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Calculation of multicomponent compound properties using generalization of thermodynamics in derivatives of fractional order

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Abstract. The generalization of thermodynamics in formalism of fractional derivatives is presented. One-parametric “fractal” state equation with second virial coefficient is obtained. The calculation of entropy S and compressibility z of the refrigerant freon R409B for the pressure range from 0.01 to 3.8 MPa and temperature range from 210 to 370 K is given.

1. Introduction

Recently, there are intensive studies on the generalization of statistical physics and both equilibrium and non-equilibrium thermodynamics [1–5]. Software environments for calculation of thermophysical parameters of matter are also being developed [6].

The standard approach to account non-local effects results in appearance of an integral operator in differential equations, and the kernel of the integral operator contains the information about non-locality nature. To solve such equations it is required to present the integral operator as a series of differential operators with the ascending rate of differentiation. Obtained equations appear to be too complex and not always can be solved. In this context the technique of integro-differentiation of fractional order is the subject of interest [7, 8]. Derivatives of fractional order being the combination of a traditional operations of differentiation and integration present a new approach in the theory of non-local differential equations. Recently fractional calculus is applied in all directions of advancement of science.

Development of modern technologies of renewable energy requires creation of new refrigerants and calculation of their thermal characteristics. One of such refrigerants is freon R409B for which on a base of fractal state equation we have calculated thermalphysic parameters (entropy S and compressibility z).

2. Fractal state equation with accounting of second virial coefficient

To obtain the state equation we use expression from [8]

$$P = - \frac{\Gamma(2 - \alpha)}{V^{1-\alpha}} \frac{\partial^\alpha F}{\partial V^\alpha} \bigg|_T, \quad (1)$$

where F is the Helmholtz potential.



The derivative of fractional order is defined by expression

$$\frac{\partial^\alpha F(V)}{\partial V^\alpha} = \frac{1}{\Gamma(1-\alpha)} \frac{\partial}{\partial V} \int_0^V \frac{F(\nu)}{(V-\nu)^\alpha} d\nu, \quad (2)$$

$0 < \alpha \leq 1$ is the rate of derivative of fractional order.

Ration (1) for the case $\alpha = 1$ is the base of standard approach of the derivation of the state equation, in other cases we have a new one-parametric class of state equations. Expression of Helmholtz potential for the case of classical statistical physics [9] has the form $F = -kT \ln Z$, where Z is the statistical summ, that is generally given by the expression

$$Z = \frac{1}{(2\pi\hbar)^{3N} N!} \int \cdots \int \exp\left(-\frac{H}{kT}\right) d\vec{p}_1 \cdots d\vec{p}_N d\vec{r}_1 \cdots d\vec{r}_N, \quad (3)$$

where N is the number of particles in the system, p is the particle impulse, r is the particle coordinate.

Freon R409B consists of three components. To account that we use expression

$$H = \sum_{n=1}^{N_1} \frac{p_n^2}{2m_1} + \sum_{n=1}^{N_2} \frac{p_n^2}{2m_2} + \sum_{n=1}^{N_3} \frac{p_n^2}{2m_3} + U(r_1, \cdots r_{N_1}, r_{n+1}, \cdots r_{N_2}, \cdots r_{N_1+N_2+N_3}). \quad (4)$$

The expression (4) represents the sum of kinetic and potential energies of the particles. $N = N_1 + N_2 + N_3$. Substituting (4) into (3) we obtain

$$Z = \frac{Q(N, V, T)}{N! \Lambda^{3N}}, \quad (5)$$

where $\Lambda = \sqrt{2\pi\hbar^2/m_1^x m_2^y m_3^z kT}$ is the thermal wave-length of the particle.

$$Q(N, V, T) = \int \cdots \int \exp\left(-\frac{U}{kT}\right) dr_1 \cdots dr_{N_1+N_2+N_3}$$

is the configuration integral. Represent (5) in the following form

$$Z = \frac{V^N}{N! \Lambda^{3N}} \left[1 + \frac{1}{V^N} \int \cdots \int \left(\exp\left(-\frac{U}{kT}\right) - 1 \right) d\vec{r}_1 \cdots d\vec{r}_{N_1+N_2+N_3} \right]. \quad (6)$$

For the Helmholtz potential we obtain

$$F = -kT \ln Z = -kT \left[\ln \frac{V^N}{N! \Lambda^{3N}} + \ln \left(1 + \frac{1}{V^N} \int \cdots \int \left(\exp\left(-\frac{U}{kT}\right) - 1 \right) d\vec{r}_1 \cdots d\vec{r}_{N_1+N_2+N_3} \right) \right]. \quad (7)$$

Substituting (7) into (1) we obtain the following state equation

$$P = kT \frac{\Gamma(2-\alpha)}{V^{1-\alpha}} \frac{\partial^\alpha}{\partial V^\alpha} \left[\ln \left(\frac{V^N}{N! \Lambda^{3N}} \right) + \ln \left(1 + \frac{1}{V^N} \int \cdots \int \left(\exp\left(-\frac{U}{kT}\right) - 1 \right) d\vec{r}_1 \cdots d\vec{r}_{N_1+N_2+N_3} \right) \right]. \quad (8)$$

Calculating the derivative fractional order, as in [10], we obtain the following fractal state equation for the three-component system

$$P = \frac{NkT}{V} \left\{ 1 + \frac{N}{V} \sum_{i=1}^3 x_i^2 B_i + \frac{N}{V} \sum_{i \leq j=1}^3 x_i x_j B_{ij} + (1-\alpha) \left(\ln \left(\frac{eV}{N} \left[\frac{m_i^{x_i} kT}{2\pi\hbar^2} \right]^{3/2} \right) + \right. \right. \\ \left. \left. + \psi(1) - \psi(2-\alpha) - \frac{N}{V} \sum_{i=1}^3 x_i^2 B_i - \frac{N}{V} \sum_{i \leq j=1}^3 x_i x_j B_{ij} \right) \right\}, \quad (9)$$

where $x_i = \frac{N_i}{N}$, B_i , $B_{i<j}$ are virial coefficients for the compound, $i, j = 1, 2, 3$. For further calculations we assume that virial coefficients are equal.

Finally the state equation is

$$P = \rho R_{\text{cm}} T \left\{ 1 + \rho B + (1 - \alpha) \left(\ln \left(\frac{eM}{\rho N_A} \left[\frac{m_1^x m_2^y m_3^z kT}{2\pi \hbar^2} \right]^{3/2} \right) + \psi(1) - \psi(2 - \alpha) - \rho B \right) \right\}, \quad (10)$$

where $R_{\text{cm}} = 86.009$ is the specific gas constant in J/(kg·K), $M = 96.67 \times 10^{-3}$ is the molecular weight in kg/mol, m_1^x is the mass fraction of the component R22 in compound, m_2^y is the mass fraction of the component R124, m_3^z is the mass fraction of the component R142.

Compressibility factor for a multicomponent mixture is

$$z = 1 + \rho B + (1 - \alpha) \left(\ln \left(\frac{eM}{\rho N_A} \left[\frac{m_1^x m_2^y m_3^z kT}{2\pi \hbar^2} \right]^{3/2} \right) + \psi(1) - \psi(2 - \alpha) - \rho B \right). \quad (11)$$

For the entropy we proceed from the expression

$$S = -\frac{\Gamma(2 - \alpha)}{T^{1-\alpha}} \frac{\partial^\alpha F}{\partial T_V^\alpha}. \quad (12)$$

After calculations analogous to the derivation of the state equation in [8] and the entropy of single-component compound calculation in [10], we get the following expression for the entropy

$$\begin{aligned} S = & \frac{3}{2} Nk \left[\frac{1}{2 - \alpha} + \ln \left(\left(\frac{eV}{N} \right)^{2/3} \frac{mkT}{2\pi \hbar^2} \right) + \psi(2) - \psi(3 - \alpha) \right] + \\ & + k \left[\ln \left(1 - \frac{A(T)}{V} \right) - \frac{1}{2 - \alpha} \frac{N^2 a/T}{1 - \frac{A(T)}{V}} + \psi(2) - \psi(3 - \alpha) \right] - \\ & - k(1 - \alpha) \left[(2 - \alpha) \sum_{n=1}^{\infty} \frac{[(1 - N^2 b/V)(1 - A(T)/V)]^{n+1}}{(n+1)(n+2-\alpha)(n+3-\alpha)} + \right. \\ & \left. + \frac{N^2 a/T}{1 - \frac{A(T)}{V}} \sum_{n=1}^{\infty} \frac{[(1 - N^2 b/V)(1 - A(T)/V)]^{n+1}}{(n+2-\alpha)(n+3-\alpha)} \right], \end{aligned} \quad (13)$$

where $A(T) = N^2 B(T)$, $B(T) = \frac{1}{2} \int_0^\infty (1 - \exp(-\frac{U(r)}{kT})) dr$. The first term corresponds to the case of an ideal gas, the second and third terms correspond to account for the second virial coefficient $B(T) = (b - \frac{a}{kT})$. For $A(T)/V \ll 1$ we have

$$S = \frac{3}{2} Nk \left[\frac{1}{2 - \alpha} + \ln \left(\left(\frac{eV}{N} \right)^{2/3} \frac{mkT}{2\pi \hbar^2} \right) + \psi(2) - \psi(3 - \alpha) \right] - Nk \left[\frac{Nb}{V} - (1 - \alpha) \frac{Na}{VT} \right]. \quad (14)$$

The specific heat at constant volume we determine by the following generalized expression

$$C_V = T^\alpha \frac{\partial^\alpha S}{\partial T_V^\alpha}. \quad (15)$$

The derivative of fractional order (15) in more detail calculated in [10]. Finally, for the isochoric heat capacity we obtain the following expression

$$C_V = \frac{3}{2\Gamma(2 - \alpha)} Nk \left\{ 1 - \frac{2}{3} \frac{Na}{VkT} + (1 - \alpha) \left(\ln \left(\frac{eV}{N} \right)^{2/3} \frac{mkT}{2\pi \hbar^2} \right) - 1 - \frac{2}{3} \frac{N}{V} \left(b - \frac{a}{kT} \right) \right\}. \quad (16)$$

Table 1. The entropy S and the heat capacity C_V of neon for $B = -6.738344 \times 10^{-4} \text{ m}^3/\text{kg}$ and $T = 500 \text{ K}$.

P , MPa	ρ , kg/m ³	z	α	S [11], kJ/(kg K)	S , kJ/(kg K)	C_V [11], kJ/(kg K)	C_V , kJ/(kg K)
1	4.84	1.0033	0.9996	6.839	6.83895	0.618	0.61957
5	23.88	1.0165	0.9976	6.175	6.17502	0.619	0.62628
10	47.00	1.0329	0.9950	5.888	5.88802	0.620	0.63443
16	73.80	1.0526	0.9918	5.694	5.69422	0.622	0.64404
20	91.12	1.0656	0.9896	5.601	5.60102	0.623	0.65036
30	132.62	1.0982	0.9842	5.432	5.43217	0.625	0.66587
40	171.75	1.1307	0.9788	5.312	5.31231	0.628	0.68108
50	208.73	1.1630	0.9734	5.218	5.21818	0.630	0.69592

The results of calculations of S and heat capacity C_V for single-component compound (neon) compared to the experimental values in [11] are presented in table 1.

For calculations we used $T = 500 \text{ K}$, pressure range ΔP from 1 to 50 MPa and second virial coefficient $B = -6.738344 \times 10^{-4} \text{ m}^3/\text{kg}$. The application of similar technique for argon recently was presented in [10].

The calculation error of heat capacity is $\sim 10\%$. It can be caused by the error of measurement of experimental values of P , ρ , T and admitted simplifications in the calculation of the fractal derivatives.

Finally, we obtain the following expression for the entropy of a mixture

$$S = R_{\text{cm}} \left[\ln \left(\frac{eM}{\rho N_A} \left[\frac{m_1^x m_2^y m_3^z kT}{2\pi \hbar^2} \right]^{3/2} \right) + \frac{3}{2} \left[\frac{1}{2-\alpha} + \psi(2) - \psi(3-\alpha) \right] - R_{\text{cm}} \rho \left[b - (1-\alpha) \frac{a}{R_{\text{cm}} T} \right] \right]. \quad (17)$$

3. Calculation of entropy and compressibility of freon R409B

For calculating α parameter rewrite (10) in the form

$$P = \rho R_{\text{cm}} T \left\{ 1 + \rho B + (1-\alpha) \left(\ln \left(\frac{ek}{\rho R_{\text{cm}}} \left[\frac{m_{\text{cm}} kT}{2\pi \hbar^2} \right]^{3/2} \right) + \psi(1) - \psi(2-\alpha) - \rho B \right) \right\}, \quad (18)$$

where P is the pressure in Pa, ρ is the density in kg/m³, $B(a, b, T) = b - \frac{a}{kT}$ is the second virial coefficient in m³/kg, a and b are the Van der Waals constants, T is the temperature in K, α is the parameter, $e = 2.7182818 \dots$ is the exponent, N_A is the Avogadro constant, $m_{\text{cm}} = m_1^x m_2^y m_3^z$, k is the Boltzmann constant, $\hbar$ is the Planck constant, $\psi(x)$ is the psi-function of the number x .

Accordingly, the expressions for the compressibility factor and entropy take the form

$$z = 1 + \rho B + (1-\alpha) \left(\ln \left(\frac{ek}{\rho R_{\text{cm}}} \left[\frac{m_{\text{cm}} kT}{2\pi \hbar^2} \right]^{3/2} \right) + \psi(1) - \psi(2-\alpha) - \rho B \right), \quad (19)$$

$$S = R_{\text{cm}} \left\{ \left[\ln \left(\frac{ek}{\rho R_{\text{cm}}} \left[\frac{m_{\text{cm}} kT}{2\pi \hbar^2} \right]^{3/2} \right) + \frac{3}{2} \left[\frac{1}{2-\alpha} + \psi(2) - \psi(3-\alpha) \right] - \rho \left[b - (1-\alpha) \frac{a}{R_{\text{cm}} T} \right] \right] \right\}. \quad (20)$$

To find the van der Waals constants a and b , the following system of equations was solved for different values of the temperature T :

$$\begin{cases} S = S(a, b, T), \\ B = B(a, b, T). \end{cases} \quad (21)$$

Table 2. The entropy S and the compressibility z of freon R409B.

T , K	P , MPa	ρ , kg/m ³	S [6], kJ/(kg K)	S , kJ/(kg K)	α	z	$b \times 10^{-3}$, m ³ /kg	$a \times 10^{-22}$, Pa m ⁶ /kg ²
210	0.014480	0.80868	1.8489	1.849	0.9966	0.991	-60.76	0.94
220	0.027147	1.4547	1.8204	1.820	0.9936	0.986	-46.62	1.41
230	0.047651	2.4595	1.7966	1.797	0.9889	0.979	-35.17	1.84
240	0.079073	3.9476	1.7746	1.775	0.9817	0.970	-26.10	2.22
250	0.12505	6.0642	1.7598	1.760	0.9713	0.959	-20.50	2.51
270	0.27780	12.882	1.7335	1.733	0.9380	0.929	-12.73	2.99
300	0.73452	33.082	1.7053	1.705	0.8466	0.860	-6.86	3.57
330	1.6075	74.629	1.6815	1.681	0.6977	0.759	-3.91	4.06
350	2.5194	126.14	1.6613	1.661	0.5981	0.663	-2.62	4.37
370	3.8017	229.66	1.6238	1.624	0.4093	0.520	-1.56	4.68

Here the first equation corresponds to the entropy calculation expression (20) and the second equation corresponds the second second virial coefficient expression given above. The systems of equations were solved by means of numerical computation in the MathCad environment.

For every compound the Van der Waals constants must be independent of temperature. Indeed for a different temperatures it is needed to match a different constants a and b [12], that means that they depend of temperature.

The results of calculation are presented in table 2. For the comparison in the same table we also present the calculation of entropy using REFPROP [6]. We have considered that freon R409B consists of components R22, R124, R142B (compound—65/25/10 (%)). The maximum deviation of the entropy S , calculated by the formula (20), from the value of entropy S [6], calculated in the environment REFPROP, is $\sim 0.5\%$.

4. Conclusion

Peculiarity of the proposed generalization of equilibrium thermodynamics on the base of fractal calculus is the additional parameter—rate of the derivative of fractional order by thermodynamic parameters that allows to theoretically calculate values of thermodynamic characteristics on the base of obtained state equation. From the expression for the statistical sum we can derive one-parameter state equation and obtain analytic expressions for thermodynamic characteristics of matter. On the base of experimentally measured values of P , V , T and obtained “fractal” state equation we can calculate the rate of the derivative of fractional order by thermodynamic parameters and further calculate thermodynamic characteristics using obtained analytic expressions. The results of our calculation are evidence of the availability of considered approach.

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