The Joule-Thomson Effect for Refrigerants with Dopants of the Fullerenes and Carbon Nanotubes

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The importance of thermodynamic and phase behavior of working fluids embedded with nanostructured materials is fundamental to new nanotechnology applications. The fullerenes (C₆₀) and carbon nanotubes (CNT) adding to refrigerants change their thermodynamic properties the Joule - Thomson effect such as dislocation of critical point, gas – liquid equilibria shift at alias. Algorithm of refrigerant thermodynamic property calculations based on the NIST (National Institute of Standards and Technologies) equation of state at different carbon nanotube concentrations is proposed. Thermodynamic properties of carbon dioxide in the C₆₀ and CNT presence are given. Considering the extremely large number of different both nanoparticle types and reference fluids, it is obvious that there is need for developing theoretically sound methods of the prompt estimation thermodynamic properties and phase equilibria for emerging working media. The effect of nanoparticles on the critical point shift for classical fluids doped by nanoparticles is examined. The regular and singular parts of thermodynamic surface of reference fluid and nanofluid (volume nanoparticle concentration < 5%) are suggested to coincide in the reduced form. The shift of critical point for nanoliquids of industrial interest is theoretically predicted. Results of calculations of phase equilibria for some nanofluids are described.

Keywords: fullerene; carbon nanotubes; carbon dioxide; Joule-Thomson effects; nanofluids; saturation curve; thermodynamic properties.

1. Introduction

Nanofluids (NF) - solutions of nanoparticles, whose sizes range from 20 to 100 Å, are objects of intensive research, thanks to previously unknown effects and an anomalous increase in the thermal conductivity. The great interest in studying the behavior of nanofluids is explained by a wide range of applications: from production and
energy conversion, transport of oil, refrigeration and air conditioning to electronics, the textile industry and paper production. According to the ratings agency Thomson - Reuters, research in the field of nanofluids refers to the "leading edge of research".

The subject of research is the effect of nanostructured material additives on the thermophysical properties and efficiency of working fluids and heat transfer media in energy conversion systems. Development of scientific and technical bases for the implementation of new nanofluids in the heat and power systems. Research methods - mathematical modeling of the thermophysical properties of working and heat transfer media, neural network methods for predicting the thermodynamic efficiency of unexplored substances, laboratory experiments, comparing and analyzing the results of numerical simulation with the results of experimental studies. Scientific novelty of the results given in the work.

The following new scientific results were obtained: for the first time, an approach to modeling the thermodynamic characteristics of classical working fluids and coolants with the addition of nanostructured materials based on the thermodynamic similarity of nano- and near-critical fluids was developed and presented. The published literature reviews cover a wide range of applications and properties of nanofluids [1–12]. Key features of nanoparticles include the nonlinear relationship between the thermophysical properties and the bulk concentration of nanoparticles [1], as well as the significant intensification of critical heat fluxes at boiling [2–5]. The use of NF allows you to create a new class of working fluids and coolants for various technological applications, achieving an increase in energy efficiency, lower operating cost, size reduction and reduction of environmental pollution [6 - 12]. Examples of successful application of nanofluids for solving practical problems include [1–12]:

- engine cooling;
- additives in lubricating oils;
- coolants in shirts diesel - generators;
- heating and cooling buildings;
- cooling media in electronics;
- additives in transformer oil;
- cooling media for nuclear reactors;
- solar systems for heating;
- artificial cold (refrigerator chillers);
- military equipment;
- space;
- cooling of high-power lasers;
- biomedical applications.

Two aspects attract industry attention to the introduction of nanofluids - the increase in thermal conductivity and the intensification of convective heat transfer processes as compared with conventional heat transfer media.

Thus, the topic of this study, in which scientific and technical approaches are being developed, is to solve a number of important problems of technical thermal physics and power engineering,

to increase the efficiency of energy conversion systems using a promising class of working fluids and heat carriers nanofluids,

to search for working fluids that reduce the compression pressure in CO₂ compressors.

As an objective we also consider ways to intensify the processes of energy and momentum transfer in microchannels in the flow of nanofluids through nano edges and to compare the effectiveness of hydrodynamic processes with microstructural elements.

The main goal of this work is to evaluate the addition of nanostructured materials and its impact to changes in the thermodynamic properties of refrigerants. As a system, on which the approach to determining the thermodynamic properties of refrigerants with nanostructured materials is tested, a mixture of carbon dioxide is considered - R744 with fullerene and carbon nanotubes.

2. Impact of nanoparticles on the critical point shift

A critical point is the singular point of the pressure-density-temperature surface that designates conditions under which a liquid and its vapor phase can coexist. Knowledge of critical point (line) gives information about thermodynamic behavior of pure substance (binary mixture). Nanoparticles change the intermolecular interactions between nanofluid components and shift the location of singularities. It is suggested that the liquids with small impurities do not violate the corresponding state principle and the dimensionless thermodynamic surfaces of reference liquid and nanofluid are coinciding [5], [6].

Estimation of the change for CO₂ critical point with different: CNT – Fig. 1a, fullerenes – Fig. 1b.

![Figure 1](image)

**Figure 1 – The bulk density of the CNT and C₆₀ nanoparticles**

The portrait of thermodynamic behavior near critical point for selected fluids was obtained via application of the fundamental equations of state [7, 8]. The variations of critical temperature and density after adding of different nanoparticles are provided in Table 1 and in Figs. 1 - 3. The growth of nanoparticle concentration leads to insignificant change of critical temperature for the CO₂ with graphene derivatives nanoliquid.

| Napoparticles | Δρₜ, kg/m³ | Δρₜ, kg/m³ | ΔTc, K | ΔTc, K |
|---------------|------------|------------|--------|--------|
| CNT           | 5.7        | 22.6       | 0.01   | 0.11   |
| C₆₀           | 7.5        | 33.2       | 0.01   | 0.13   |

Table 1 – Effects of CNT and C₆₀ on the shift of critical temperature (∆Tc = Tₙ - Tₙ₀) and density (∆ρₜ = ρₜ₀ₙ - ρₜ₀)
The critical point identifies the thermodynamic behavior of a pure substance in a wide range of state parameters. The addition of nanoparticles redistributes intermolecular interactions between particles of a liquid and leads to a shift of the equilibrium liquid – vapor line. To assess the thermodynamic behavior of nanofluids, we assume that liquids with small additions of nanoparticles satisfy the principle of the corresponding states [13]. From this, it follows that the regular and singular parts of the thermodynamic surface of the base fluid and the nanofluid coincide. It is assumed that equation is valid for both pure substance and nanofluid. The application of this equation is based on the principle of isomorphism. The scaling parameters obtained from the data for the pure substance were used to determine the critical parameters of the nanofluid. Because of the calculations, it was found that the position of the critical temperature for carbon dioxide ($T_c = 304.13K$) is shifted by 0.1K in the range of volume concentrations of carbon nanotubes not exceeding 5% ($T_{cnf} = 304.27K$). The accuracy of the algorithm was tested on the prediction of critical parameters and parameters of the critical point of some substances (ammonia, isobutane and toluene). The accuracy of the description of the density according to the equation of state in the temperature range 290 ... 300K is less than 0.1% in the liquid phase and indirectly confirms the reliability of the prediction of critical parameters and parameters of the critical point of some substances (ammonia, isobutane and toluene). The calculations showed the reproduction of data [16] with the accuracy of standard reference data. The shift of the critical point $\Delta T_c = T_{cnf} - T_{cnf}$ in natural refrigerants with the addition of carbon nanotubes.

3. Thermodynamic properties of the nanofluids

The fundamental equations of state in reduced form [7], [8] are used to restore thermodynamic surface in vicinity of singular point. Compressibility factor ($Z$) of nanofluid in the range 0 … 5% volume concentrations $\varphi$ of nanoparticles (np) was found via scaled reference fluid properties

$Z = Z(\rho_{cnf}/\rho, T/T_{cnf})$. (1)

Critical parameters of nanofluid $(\rho_{cnf}, T_{cnf})$ were calculated from fundamental equation of state in vicinity of critical point. The density of nanofluid (nf) was determined via reference fluid density ($\rho_f$) by standard approximation [14]:

$\rho_{nf} = (1 - \varphi)\rho_f + \varphi\rho_{np}$ (2)

To estimate the nanofluid critical parameters an algorithm from [13] was applied. From the fundamental EoS for reference liquid the $\rho - \rho - T$ data in vicinity of...
critical point were generated to establish the fitting parameters in the power law equations [13]

\[
\frac{\rho_0}{\rho_\sigma} - 1 = N_1(1 - \frac{T_\sigma}{T_c})^{\pm N_2}(1 - \frac{T_\sigma}{T_c})^\beta
\]  

(3)

Here \( \rho_0 \) and \( T_c \) are critical density and temperature; \( N_1, N_2, \beta \) are fitting parameters; \( \rho_\sigma \) and \( T_\sigma \) are density and temperature along saturation curve.

An equation is valid both reference liquid and nanofluids only in the critical domain. The fitting parameters in equation (3) were restored from the \( \rho - T \) data for reference liquid and then used to estimate critical parameters of nanofluid. Reliability and accuracy of algorithm tested at limit \( \varphi = 0 \) to reproduce the critical points of reference liquids. The results of our calculations reproduce the EoS data from [11] within experimental accuracy of density measurements for given substance.

Thermodynamic functions are calculated on the basis of algebraic transformations and the operation of differentiation according to standard relations for characteristic functions. Similarly, expressions for calculating enthalpy and entropy are found from the relationships given below.

A complete list of the calculated relations for thermodynamic functions according to the equation of state (1) - (12) is given in [16]. Ideal-gas functions and the coefficients of equation for CO \(_2\) are given in [18]. Algebraic expressions for calculating properties were programmed into MATLAB. Table 2 shows the results of calculations of the thermodynamic functions of R744 for various volume concentrations of the fullerenes and carbon nanotubes. The Appendix contains tables of thermodynamic properties of some technically important substances with various nanoparticle additives.

To calculate the thermodynamic properties, we used the models of simplified fundamental equations of state NIST (National Institute of Standards and Technologies) for 20 technically important substances developed in [15]. The equations of state are presented in the form of a superposition of the Helmholtz free energy for an ideal gas (index “0”) and interacting particles (index “i”):

\[
\sigma(\rho,T) = \sigma^0(\rho,T) + \sigma^i(\rho,T)
\]  

(4)

In the dimensionless form, the equation has the form

\[
\frac{\sigma(\rho,T)}{R_T} = \alpha(\delta,\tau) = \alpha^0(\delta,\tau) + \alpha^i(\delta,\tau)
\]  

(5)

where \( R \) is the universal gas constant, \( \alpha \) is the dimensionless free energy of the Helmholtz, \( \tau = T_c / T \) and \( \delta = \rho / \rho_\sigma \) are the dimensionless temperature and density.

The Helmholtz free energy of an ideal gas is determined by the enthalpy (h) and entropy (s):

\[
\sigma^0 = h^0 - R_T - Ts^0
\]  

(6)

The functional form of the components of the dimensionless free energy of Helmholtz (5), proposed in [15], is written as follows:
Table 2 – The Joule – Thomson effect and thermodynamic properties of R744 with dopants of the fullerenes and carbon nanotubes

| Temperature, K | Pressure, MPa | Liquid Enthalpy (l) kJ/kg | Vapor Enthalpy (v) kJ/kg | Liquid Entropy (l) kJ/kg - K | Vapor Entropy (v) kJ/kg - K | Liquid Joule-Thomson K/MPa | Vapor Joule-Thomson K/MPa |
|---------------|--------------|---------------------------|--------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|
| 250.00        | 1.7850       | 1046.0                    | 46,644                   | 147.71                      | 437.04                      | 0.80675                   | 1.9641                    |
| 260.00        | 2.4188       | 998.89                    | 64,417                   | 169.44                      | 435.92                      | 0.88954                   | 1.9144                    |
| 270.00        | 3.2033       | 945.83                    | 88,374                   | 192.41                      | 432.56                      | 0.97317                   | 1.8626                    |
| 280.00        | 4.1607       | 883.58                    | 121.74                   | 217.30                      | 425.94                      | 1.0598                    | 1.8050                    |
| 290.00        | 5.3177       | 804.67                    | 171.96                   | 245.63                      | 413.75                      | 1.1544                    | 1.7341                    |
| 300.00        | 6.7131       | 679.24                    | 268.58                   | 283.38                      | 387.08                      | 1.2759                    | 1.6215                    |

Volume concentrations $\phi$ of the fullerences $\phi = 1\%$

| Temperature, K | Pressure, MPa | Volume concentrations $\phi$ of the fullerences $\phi = 1\%$ |
|---------------|--------------|-------------------------------------------------------------|
| 250.00        | 1.7558       | 1048.3                                                      |
| 260.00        | 2.3846       | 1001.3                                                      |
| 270.00        | 3.1574       | 948.85                                                      |
| 280.00        | 4.5536       | 857.70                                                      |
| 290.00        | 5.2457       | 809.90                                                      |
| 300.00        | 6.6597       | 685.70                                                      |

Volume concentrations $\phi$ of the fullerences $\phi = 5\%$

| Temperature, K | Pressure, MPa | Volume concentrations $\phi$ of the fullerences $\phi = 5\%$ |
|---------------|--------------|-------------------------------------------------------------|
| 250.00        | 1.6216       | 1059.2                                                      |
| 260.00        | 2.2019       | 1014.4                                                      |
| 270.00        | 2.9283       | 964.03                                                      |
| 280.00        | 4.4046       | 867.58                                                      |
| 290.00        | 4.9719       | 829.27                                                      |
| 300.00        | 6.4938       | 704.28                                                      |

Volume concentrations $\phi$ of the carbon nanotubes $\phi = 1\%$

| Temperature, K | Pressure, MPa | Volume concentrations $\phi$ of the carbon nanotubes $\phi = 1\%$ |
|---------------|--------------|-----------------------------------------------------------------|
| 250.00        | 1.7097       | 1052.0                                                         |
| 260.00        | 2.3395       | 1004.5                                                         |
| 270.00        | 3.1095       | 952.00                                                        |
| 280.00        | 4.5040       | 861.00                                                        |
| 290.00        | 5.2012       | 813.10                                                        |
| 300.00        | 6.6358       | 688.50                                                        |

Volume concentrations $\phi$ of the carbon nanotubes $\phi = 5\%$

| Temperature, K | Pressure, MPa | Volume concentrations $\phi$ of the carbon nanotubes $\phi = 5\%$ |
|---------------|--------------|-----------------------------------------------------------------|
| 250.00        | 0.89452      | 1128.5                                                         |
| 260.00        | 1.3652       | 1081.3                                                         |
| 270.00        | 2.0180       | 1028.0                                                        |
| 280.00        | 3.5072       | 926.00                                                        |
| 290.00        | 4.4104       | 867.20                                                        |
| 300.00        | 6.3222       | 721.70                                                        |
Conclusions

This work is one of the first attempts to calculate the thermodynamic properties of refrigerants with nanoparticle additives. Carbon dioxide was chosen as a basic substance as one of the promising natural refrigerants with minimal global warming potential. For the first time, detailed tables of the basic thermodynamic properties of the R744 + system of the fullerenes and carbon nanotubes are presented. An estimate of the phase equilibrium shift and the critical point showed that the effect of the fullerenes and carbon nanotubes hardly changes the thermodynamic behavior of the refrigerant at low volumetric concentrations of nanoparticles. More significant is the increase in the thermal conductivity of such systems, which requires nonequilibrium thermodynamic approaches.

The enormous potential of nanofluids for use in the new generation of cooling systems for microelectronics, laser technology and optoelectronics necessitates significant interdisciplinary efforts by specialists in the fields of refrigeration, organic and physical chemistry, materials science, spectroscopy, biology, physics, computer science, hydrodynamics. On the one hand, it is obvious that nanofluids can find wide application in a large number of applications. On the other hand, it is also clear that the commercial application of nanofluids is still at the very beginning. Therefore, fundamental research in this area broadens the horizons for the subsequent application of this promising class of substances in industry. This study is one of the first attempts to establish and demonstrate multiple links existing between the critical point shift in classical fluids and phase equilibria phenomena in mixtures embedded with nanostructured materials. From the very beginning of these efforts, the obtained results serve very useful information for scientists and engineers working in the field of emerging nanotechnology applications. The examples the critical point shift for CO2 with different types of nanoparticle doping: graphene genealogic tree (CNT, fullerenes) are given. There is no doubt that, this extension of our knowledge about thermodynamic and phase behavior of nanofluids will lead to the creation of reliable engineering recipes for solving the actual problems of nanotechnologies.

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