The accuracy of the theories based on statistical physics for the thermodynamic modeling of state parameters of dense pure gases (fluids)

S A Gubin\textsuperscript{1,2} and S B Victorov\textsuperscript{3}
\textsuperscript{1}National Research Nuclear University "MEPhI", Moscow, Russia
\textsuperscript{2}State Centre «Interphysica», Moscow, Russia
\textsuperscript{3}OpenSearchServer, Paris, France

gubin sa@mail.ru

Abstract. A comparison of the accuracy of calculations of the parameters of the state of dense supercritical gases (fluids) using the equations of state (EOS), obtained using the three best one fluid theories HMSA/C, MRCSR and KLRR-T, based on the given potentials of intermolecular interactions and the laws of statistical mechanics is carried out. The best agreement of the calculated state parameters with Monte Carlo data was obtained for the EOS based on the HMSA/C and KLRR-T theories.

1. Introduction
A reliable model of the wide-range equation of state (EOS) (or equation of thermodynamic potential) is needed to calculate the thermodynamic properties of the gas-liquid phase (included supercritical fluid) in the range from normal conditions to pressures of 100 GPa and temperatures to15000 K. Special EOS models should be used for thermodynamic calculations in conditions where the gas is super-dense. Such EOS models allow us to calculate problems with chemical reaction in physics and chemistry of shock and detonation waves, astrophysical problems about the inner layers of giant planets and many others.

Most EOS models do not have a rigorous theoretical justification, i.e. they are empirical or semi-empirical. The functional form and constants of the used parameters of the EOS model are selected from the condition of the best agreement of the calculated values with the available experimental data. The use of empirical and semi-empirical EOS models does not allow to predict correctly of the state parameters outside the experimental range of such EOS. In recent decades interest has increased significantly to theoretically substantiated EOS models based on the predefined intermolecular interactions potential \( \varphi(r) \) \( (r – \text{distance between molecules}) \). Calculation of thermodynamic parameters of the chemical system is carried out by such EOS models which are based only on the interaction potentials of molecules. No other information on the properties of the substances is required. Theoretical models of EOS provide reliable prediction of thermodynamic properties of dense gases, demonstrating agreement with the results of computer simulation by the Monte Carlo (MC) and molecular dynamics (MD) methods.

Direct computer simulation using MC method allows us to calculate accurately the thermodynamic properties of a system of molecules interacting with each other with a given potential. Therefore, MC
modeling is a computer experiment to confirm the reliability of the theoretical models of EOS obtained on the basis of theories with a given intermolecular potential. However, calculations using the MC or MD methods require considerable computer time. At the same time, the rate of calculation of thermodynamic properties of matter on the basis of exact theories for thermodynamic potentials or EOS based on statistical mechanics is thousands of times higher than the rate of calculations by MC and MD methods, while maintaining high accuracy of calculations. Therefore, it is advisable to develop special theories based on statistical mechanics to obtain theoretical models of EOS based on the given interaction potentials of molecules for the modeling of thermodynamic properties of substances.

2. Problem statement

Only one component fluid systems are considered in the work. The extension of the theory for multicomponent mixtures (different molecules) is carried out by applying the van Der Waals effective potential model [1 - 4]. The ensemble of identical molecules with a spherical symmetric potential of intermolecular interaction Exp-6 [2, 3, 5] is considered at fixed temperature $T$, specific volume $V$ and number of particles $N$. Only pair interactions are considered.

A reliable model of the full thermodynamic potential of one fluid can be obtained in the presence of a theory that allows to reasonably calculate the excess energy of the Helmholtz $\Delta F^{ex}(T,V,N,\phi(r))$ system using the Exp-6 potential. The thermodynamic properties of the system are determined by the differentiation of the Helmholtz energy of the ensemble of molecules at given values $T$, $V$, $N$. In this case the Helmholtz energy $F(T,V,N,\phi(r))$ (also any other thermodynamic characteristic obtained by the Helmholtz energy differentiation) of the system is the sum of the Helmholtz energy of an ideal gas and the excess value of the Helmholtz energy due to intermolecular interaction. Thus, the main task of the considered theories is to calculate the exact excess energy of the Helmholtz $\Delta F^{ex}(T,V,N,\phi(r))$.

Today there are three theories providing the highest accuracy of calculation of thermodynamic properties of one fluid, whose molecules interact with a given potential in a wide range of pressures and temperatures including high densities. There are variational perturbation theory MCRSR [5, 6], the theory of integral equations HMSA/C [2, 7] and the KLRR perturbation theory [3, 8]. These theories are developed on the basis of statistical mechanics and have deep physical justifications. Calculations based on these theories are consistent with the results of the MC simulation. It makes possible to calculate reliably the thermodynamic properties of a fluid in a wide range from normal conditions to extremely high pressure (hundreds of GPa) and temperature (up to 15000 K) thousands of times faster than MC calculations and MD modeling. Powerful computer codes CHEQ [5], CHEETAH [2], CARTE [8], TDS [9] are developed on the basis of these theories. The variational perturbation theory MCRSR [6] was applied in computer codes CHEQ [5] and CARTE [8]. The KLRR-T perturbation theory [3] was used to create our modified perturbation theory THEOSTAR [4] for the TDS code [9], HMSA/C [2] for CHEETAH.

Due to the fact that different modeling assumptions are used in the construction of such theories, the calculation based on different theories with the same potential can lead to different results for the thermodynamic parameters of the substance. Hence the question arises which of the theories gives the most acceptable model of EOS and the real definition of the thermodynamic characteristics of the system. The theory providing a better agreement with the results of the computer experiment for the same intermolecular potential is correct.

3. Objective

The aim of this work is to compare the accuracy of the calculations for the three best physically one fluid theories based on statistical mechanics (variational perturbation theory MCRSR [6], the theory of integral equations HMSA/C [2] and modified perturbation theory KLRR-T [7, 11]) to determine the most accurate theory. The excess value of the Helmholtz energy of the studied system $\Delta F^{ex}$ is different for each theory.
The basic idea of any perturbation theory (variational theory too) is to represent the potential \( \varphi(r) \) of a system as a sum of the basic potential \( \varphi_0(r) \) and a small perturbation \( \varphi_1(r) \): \( \varphi(r) = \varphi_0(r) + \varphi_1(r) \).

The excess energy of Helmholtz of the investigated one-component system \( \Delta F^{\text{ex}} \) is represented by the terms of the zero and first order expansion into infinite series for variational theory and perturbation theory:

\[
\Delta F^{\text{ex}} = \Delta F_0 + 2\pi \rho_N \int_0^\infty \varphi(r)r^2 g(r)dr .
\]  

Here \( \Delta F_0 \) – the excessive Helmholtz energy of some basic system, \( \varphi_0(r) \) – perturbing potential, \( g_0(r) \) – radial distribution function of molecules in basic system, \( \rho_N = N/V \) – the number density. Only terms of the zero and first order of series expansion for excess Helmholtz energy are used for the investigated one fluid system. It is shown that the higher order terms can be neglected in expansion (1) because of their mutual compensation (the series members have alternating signs).

Under the assumption that the excessive value of the Helmholtz energy of the basis system coincides with the hard sphere fluid, the expression for the excessive \( \Delta F^{\text{ex}} \) in the variational perturbation theories is represented as:

\[
\Delta F^{\text{ex}} \leq \Delta F_{0\text{HS}} + 2\pi \rho_N \int_0^\infty \varphi(r)r^2 g_{\rho\gamma}(r,d)dr
\]

Here \( g_0 = g_{\rho\gamma}(r,d) \) is the radial distribution of hard sphere one fluid. It is supposed that the excessive Helmholtz energy of the reference system coincides with the excessive Helmholtz energy of a certain effective hard sphere fluid \( \Delta F_0 = \Delta F_{0\text{HS}} \). Next the variational parameter (for example, the diameter of hard spheres \( d \)) is selected. The value of the variational parameter is determined in such way that \( \Delta F^{\text{ex}} \) reaches a minimum at fixed \( T, V \) and \( N \). The found minimum value \( \Delta F^{\text{ex}} \) corresponds to the equilibrium state of the system (for data \( T, V \) and \( N \)). The need for multiple numerical integration and differentiation leads to significant computer time costs in the application of MCRSR, variational theories, but, of course, these costs are not comparable with the time of MC or MD calculation.

The problem that necessarily arises when using a hard sphere fluid in variational and perturbation theories is the choice of the hard spheres diameter on which all the properties of the basis system are depend. Different ways of solving this problem are proposed in various perturbation theories. The value of \( \Delta F^{\text{ex}} \) is calculated after determining the diameter of hard spheres. All necessary thermodynamic parameters of the system can be expressed in terms of the corresponding first and second derivatives of the excessive Helmholtz energy \( \Delta F^{\text{ex}} \).

Direct calculation \( \Delta F^{\text{ex}} \) for all values of \( T \) and \( V \) based on known properties of the basis system (\( \Delta F_0 = \Delta F_{0\text{HS}} \) and \( g_0 = g_{\rho\gamma}(r,d) \)) is carried out using a reasonable decomposition of the given potential \( \varphi(r) \) on basic and perturbing potentials in the theories of perturbations (in contrast to variational theory).

The problem of break point choosing of the thermodynamic potential is successfully solved in [4], arises in perturbation theories, in addition to the problem of choosing the diameter of hard spheres. The Laplace transform is used to find \( g_{\rho\gamma}(r,d) \) in deriving perturbation theories, as well as in variational theories.

The theoretical model of EOS one fluid with potential Exp-6 (KLRR-T) implemented in the form of computational subroutines is based on the version of the theory of perturbation THEOSTAR proposed by us [4]. A high-precision approximation in the form of a polynomial of the 7th order (error less than \( 5 \times 10^{-5} \)) is proposed by us in this model for the calculation of the energy Helmholtz term. This term is responsible for the attraction forces of molecules. The contribution of this term, which was neglected in [10], is taken into account for calculating the total Helmholtz energy. High-speed algorithms and routines that significantly reduce the calculation time on the computer are developed.

The one-component theory HMSA/C based on the application of the Ornstein Zernike equation in conjunction with the closing equation HMSA allows to calculate accurately the radial distribution functions of molecules according to the given parameters of intermolecular potentials, pressure, excess
internal energy. These data are sufficient to find the excess energy of Helmholtz using general thermodynamic relations (Maxwell’s differential equation and the definition of thermodynamic potentials).

4. Discussion

The accuracy of the theories was tested by comparing the results with those obtained by the MC simulation. The statistics of comparisons of the calculations accuracy on the best theories HMSA/C, MCRSR and the improved version of the theory KLRR-T [7, 11] for a one fluid with the potential Exp-6 are shown in table 1. The values of relative deviations of compressibility factor (dimensionless pressure) $Z$ and dimensionless excess internal energy $U^*$ computed by the presented theories from the MC simulations [2] are given in table 1. Dimensionless values of pressure $Z$ and excess internal energy $U^*$ were calculated using the following relations:

$$Z = \frac{PV}{Nk_BT} = 1 + \rho^* \left( \frac{\partial F^*}{\partial \rho^*} \right)_T^*$$

$$U^* = \frac{\Delta U}{Nk_BT} = \beta^* \left( \frac{\partial F^*}{\partial \beta^*} \right)_{\rho^*} = -T^* \left( \frac{\partial F^*}{\partial T^*} \right)_{\rho^*}$$

$$(2)$$

Dimensionless parameters in expansion (2) are marked by the index *: $\rho^*$ – density, $k_B$ – Boltzmann constant, $\beta^* = \frac{1}{k_BT}$ here. The same characteristic of the Exp-6 potentials for three different values of parameter determining the repulsive stiffness $\alpha$ were used in these calculations on the basis of MC and compared theories, table 1. The comparison was performed for MC points taken from [2]. These points cover the entire wide range of temperatures, pressures and densities. The calculations on the best theories give close deviations from the MC data (the comparison of the results in the table 1).

**Table 1.** The statistics of the relative deviations of calculated compressibility factor $Z$ and excess internal energy $U^*$ of a one component supercritical fluid from the MC results

| Method    | Over 55 MC points for $\alpha = 11.5$ | Over 19 MC points for $\alpha = 13.5$ | Over 18 MC points for $\alpha = 15.5$ |
|-----------|--------------------------------------|--------------------------------------|--------------------------------------|
|           | $\delta U^*$, % | $\delta Z$, % | $\delta U^*$, % | $\delta Z$, % | $\delta U^*$, % | $\delta Z$, % |
| KLRR-T    | 0.60 | 0.87 | 0.55 | 0.60 | 0.50 | 0.75 | 0.75 | 1.26 |
| MCRSR     | 2.07 | 2.46 | 2.92 | 1.87 | 1.78 | 2.29 | 1.52 | 3.24 |
| HMSA/C    | 0.72 | 1.89 | 0.46 | 1.19 | 0.72 | 1.69 | 0.98 | 2.85 |
| Relative average deviation, % | | | | | | | | |
| KLRR-T    | 0.90 | 1.44 | 0.62 | 0.76 | 0.56 | 0.99 | 1.32 | 2.16 |
| MCRSR     | 2.33 | 3.29 | 3.10 | 2.14 | 1.86 | 2.85 | 1.79 | 4.45 |
| HMSA/C    | 0.84 | 3.64 | 0.54 | 1.32 | 0.80 | 2.28 | 1.10 | 5.78 |
| Relative root mean square deviation, % | | | | | | | | |
| KLRR-T    | 5.30 | 7.00 | 1.48 | 1.72 | 1.05 | 2.96 | 5.30 | 7.00 |
| MCRSR     | 5.06 | 11.56 | 4.11 | 3.87 | 2.40 | 4.82 | 5.06 | 11.56 |
| HMSA/C    | 2.43 | 23.42 | 1.08 | 2.20 | 1.63 | 7.62 | 2.43 | 23.42 |
| Relative maximum deviation, % | | | | | | | | |

Note that the variational theory and HMSA/C theory use functions that correct excess Helmholtz energy so that the excess pressure and internal energy are in good agreement with the results of Monte Carlo computer experiments [2]. Whereas there are no correcting functions in the improved version KLRR-T [7, 11]. Consequently the theory MCRSR is less accurate compared to an improved version of the KLRR-T [7, 11] and HMSA/C [2] theory even with the use of the correction functions (table 1).
Calculations based on our improved version of the KLRR theory [7, 11] are more precise in comparison with estimations based on the theory HMSA/C.

We presented an EOS model that allows for reliably computing of the thermodynamic properties for systems over a wide range of temperatures and densities covering both the high-pressure area up to hundreds gigapascals and the region of moderate pressures. High predictive abilities of the presented EOS model allow one to apply it to solving a variety of practical and theoretical tasks in geophysics and astrophysics and in the chemistry and high energy physics.

Acknowledgments
This work is supported by the Russian Science Foundation under grant 16-19-00188.

References
[1] Ree F H 1983 J. Chem. Phys. 78 409
[2] Fried L E, Howard W M 1998 J. Chem. Phys 109 7338
[3] Kang H S, Lee C S, Ree T, Ree F H 1985 J. Chem. Phys. 82 414
[4] Victorov S B, El-Rabii H, Gubin S A, Maklashova I V, Bogdanova Y A 2010 J. of Energetic Materials 28 35
[5] Ree F H 1984 J. Chem. Phys. 81 1251
[6] Ross M J 1979 Chem. Phys. 71 1567
[7] Anikeev A A, Viktorov S B, Gubin S A 2014 J. Phys. Chem. B 8 56
[8] Dubois V, Desbiens N, Auroux E 2010 Chem. Phys. Let. 494 306
[9] Victorov S B, Gubin S A, Maklashova I V, Revyakin I I 2001 Proc. of the 32nd Int. Ann. Conf. of ICT. 69/1
[10] Byers-Brown W, Horton T V 1988 Mol. Phys. 63 125
[11] Victorov S B, Gubin SA 2006 Proc. of the 13th Int. Detonation Symp 1118