and the bulk modulus have been also obtained. In the proposed approach, the main task is to determine the parameters of the equation from the experimental data of the phase diagrams of the substances under study. The equations can then be used to predict the thermodynamic properties of substances that can be seen as fractals.

The model presented in this study has been validated against experimental data available in the literature. In particular, values of the fractional exponent have been determined for various metals. The results showed that the proposed model fits the experimental data quite well.

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References

1. Zharkov, V.N.; Kalinin, V.A. *Equations of State of Solids at High Pressures and Temperatures*; Nauka: Moscow, Russia, 1968.
2. Bushman, A.V.; Fortov, V.E. Models of the equation of state of matter. *Adv. Phys. Sci.* **1983**, *140*, 177–232.
3. Fortov, E.A. *Thermodynamics and Equations of State for Matter: From Ideal Gas to Quark-Gluon Plasma*; World Scientific: Singapore, 2016.
4. Kontogeorgis, M.G.; Liang, X.D.; Arya, A.; Tsivintzelis, I. Equations of state in three centuries. Are we closer to arriving to a single model for all applications? *Chem. Eng. Sci. X* **2020**, *7*, 100060.
5. Oldham, K.; Spanier, J. *The Fractional Calculus*; Academic Press: Cambridge, MA, USA, 1974.
6. Hilfer, R. *Applications of Fractional Calculus in Physics*; World Scientific: Singapore, 2000.
7. Kulish, V. A Non-field Analytical Method for Solving Energy Transport Equations. *J. Heat Transfer.* **2020**, *142*, 042102. [CrossRef]
8. Rekhviashvili, S.S. Application of Fractional Integro-Differentiation to the Calculation of the Thermodynamic Properties of Surfaces. *Phys. Solid State* **2007**, *49*, 796–799. [CrossRef]
9. Rekhviashvili, S.S. Equation of State of a Solid with Fractal Structure. *Tech. Phys. Lett.* **2010**, *36*, 798–800. [CrossRef]
10. Liley, P.E. Some Simple Equations for Refrigerant 134a Properties. *Int. J. Mech. Eng. Educ.* **1996**, *24*, 191–194. [CrossRef]
11. Herrick, D.R.; O'Connor, S. Inverse virial symmetry of diatomic potential curves. *J. Chem. Phys.* **1998**, *109*, 11–19. [CrossRef]
12. Stacey, F.D.; Hodgkinson, J.H. Thermodynamics with the Grüneisen parameter: Fundamentals and applications to high pressure physics and geophysics. *Phys. Earth Planet. Inter.* **2019**, *286*, 42–68. [CrossRef]
13. Trunin, R.F.; Simakov, G.V.; Sutulov, Y.N.; Medvedev, A.B.; Rogozkin, B.D.; Fedorov, Y.E. Compressibility of porous metals at shock waves. *J. Exp. Theor. Phys.* **1989**, *96*, 1024–1038.
14. Sin'ko, G.V.; Smirnov, N.A. Ab Initio Calculations of Elastic Constants and Thermodynamic Properties of BCC, FCC, and HCP Al Crystals under Pressure. *J. Phys. Condens. Matter* **2002**, *14*, 6989–7005.
15. Sin'ko, G.V.; Smirnov, N.A. Relative Stability and Elastic Properties of HCP, BCC, and FCC Beryllium under Pressure. *Phys. Rev. B Condens. Matter Mater. Phys.* **2005**, *71*, 214108. [CrossRef]
16. Katsnelson, M.I.; Sin'ko, G.V.; Smirnov, N.A.; Trefilov, A.V.; Khromov, K.Y. Structure, Elastic Moduli, and Thermodynamics of Sodium and Potassium at Ultrahigh Pressures. *Phys. Rev. B Condens. Matter Mater. Phys.* **2000**, *61*, 14420–14424. [CrossRef]
17. Sin'ko, G.V.; Smirnov, N.A. Ab Initio Calculations of Elastic Properties of Magnesium under Pressure. *Phys. Rev. B Condens. Matter Mater. Phys.* **2009**, *80*, 104113. [CrossRef]
18. Rudin, S.; Jones, M.D.; Greeff, C.W.; Albers, R.C. First-Principles-Based Thermodynamic Description of Solid Copper Using the Tight-Binding Approach. *Phys. Rev. B Condens. Matter Mater. Phys.* **2002**, *65*, 235114. [CrossRef]

19. Christensen, N.E.; Ruoff, A.L.; Rodriquez, C.O. Pressure Strengthening: A Way to Multimegabar Static Pressures. *Phys. Rev. B Condens. Matter* **1995**, *52*, 9121–9124. [CrossRef] [PubMed]
20. Ruoff, A.L.; Rodriquez, C.O.; Christensen, N.E. Elastic Moduli of Tungsten to 15 Mbar, Phase Transition at 6.5 Mbar, and Rheology to 6 Mbar. *Phys. Rev. B Condens. Matter Mater. Phys.* **1998**, *58*, 2998–3002. [CrossRef]
21. Apfelbaum, E.M.; Vorob'ev, V.S.; Martynov, G.A. The unit compressibility factor and critical parameters of mercury. *Chem. Phys. Lett.* **2005**, *413*, 342–345. [CrossRef]
22. Apfelbaum, E.M.; Vorob'ev, V.S. The Line of the Unit Compressibility Factor (Zeno-Line) for Crystal States. *J. Phys. Chem. B* **2020**, *124*, 5021–5027. [CrossRef] [PubMed]