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To the fractal equation of state

R A. Magomedov1, R R Meilanov1, R P Meilanov1, E N Akhmedov1, V D Beybalaev1,2 and A A Aliverdiev1,2

1 Institute for Geothermal Research of the Dagestan Scientific Center of the Russian Academy of Sciences, Shamilya 39A, Makhachkala, Dagestan 367030, Russian Federation
2 Dagestan State University, M Gadzhieva 43A, Makhachkala, Dagestan 367000, Russia

E-mail: aliverdi@mail.ru

Abstract. The generalization of thermodynamics in the formalism of fractional order derivatives, allowing to take into account non-local effects in the thermodynamic processes, is made to the development of approach proposed in our recent publications. A one-parameter (depending on the fractional order derivative index) equation of state is derived. On its basis the calculation of entropy, isochoric heat capacity and compressibility factor for a monatomic gas and multi-component systems in a wide temperature and pressure range is realized. Thus, the thermodynamics in fractional calculus contains the traditional thermodynamics as a special case and expands the scope of its application.

1. Introduction

As usual for the study of non-equilibrium processes there are two mutually complementary approaches: (i) microscopic and (ii) phenomenological. A microscopic approach based on the kinetic equations gives a rigorous and consistent derivation of equations for conserved quantities [1-3]. A phenomenological approach is based on the application of the principles of non-equilibrium thermodynamics [4]. Transport phenomena express fundamental aspects of the structure and properties of matter and their investigation requires the involvement of the full arsenal of theoretical and mathematical physics and the development of new approaches.

The description of non-equilibrium processes by the statistical methods presupposes the presence of parameters of a "reduced description". It is important that along with the hierarchy of time scales that allow us to introduce "reduced parameters", there is also a certain subordination between slowly and rapidly changing quantities, thanks to the appearance of a special kind of correlations of the particles in the system. These correlations lead to the fact that the parameters of the short description begin to determine the state of the system and there is no necessity to average the microscopic dynamics of the system every time [2].

But it is necessary to note that the characteristic times of correlations of microscopic variables $\tau_{mic}$ should be significantly less than the characteristic times of variation of macroscopic times $\tau_{mac}$: $\tau_{mic} \ll \tau_{mac}$. This relation underlies the various procedures for averaging the many-particle distribution functions with the subsequent derivation of the traditional equations of motion for transport phenomena. However, for a wide class of substances, especially those having a fractal structure, there is a slow relaxation of fast processes. These processes proceed according to a power law $\tau^{-\alpha}$. These
fast processes don’t have time to relax for times of order $\tau_{\text{mac}}$, and for them the condition $\tau_{\text{mic}} \ll \tau_{\text{mac}}$ is violated and instead it the condition $\tau_{\text{mic}} \approx \tau_{\text{mac}}$ holds. Finally this leads to divergent magnitudes in the kinetic coefficients and to a clear display of non-local properties, memory effects, self-organization, etc.

The absence of local approximations, both in terms of spatial and temporal characteristics in such systems leads to the abandonment of traditional averaging methods in statistical analysis. So, for the correct description we must simultaneously consider both microscopic and macroscopic space-time scales, and it is fundamentally different from any traditional approach. As a result, instead of the known equations of mathematical physics, it is necessary to start from the equations of the mathematical apparatus of fractional order integration-and-differentiation.

The study of non-equilibrium processes in terms of the principle of local disequilibrium requires to consider memory effects (non-locality in time), spatial correlations (coordinate non-locality) and the development of innovative analysis methods. Some of these methods are based on the mathematical apparatus of fractional derivatives. [5-9] In the case of the equilibrium thermodynamics the transition to fractional derivatives on the thermodynamic parameters (temperature, volume) also contributes to the theory the rate of derivative of fractional order ($\alpha$), that implicitly takes into account the non-locality of the collision integral, thereby leading to the expansion of the area of applicability of the one-parameter family equations of state to fractal equation of state.

Here we present a calculation of the coefficient of compressibility and entropy for neon, argon and water made using the parameter $\alpha$ calculated from the fractal equation of state in comparison with experimental tabulated data.

2. Fractal equation of state taking into account the second virial coefficient
As we have shown in our recent papers [10, 11], the generalization of Legendre transformations to the fractional derivatives can be performed starting from the expression for the fractional order total differential of a function of two variables $L(x,y)$:

$$d^{\alpha}L(x,y) = \frac{\partial^{\alpha}L(x,y)}{\partial x^{\alpha}}dx^{\alpha} + \frac{\partial^{\alpha}L(x,y)}{\partial y^{\alpha}}dy^{\alpha}. \quad (1)$$

Here the derivatives of fractional order are defined as [12]

$$\frac{\partial^{\alpha}L(x,y)}{\partial x^{\alpha}} = \frac{1}{\Gamma(1-\alpha)} \frac{\partial}{\partial x} \int L(\xi,y) d\xi, \quad 0 < \alpha \leq 1, \quad \Gamma(z) \text{ is Euler gamma function, } dx^\alpha = \frac{(dx)^\alpha}{\Gamma(1+\alpha)}$$

the "generalized" infinitesimal increment of the independent variable. A detailed derivation and mathematical justification of complete differential in a generalization for fractional derivatives is given in the appendix of our resent paper [10].

Applying the generalized total differential to the Helmholtz potential

$$dF = -PdV -TdS. \quad (2)$$

we obtain:

$$d^{\alpha}F = \frac{P \cdot V^{1-\alpha}}{\Gamma(1-\alpha)}dV^{\alpha} - \frac{S \cdot T^{1-\alpha}}{\Gamma(1-\alpha)}dT^{\alpha}. \quad (3)$$

Here $\alpha$ is the rate of derivative of fractional order ($0 < \alpha \leq 1$), $F = -kT \cdot \ln(Z)$ is the Helmholtz potential, $Z = \sum_i \exp(-\varepsilon_i/kT)$ is the statistical sum (the partition function) [12], and the derivative of a fractional order is given by

$$\frac{\partial^{\alpha}F(V)}{\partial V^{\alpha}} = \frac{1}{\Gamma(1-\alpha)} \frac{\partial}{\partial V} \int_0^V F(v) (V-v)^{\alpha-1}dv. \quad (4)$$
Hence we have:

\[ P = -\frac{\Gamma(2-\alpha)}{\Gamma^{1-\alpha}} \frac{\partial^\alpha F}{\partial V^\alpha} |_{r} \]  

Equations (3)-(5) for \( \alpha = 1 \) coincide with the corresponding expressions of traditional thermodynamics. For \( \alpha \neq 1 \) if we start from the expression for the statistical sum

\[ Z = \frac{1}{(2\pi \hbar)^{3N}} \int \ldots \int dp_1 \ldots dp_N dr_1 \ldots dr_N \exp\left(\frac{-H}{kT}\right) \]  

for an ideal gas and use expression (2), than we can obtain the following one-parametric “fractal” equation of state with second virial coefficient \((B)\) for noble gases [8]:

\[ P = \rho RT \left\{ 1 + \rho B + (1 - \alpha) \left[ \ln \left( \frac{eM}{\rho N_A} \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} \right) + \psi(1) - \psi(2-\alpha) - \rho B \right] \right\}. \]

Here \( P \) is the pressure, \( \psi(x) \) is the Euler \( \psi \)-function of the number \( x \), \( \psi(x) = \frac{d}{dx} \ln \Gamma(x) = \frac{\Gamma'(x)}{\Gamma(x)} \), \( \rho \) is the density, \( T \) is the temperature, \( k \) is a Boltzmann constant, \( N_A \) is the Avogadro's number, \( R \) is the universal gas constant, \( a \) and \( b \) are Van-der-Waals constants \((B(T) = b - \frac{a}{kT})\), \( M \) is the molar mass, \( m \) is the mass of atom, \( e \) is the exponent \((2.71828\ldots)\), \( h \) is the Plank constant. On the base of (3) we can find the compressibility factor \((z)\) and the entropy \((S)\):

\[ z = 1 + \rho B + (1 - \alpha) \left[ \ln \left( \frac{eM}{\rho N_A} \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} \right) + \psi(1) - \psi(2-\alpha) - \rho B \right], \]

\[ S = \frac{3}{2} \frac{R}{M} \left[ \ln \left( \frac{eM}{\rho N_A} \right)^{2/3} \left( \frac{mkT}{2\pi \hbar^2} \right)^{1/2} + \frac{1}{2 - \alpha} + \psi(2) - \psi(3 - \alpha) - \right. \]

\[ - \left. \frac{2}{3} \frac{\rho}{M} \left( b - (1 - \alpha) \frac{5 - 2\alpha}{(2 - \alpha)(3 - \alpha)} \right) \right\}. \]

Here \( M \) is the molar mass, \( P_c = \frac{a}{27b^2} \) is the critical pressure. Assuming \( \alpha = 1 \) in Eqn. (6) give us the equation of state for ideal gas. It can be argued that the transition to a fractional derivative in thermodynamics means an implicit consideration of the interaction between particles, since the equation of state (6) is a fractal equation of state, different from the equation of state for an ideal gas.

3. Results and discussion
The comparison of the values calculated from formulas (4) - (7) and tabulated values for Neon and Argon for pressures from 1 to 10 MPa for argon, together with the corresponding gas density at the temperature of 500 K, are given in Tables 1.

We can see that for both neon and argon up to 10 MPa, the difference of the coefficient \( \alpha \) from one is very small: for 10 MPa this is the fifth sign after the point for neon and the fourth sign after the point for argon. In general, however, the behavior for both substances has a very little impact on nonlocal effects.
Table 1. The heat properties of Neon and Argon for $T=500$ K

| P, MPa | $\rho$, kg/m$^3$ | $z$ [14] | $z$ | $S \times 10^3$, J/(kg K) [14] | $S \times 10^3$, J/(kg K) | $\alpha$ |
|-----|-------|-------|------|-----------------|-----------------|-------|
| Neon, $B_2=6.738 \times 10^{-3}$ m$^3$/kg [13] |
| 1.0 | 4.84 | 1.0033 | 1.00326 | 6.839 | 6.83900 | 0.99999 |
| 2.0 | 9.65 | 1.0066 | 1.00657 | 6.553 | 6.55294 | 0.99999 |
| 3.0 | 14.42 | 1.0099 | 1.01003 | 6.386 | 6.38601 | 0.99998 |
| 4.0 | 19.17 | 1.0132 | 1.01305 | 6.267 | 6.26690 | 0.99997 |
| 5.0 | 23.88 | 1.0165 | 1.01650 | 6.175 | 6.17501 | 0.99997 |
| 6.0 | 28.57 | 1.0197 | 1.01958 | 6.100 | 6.09992 | 0.99997 |
| 8.0 | 37.84 | 1.0263 | 1.02640 | 5.981 | 5.98096 | 0.99993 |
| 10.0 | 47.00 | 1.0329 | 1.03296 | 5.888 | 5.88802 | 0.99991 |
| Argon, $B_2=1.827 \times 10^{-4}$ m$^3$/kg [13] |
| 1.0 | 0.96 | 1.0002 | 1.00097 | 4.145 | 6.83900 | 0.99996 |
| 2.0 | 9.59 | 1.0017 | 1.00200 | 3.664 | 6.55294 | 0.99998 |
| 3.0 | 19.15 | 1.0035 | 1.00358 | 3.519 | 6.38601 | 0.99999 |
| 4.0 | 28.67 | 1.0054 | 1.00550 | 3.433 | 6.26690 | 0.99998 |
| 5.0 | 38.16 | 1.0074 | 1.00726 | 3.372 | 6.17501 | 0.99998 |
| 6.0 | 47.60 | 1.0095 | 1.00938 | 3.324 | 6.09992 | 0.99995 |
| 8.0 | 57.00 | 1.0116 | 1.01150 | 3.284 | 5.98096 | 0.99992 |
| 10.0 | 75.66 | 1.0161 | 1.16048 | 3.222 | 5.88802 | 0.99984 |

Table 2. The heat properties of Argon and water vapor for $T=900$ K

| P, MPa | $\rho$, kg/m$^3$ | $z$ [14] | $z$ | $S \times 10^3$, J/(kg K) [14] | $S \times 10^3$, J/(kg K) | $\alpha$ |
|-----|-------|-------|------|-----------------|-----------------|-------|
| Argon, $B_2=5.007 \times 10^{-4}$ m$^3$/kg [13] |
| 1.0 | 5.32 | 1.0026 | 1.00287 | 3.971 | 3.970590 | 0.99999 |
| 2.0 | 10.62 | 1.0051 | 1.00552 | 3.827 | 3.826590 | 0.99999 |
| 3.0 | 15.89 | 1.0077 | 1.00815 | 3.742 | 3.741589 | 0.99999 |
| 4.0 | 21.14 | 1.0103 | 1.01077 | 3.682 | 3.681589 | 0.99999 |
| 5.0 | 26.35 | 1.0129 | 1.01338 | 3.635 | 3.634588 | 0.99999 |
| 6.0 | 31.54 | 1.0156 | 1.01594 | 3.597 | 3.596571 | 0.99999 |
| 8.0 | 41.84 | 1.0208 | 1.02109 | 3.536 | 3.535590 | 0.99999 |
| 10.0 | 52.03 | 1.0261 | 1.02620 | 3.489 | 3.488595 | 0.99999 |
| 12.0 | 62.11 | 1.0315 | 1.03138 | 3.450 | 3.449594 | 0.99998 |
| 16.0 | 81.95 | 1.0423 | 1.04236 | 3.389 | 3.388592 | 0.99991 |
| 20.0 | 101.37 | 1.0532 | 1.05323 | 3.342 | 3.341579 | 0.99983 |
| Water, $B_2=-1.934 \times 10^{-3}$ m$^3$/kg [15] |
| 1.0 | 2.42 | 0.9958 | 0.99613 | 8.096 | 8.09606 | 0.9999 |
| 2.0 | 4.86 | 0.9916 | 0.99216 | 7.770 | 7.77005 | 0.9999 |
| 3.0 | 7.31 | 0.9874 | 0.98802 | 7.577 | 7.57694 | 0.9999 |
| 4.0 | 9.79 | 0.9832 | 0.98368 | 7.438 | 7.43797 | 0.9998 |
| 5.0 | 12.30 | 0.9790 | 0.97916 | 7.329 | 7.32896 | 0.9998 |
| 6.0 | 14.82 | 0.9748 | 0.97425 | 7.238 | 7.23803 | 0.9998 |
| 8.0 | 19.93 | 0.9662 | 0.96574 | 7.093 | 7.09305 | 0.9997 |
| 10.0 | 25.14 | 0.9577 | 0.95756 | 6.977 | 6.97701 | 0.9996 |
| 20.0 | 52.68 | 0.9140 | 0.91401 | 6.589 | 6.58898 | 0.9988 |
Table 2 presents the calculated and tabulated data for Argon and water for \( T = 900 \) K. To get into the zone of possible nonlocal effects, we maximized (as far as reference data allowed) the range of pressures. As it was expected, there is a significantly greater difference in the behavior of substances: a noble gas Argon and water. At a pressure of 20 MPa, the coefficient \( \alpha \) for water differs from unity already in the third sign after the point.

The situation changes radically on the saturation line. The data for the point \( (P=22.56 \) MPa, \( T=647.15 \) K) for both water vapor and liquid are presented in Table 3. We see that the rate \( \alpha \) here is markedly different from one and there is a jump in the phase transition. But even before the phase transition, the fractional order rate is already significantly different from one.

|          | \( B_2 \), m\(^3\)/kg | \( \rho \), kg/m\(^3\) | \( z \) | \( S \times 10^3 \), J/(kg K) | \( S \times 10^3 \), J/(kg K) | \( \alpha \) |
|----------|------------------------|----------------------|------|----------------------------|----------------------------|---------|
| vapour   | -25\( \times 10^{-3} \) | 288                  | 0.2623 | 1.0755                     | 1.07547                    | 0.6378  |
| liquid   | -25\( \times 10^{-3} \) | 357.14               | 0.2115 | 1.0332                     | 1.03318                    | 0.5781  |

To clarify the physical meaning of fractional order derivatives in terms of thermodynamic parameters, we note that under conditions where the hypothesis of molecular chaos is not fulfilled, the role of fluctuations in the thermodynamic parameters becomes important. In this case, the principle of local equilibrium is violated, and the principle of local disequilibrium takes place. The fluctuations of the thermodynamic parameters contribute to the thermodynamic process, which in turn leads to the appearance of power "tails" of the distribution function [3]. In terms of its physical meaning, the transition to fractional derivatives with respect to thermodynamic parameters can be interpreted as a way of taking into account the principle of local disequilibrium, when the thermodynamic process occurs under conditions of large fluctuations. That is, the transition from one equilibrium state to another does not occur through a set of equilibrium states of the system, but the contribution is made by fluctuations and non-equilibrium states that do not have time to fully relax to the equilibrium state. The measure of the fluctuations is the fractional order derivative rate.

4. Conclusion
As we can see the results of our calculations are in satisfactory agreement with the experimentally measured data. In addition, it is possible to extrapolate the equation of state to the extreme thermodynamic parameters, where experiments are difficult or impossible. The thermodynamics of fractional calculus, containing a traditional thermodynamics (which is based on the principle of local equilibrium) as a special case, is expanding its scope, encompassing the processes under fulfillment of the principle of local non-equilibrium.

We have shown that proceeding from the generalization of the equilibrium thermodynamics to the case of derivatives of fractional order, it is possible to give a one-parametric equation of state and, on its basis, obtain analytic expressions for the thermodynamic characteristics of matter. As shown by our calculations for noble gases (neon and argon), the results are in satisfactory agreement with experimentally measured data. As follows from the analysis of the results, the transition to fractional derivatives with respect to time and coordinate is not a formal mathematical transition, but is connected with the fundamental aspects of the physics of many-particle systems.

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