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Thermophysical Properties of Carbon Dioxide in Critical Point Region[1]

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ABSTRACT

New method has been proposed for constructing thermodynamic perturbation theory. The method is based on the expressions for Helmholtz free energy and radial distribution function. Low- and high-density limits of those expressions have been used to describe gas and liquid phases correspondingly. Wide region around critical point is treated as a region of moderate (intermediate) density. New expression for free energy has been developed using certain simplifying assumptions. It has been applied for predicting thermodynamic properties of argon and carbon dioxide. Comparison of predicted values and experimental data suggests appropriateness of the developed method for description of thermodynamic properties in wide region around critical point.

KEY WORDS: argon; carbon dioxide; critical point region; thermodynamic perturbation theory.

1. INTRODUCTION

In paper [1], authors analyzed heat transfer processes during heating of water by gaseous carbon dioxide along overcritical isobars (carbon dioxide heat pump). Such kind of analysis appeared to be insufficient to describe properties of carbon dioxide in near overcritical region in the frame of equation of state [2] (especially, in description of isobaric capacity). That posed the problem of predicting thermophysical properties based on theoretically consistent approach without using polynomials containing numerous coefficients. An example of such theoretically consistent approach is thermodynamic perturbation theory. The most successful version of it was suggested in yearly publications by Barker-Henderson. Based on it, properties of moderately dense gas and low-temperature liquid [5] can be predicted by utilizing concept of universal effective pseudopotential of intermolecular interactions. Nevertheless, satisfactory description was not achieved in the region approaching critical point of liquid-vapor equilibrium.

Numerous researchers on critical phenomena suggest different ideas explaining such observations. Apparently, the following statements can be considered as valid:

- wide region around critical point can be considered as region of moderate density (intermediate between moderately dense gas and highly dense liquid);
- in the region of such moderate density there are no principal changes in potentials, and nature of intermolecular interactions;
- screening of paired intermolecular interactions is described by continuous and bounded function of density and temperature.

Present authors addressed the problem of constructing thermodynamic perturbation theory, which would allow to describe properties of a fluid in wide region around critical point. For the above statements the problem of construction would be that of density interpolation in classical Van der Waals approach. The posed problem has been solved methodologically. The simplest case of the screening function and model Lennard-Jones potential containing temperature and pressure independent parameters has been studied. Even in this simplest case better agreement with

experimental data has been achieved comparing to other well-known versions of thermodynamic perturbation theories.

2. THEORETICAL ASPECTS

Introduction of perturbing part $\Phi_1(R)$, relative to intermolecular potential $\Phi_0(R)$ of the base system of hard sphere particles, with the help of dimensionless coefficient λ:

$$\Phi(R,\lambda) = \Phi_0(R) + \lambda\Phi_1(R), \quad 0 \le \lambda \le 1 \tag{1}$$

yields the following expression for Helmholtz free energy:

$$\frac{F}{Nk_BT} = \frac{F_0}{Nk_BT} + \frac{2\pi n}{k_BT}\int_0^1 d\lambda \int_0^\infty g(R,\lambda)\,\Phi_1(R)\,R^2\,dR\,. \tag{2}$$

In equation (2), F_0 is Helmholtz free energy of hard sphere system of the same density, $g(R,\lambda)$ - particle radial distribution function, N - number of particle in the system, n - particle density, T - temperature, k_B - Boltzman constant, R - distance between particles in liquid.

Relation (2) is exact for any density and temperature and can be solved if exact correlation between $g(R,\lambda)$ and $\Phi_1(R)$ is available. If consideration is limited by dense liquid case, then $g(R)$ can be replaced by radial distribution function of hard sphere system $g_0(R)$. Thus,

$$\frac{F - F_0}{Nk_BT} \cong \frac{2\pi n}{k_BT}\int_0^\infty g_0(R)\,\Phi_1(R)\,R^2\,dR\,. \tag{3}$$

Expression (3) is often called high-temperature approximation. However, according to equation (3), comparison of values predicted with molecular dynamics (MD) and Monte-Carlo (MC) computer simulations shows the equation (3) is sufficiently correct in region of high density and all temperature values. Equation (3) is better than that of Percus-Yevick energy approximation [4]. On the other side, equation (3) was used in [5] for predicting thermodynamic properties of polar molecules in gaseous and liquid phases. The intermolecular interaction is described by Lennard-Jones potential containing temperature-dependent parameters

$$\Phi(R) = 4\,\varepsilon(T)\left[\left(\frac{\sigma(T)}{R}\right)^{12} - \left(\frac{\sigma(T)}{R}\right)^{6}\right]\,. \tag{4}$$

Selected set of parameters $\sigma(T)$ and $\varepsilon(T)$ allows to describe moderate dense gas and low-temperature liquid ($T < T_c$, T_c - critical temperature).

Analyzing obtained results, authors of the present paper consider it possible to accept equation (3) as high-density limit for free energy. At the same time, low-density limit is known as

$$\frac{F - F_0}{Nk_BT} \cong 2\pi n \int_0^\infty \left[1 - \exp\left(- \frac{\Phi_1(R)}{k_BT} \right) \right] R^2 \, dR \, . \tag{5}$$

In tern, interpolation procedure for radial distribution function has been carried out in macroscopic approach

$$g(R,\lambda) = g_0(R) \exp\left[- \frac{\lambda \, \Phi_1(R)}{k_BT} k_BT \left(\frac{\partial n}{\partial P} \right)_T^{VDW} \right] , \tag{6}$$

where ($\partial n / \partial P$) is calculated in Van der Waals approach (VDW) and, according to (5), radial distribution function can be expressed as

$$k_BT \left(\frac{\partial n}{\partial P} \right)_T^{VDW} = \frac{S_0(q = 0)}{1 - S_0(q = 0)\eta \frac{a}{T}} \quad . \tag{7}$$

In equation (7), $S_0(q)$ is hard sphere structure factor, $\eta = \pi n d^3/6$ - packing parameter of spheres of diameter d, a - quantity dependent on density, temperature, and the parameters of intermolecular interaction potential. Substitution of equation (6) in equation (2) allows to obtain equation (5) in the limit $n \to 0$, and equation (3) in the limit $n \to \infty$. In particular, asymptotic expression is obtained for $n \to \infty$ limit in equation (6)

$$g(R) = g_0(R) \left[1 - S_0(q = 0) \frac{\Phi_1(R)}{k_BT} + \ldots \right] , \tag{8}$$

which is in agreement with Barker-Henderson macroscopic approximation for $g(R)$ [6].

In case of the potential $\Phi(R)$ (4), there are following estimations for $\eta \frac{a}{T}$:

$$\eta\left(\frac{\varepsilon}{T}\right)^{1/2}, \qquad \text{for moderate temperature,}$$

$$\eta\left(\frac{\varepsilon}{T}\right)^{1/4}, \qquad \text{for high temperature.}$$

In general case, such analysis points out that $a = f(\eta,T)$. However, it can be assumed that $a = \text{Const}$ for the purpose of approbation of the developed method and estimation of its possibilities. Then substitution of (6) in equation (2) easily yields

$$\frac{F - F_0}{Nk_BT} = 2\pi n \int_{\sigma}^{\infty} \frac{g_0(R)\left\{1 - \exp\left[-\xi(\eta,T)\frac{\Phi(R)}{k_BT}\right]\right\}}{\xi(\eta,T)} R^2\, dR\,, \tag{9}$$

where $\xi(\eta,T) = k_BT\left(\frac{\partial n}{\partial P}\right)_T^{VDW}$ acts as a screening function.

Equation (9) has the same asymptotic expression for high density as equation (3), and for low density equations (9) and (3) have the same second virial coefficient for free energy too. Thus selection of $\Phi_1(R)$ and hard sphere diameter d can be calculated according to Barker-Henderson scheme [3].

3. RESULTS

Approbation of equation (9) for the case where $a = \text{Const}$, $\sigma = \text{Const}$, $\varepsilon = \text{Const}$ has been carried out for argon and carbon dioxide. Selection of constants a, σ, ε according to (9) for the given critical parameters T_c, P_c, ρ_c has been obtained by satisfaction of the following three classical conditions:

$$P(T_c, \rho_c) = P_c\,, \qquad \left(\frac{\partial P}{\partial \rho}\right)_{T_c} = 0\,, \qquad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c} = 0\,. \tag{10}$$

Thus, there is an agreement with data on experimental compressibility z_c in critical point. Table I represents corresponding Lennard-Jones potential values obtained by means of molecular dynamics and different modifications of Percus-Yevick approximations (PY).

Analogous procedure has been used for obtaining a, σ, ε for carbon dioxide. The results for argon and carbon dioxide are as follows:

$$\sigma = 3.34 \ \mathring{A}, \quad \frac{\varepsilon}{T} = 114.84 \ K, \quad a = 3.113 \cdot T_c \qquad (Ar)$$

$$\sigma = 3.65 \ \mathring{A}, \quad \frac{\varepsilon}{T} = 239.7 \ K, \quad a = 8.339 \cdot T_c \qquad (CO_2)$$

Thermodynamic properties has been calculated according to (9) with the use of the differential equations of thermodynamics. Pressure of saturated vapor and density of corresponding gaseous and liquid phases has been obtained using Maxwell rule. Finally, ideal-gas properties has been included in Helmholtz free energy F_0 of the system of hard spheres (exactly as it was done in [5]).

Obtained numerical values are presented in Tables II, III, and IV. Analysis of the results shows that the suggested modification of the thermodynamic perturbation theory has perspective value even for describing thermodynamic properties in wide critical point region. Some details of the dependence of screening function on density and temperature are subject to further refinement. Also, in the case of polar molecules, in the potential (4) functional dependence of the parameters on density and temperature should be refined.

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Table I. Values of Compressibility Coefficient $z_c = P_c V_c / (RT_c)$ Predicted by Different Methods

Method	MD	PY (V)	PY (C)	PY (E)	PY II (V)	Eq. (9)	Argon
z_c	0.30-0.36	0.3	0.36	0.31	0.31	0.293	0.293

Table II. Comparison of Predicted Values and Experimental Data of Density of Saturated Vapor and Liquid of Carbon Dioxide

Temperature K	Density of Vapor ($kg \cdot m^3$)			Density of Liquid ($kg \cdot m^3$)		
	calc	exp [2]	δ, %	calc	exp [2]	δ, %
230	37.1	23.3	60.8	1068.7	1120.1	5.2
240	49	33.3	48.4	1028.6	1065.9	5.3
250	62.7	46.7	33.3	985.2	1043.4	5.6
260	81.8	64.4	26.5	938.2	997.5	5.9
270	107.8	88.4	21.1	886.1	946.3	5.9
280	139.7	121.7	14.8	824.3	886.2	7
290	192.8	72.1	11.6	747.6	808.9	7.5
295	242.2	210.1	15.2	699.9	752.5	7
304.2	468	468	0	468	468	0

Table III. Comparison of Predicted and Experimental Data on Density of Carbon Dioxide Along Critical Isotherm for Given Pressure

Pressure MPa	Density ($kg \cdot m^3$)		
	calc	exp [2]	δ%
1.0	18.1	18.3	- 0.82
4.5	101.5	104.9	- 3.25
8.0	623.6	679.1	- 8.17
11.5	772.6	792.9	- 2.56
15.0	829.2	841.2	- 1.43
18.5	867.8	874.4	- 0.75
22.0	897.8	900.1	- 0.26
25.5	922.7	921.5	0.13
29.0	944.2	939.9	0.46
32.5	963.0	956.0	0.73
36.0	980.0	970.5	0.98
39.5	995.4	983.7	1.19
43.0	1009.6	995.8	1.38

Table IV. Comparison of Predicted and Experimental Data on Isobaric Capacity of Carbon Dioxide Along Overcritical Isobars

Pressure MPa	Temperature K	Isobaric capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$)	
		calc	exp [2]
7.5	51.10	2.074	2.100
7.5	71.33	1.363	1.543
7.5	118.19	0.944	1.225
7.5	166.00	0.820	1.142
10.0	52.09	5.523	4.175
10.0	85.22	1.697	1.744
10.0	124.11	1.117	1.336
10.0	152.04	0.969	1.237
10.5	139.00	1.059	1.325
11.0	112.75	1.337	1.482
12.5	83.99	3.767	2.286
12.5	134.10	1.252	1.410
15.0	88.51	2.698	2.581
15.0	126.18	1.580	1.636