

EQUILIBRIUM PROPERTIES OF THE GAS OF ATOMS OF WHICH A PART IS EXCITED WITHIN CLUSTER EXPANSION METHOD

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A gas of atoms some of which are in excited electronic state is under consideration. Since the lifetime of an excited state is to great extent larger than the time required for establishing the equilibrium over translational degrees of freedom the system possesses equilibrium properties. They are determined essentially by many-particle resonance interactions that appear in the system of identical differently excited atoms. The present paper contains the results of numerical calculations dealing with the examination of virial state equation and density expansion for canonical pair spatial distribution function of the system in question with the accuracy up to three-particle contributions. The obtained results permit to study the excited atoms influence on gas-liquid phase transition and the excimer molecules formation in the gas with excited atoms.

The conception of effective interatomic interactions in many-atom system usually assumes the following arguments. Consider two atoms at large enough distance so that the operator of interaction energy between atoms may be taken in the form of multipole series; often one can restrict himself by dipole-dipole approximation. Making use of Born-Oppenheimer adiabatic approximation one finds that electron terms of the system with fixed positions of nuclei play the role of the potential energy in the nuclear problem and therefore they are the effective interatomic interaction. The electron terms of the system in question may be evaluated with the help of quantum-mechanical perturbation theory. Acting according to the described scheme in the case of two neutral atoms in the ground electronic state one finds that the first non-vanishing correction appears within second order of perturbation theory and thus it is inversely proportional to the six degree of interatomic distance. This is well known van der Waals interaction. The non-vanishing corrections arise in the first order of perturbation theory in the case when identical atoms are in the states with different parity. These interactions are inversely proportional to the third degree of interatomic distance and are known as resonance dipole-dipole interactions.

Although the resonance interactions were well known in condensed matter physics (e.g. in the theory of molecular excitons) the physical situation where such interactions may lead to changes in thermodynamical properties of many-particle system got started to discuss only in mid-1960s due to V.N.Malnev and S.I.Pekar [1]. Consider a gas of atoms in which due to the external influence (e.g. irradiation with the frequency that corresponds

to excitation energy of atom) a part of atoms is in the excited electronic state (partially excited gas (PEG)). The obtained system is essentially nonequilibrium and relaxes to equilibrium. The processes of achieving the equilibrium are characterized by the following times:

- the mean free path time τ_f that is connected with short-range repulsion;
- the dipole-dipole relaxation time τ_d ;
- the relaxation time of the processes of exchange by excitation between atoms τ_{exch} ;
- the time of spontaneous decay of the excited state of an atom τ_{sp} ;
- the relaxation time of processes of transfer of electron excitation energy to the energy of translational motion τ_c ;
- the time connected with Doppler width τ_D

etc.. It is of special importance, as was noted by V.N. Malnev and S.I. Pekar, that *usually the lifetime of an excited state* ($\sim \tau_D, \tau_{sp}, \tau_c \sim 10^{-9} - 10^{-8} s$) *is to great extent larger than the time that is needed for establishing the equilibrium over translational degrees of freedom* ($\sim \tau_f \sim 10^{-11} - 10^{-10} s$). This follows both from experimental data and theoretical estimations [2-14]. Thus, one faces with the problem of noncomplete equilibrium, i.e. the equilibrium with respect to translational motion achieves for given (nonequilibrium) state of electronic subsystem. The equilibrium properties are expected to be uncommon since they are determined by resonance interactions that appear in the system of identical differently excited atoms.

The calculation of equilibrium properties of PEG, however, faces with some principal difficulties. First, it is necessary to clarify the meaning of the concept of PEG. Usually [1,15-19] it was supposed that one has, for example, N two-level atoms, N_0 of which are in the ground electronic state and N_1 of which are in excited electronic state, and $N_0 + N_1 = N$. However, such definition implies the possibility to determine the electronic state of each atom, that is impossible, in a system of interacting atoms. Therefore one should elucidate whether it is possible to give such "classical" interpretation to eigenfunctions of Hamiltonian that describes the state of the system in question in quantum picture. Considering first the eigenfunctions of electronic subsystem one easily notes that analytic with respect to interatomic interaction energy operator eigenfunctions can be really labeled by the numbers of atoms in ground and excited states. Expanding then the eigenfunctions of the total Hamiltonian in the eigenfunctions of electronic subsystem Hamiltonian one finds that it is still possible to preserve the numbers of atoms in the ground and excited states while neglecting by certain effective interatomic interactions. It seems quite natural since these effective interactions are responsible for exciting or de-exciting of atoms due to collisions and hence because of them one is unable to label Hamiltonian eigenfunctions by numbers of atoms in the ground and excited electronic states. The neglecting by these interactions leads to the mentioned already limitations on the time of consideration that should be less than τ_c . There are even faster processes owing to which the classification of Hamiltonian eigenfunctions by numbers of atoms in different electronic states is destroyed and neglecting by which imposes even smaller upper limit on the observation time (e.g. the interaction with electromagnetic field) [20].

The second problem that one faces with is how to apply Gibbs' scheme for calculation of equilibrium properties for PEG. Essentially using the revealed integrals of motion, i.e. the numbers of atoms in the ground and excited states, one can construct the equilibrium ensembles and find the distribution for them adopting ergodic hypothesis and proving Gibbs' theorems or studying the extremal properties of entropy functional. The most convenient for practical calculations is the grand thermodynamical ensemble of PEG, that is the ensemble of small subsystems of PEG that weakly interact with environment via exchange by energy and atoms in different electronic states. The probability to detect the system with N_0 atoms in the ground state and N_1 atoms in the excited one with energy $E_{j(N_0, N_1)}$ reads

$$\omega_{j(N_0, N_1)} \sim \exp \left[-\beta(E_{j(N_0, N_1)} - \mu_0 N_0 - \mu_1 N_1) \right] = z_0^{N_0} z_1^{N_1} \exp(-\beta E_{j(N_0, N_1)}).$$

Here $\beta \equiv 1/(kT)$ is the reciprocal temperature and $z_0 \equiv \exp(\beta\mu_0)$, $z_1 \equiv \exp(\beta\mu_1)$ are the activities of atoms in the ground and excited states. Note, that in comparison with the grand canonical distribution which establishes in long runs $\omega_{j(N)} \sim \exp \left[-\beta(E_{j(N)} - \mu N) \right] = z^N \exp(-\beta E_{j(N)})$, $z \equiv \exp(\beta\mu)$ is the activity of atoms, the probability of states with excited atoms is essentially larger. Really, consider two possible states of the system, first, with $N_0 - 1$ atoms in ground state with the energy E_0 and $N_1 + 1$ atoms in excited state with the energy E_1 , and second, with N_0 and N_1 atoms in the ground and excited states respectively. The ratio of probabilities of these states in the latter case is $\exp[\beta(E_0 - E_1)] \ll 1$ whereas in the former case it is equal to $[z_1 \exp(-\beta E_1)]/[z_0 \exp(-\beta E_0)] \sim N_1/N_0$. Hence the states that practically did not contribute to equilibrium properties appear to be very significant in PEG [20].

The calculation of energies of states $E_{j(N_0, N_1)}$ demands some simplifying assumptions. Assuming the atoms to be two-level ones, neglecting the effects of the statistics of the atoms, taking interatomic interaction energy operator in the electrostatic form with further restriction to the dipole approximation, adopting Born-Oppenheimer approximation and taking for the solution of a nuclear problem only the zero-order approximation in effective interatomic interaction, and taking into account the short-range repulsion by means of introducing the atom radius σ one can write the initial formula for PEG equilibrium properties calculation, i.e. *PEG grand canonical distribution*, in the form:

$$\omega_{j(N_0, N_1)} = \frac{1}{(N_0 + N_1)!} z_0^{N_0} z_1^{N_1} \frac{1}{V^N} \exp \left(-\beta \sum_{j=1}^N \frac{\hbar^2 \mathbf{k}_j^2}{2M} \right) \times \exp \left[-\beta E_{N_0, N_1; \eta}^{el}(\mathbf{R}_1, \dots, \mathbf{R}_N) \right] / \Xi(\beta, z_0, z_1, V), \quad (1)$$

all $R_{ij} \geq 2\sigma$ otherwise $\omega_{j(N_0, N_1)} = 0$. Here $\hbar \mathbf{k}_j$ is the momentum of the j th atom, M is the mass of the atom, $E_{N_0, N_1; \eta}^{el}(\mathbf{R}_1, \dots, \mathbf{R}_N) \equiv N_0 E_0 + N_1 E_1 + U_{N_0 N_1}^\eta(\dots, R_{ij}, \dots)$ is the η th eigenvalue of electronic subsystem Hamiltonian of $N = N_0 + N_1$ atoms in the spatial configuration of atoms $\mathbf{R}_1, \dots, \mathbf{R}_N$, $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$, $\Xi(\beta, z_0, z_1, V)$ is the PEG grand partition function. Note that in contrast to the corresponding formula for two component mixture (1) contains $1/(N_0 + N_1)!$ but not $1/(N_0! N_1!)$ due to the identity of atoms, and the effective long-range interatomic interaction in the

n th state in group of $N = N_0 + N_1$ atoms $U_{N_0, N_1}^n(\dots, R_{ij}, \dots)$ is essentially N -particle, has rather complicated dependence on space configuration $\mathbf{R}_1, \dots, \mathbf{R}_N$ and can be found explicitly only for few atoms in the group. For two-atom groups one has $U_{20}(R_{12}) = -\left(\sqrt{1 + \alpha_{12}^2} - 1\right)(E_1 - E_0) \approx -\frac{1}{2}\alpha_{12}^2(E_1 - E_0)$, $U_{11}^1(R_{12}) = -\alpha_{12}(E_1 - E_0)$, $U_{11}^2(R_{12}) = \alpha_{12}(E_1 - E_0)$, $U_{02}(R_{12}) = \left(\sqrt{1 + \alpha_{12}^2} - 1\right)(E_1 - E_0) \approx \frac{1}{2}\alpha_{12}^2(E_1 - E_0)$, where $\alpha_{ij} = a/(R_{ij}/\sigma)^3$, $a \equiv d^2/[\sigma^3(E_1 - E_0)]$, d is the value of the transitional electrical dipole moment between the ground and the excited states. $U_{20}(R_{12})$, $U_{02}(R_{12})$ and $U_{11}^1(R_{12})$, $U_{11}^2(R_{12})$ are familiar van der Waals and resonance dipole-dipole interactions. More complicated results of examining the resonance dipole-dipole interactions in groups of three and four two-level atoms can be found in [21].

The only method that permits one to obtain grand thermodynamical potential $\Omega(\beta, z_0, z_1, V)$ or grand canonical pair spatial distribution function $\mathcal{F}_2(R_{12}; \beta, z_0, z_1)$ is cluster expansion method within the frames of which the contributions to the mentioned quantities that arise from the groups of larger and larger number of atoms are taken into account successively. Formally within such approach one should present $\Omega(\beta, z_0, z_1, V)$ or $\mathcal{F}_2(R_{12}; \beta, z_0, z_1)$ as a series in the activities z_0 and z_1 . The contribution from the term that is proportional, for instance, to $z_0^2 z_1$ is determined by $(2 + 1)$ -atom cluster integral that originates from the group of three atoms two of which are in the ground state and one in the excited state. In such a version of the cluster expansion approach many-atom cluster integrals are finite algebraic sums of terms each of which tends to infinity with $V \rightarrow \infty$. Thus, they should be regularized, that is presented as algebraic sums of finite terms. Rather lengthy and tedious details of these calculations are omitted; these can be found in [22]. Final results can be written in the form

$$-\frac{\beta\Omega(\beta, z_0, z_1, V)}{V} = z_0 b_{10}(\beta) + z_1 b_{01}(\beta) + z_0^2 b_{20}(\beta) + z_0 z_1 b_{11}(\beta) + z_1^2 b_{02}(\beta) + z_0^3 b_{30}(\beta) + z_0^2 z_1 b_{21}(\beta) + z_0 z_1^2 b_{12}(\beta) + z_1^3 b_{03}(\beta) + \dots, \quad (2)$$

$$\begin{aligned} \mathcal{F}_2(R_{12}; \beta, z_0, z_1) = & z_0^2 f_{20}(R_{12}; \beta) + z_0 z_1 f_{11}(R_{12}; \beta) + z_1^2 f_{02}(R_{12}; \beta) + \\ & z_0^3 f_{30}(R_{12}; \beta) + z_0^2 z_1 f_{21}(R_{12}; \beta) + z_0 z_1^2 f_{12}(R_{12}; \beta) + z_1^3 f_{03}(R_{12}; \beta) \\ & + \dots, \quad \text{if } R_{12} \geq 2\sigma, \\ \mathcal{F}_2(R_{12}; \beta, z_0, z_1) = & 0, \quad \text{if } R_{12} < 2\sigma, \end{aligned} \quad (3)$$

where cluster integrals are determined by

$$\begin{aligned} b_{20}(\beta) &= \frac{1}{2} b_{10}^2(\beta) v(3i_{20} - 8), \\ b_{11}(\beta) &= \frac{1}{2} b_{10}(\beta) b_{01}(\beta) v(3i_{11} - 16), \\ b_{02}(\beta) &= \frac{1}{2} b_{01}^2(\beta) v(3i_{02} - 8), \end{aligned}$$

$$\begin{aligned}
b_{30}(\beta) &= \frac{1}{3!} b_{10}^3(\beta) v^2 \left(\frac{9}{2} i_{30} - 144 i_{20} + \frac{9}{2} \alpha_{20} + 162 \right), \\
b_{21}(\beta) &= \frac{1}{3!} b_{10}^2(\beta) b_{01}(\beta) v^2 \left(\frac{9}{2} i_{21} - 144 i_{20} - 144 i_{11} + \frac{9}{2} \alpha_{20} + \frac{9}{2} \alpha_{11} + 486 \right), \\
b_{12}(\beta) &= \frac{1}{3!} b_{10}(\beta) b_{01}^2(\beta) v^2 \left(\frac{9}{2} i_{12} - 144 i_{11} - 144 i_{02} + \frac{9}{2} \alpha_{11} + \frac{9}{2} \alpha_{02} + 486 \right), \\
b_{03}(\beta) &= \frac{1}{3!} b_{01}^3(\beta) v^2 \left(\frac{9}{2} i_{03} - 144 i_{02} + \frac{9}{2} \alpha_{02} + 162 \right); \\
f_{20}(R_{12}; \beta) &= b_{10}^2(\beta) j_{20}, \\
f_{11}(R_{12}; \beta) &= b_{10}(\beta) b_{01}(\beta) j_{11}, \\
f_{02}(R_{12}; \beta) &= b_{01}^2(\beta) j_{02}, \\
f_{30}(R_{12}; \beta) &= b_{10}^3(\beta) v \left[\frac{3}{2} j_{30} + j_{20} (F_{HS}^{(3)} - 16) \right], \\
f_{21}(R_{12}; \beta) &= b_{10}^2(\beta) b_{01}(\beta) v \left[\frac{3}{2} j_{21} + (j_{20} + j_{11}) (F_{HS}^{(3)} - 16) \right], \\
f_{12}(R_{12}; \beta) &= b_{10}(\beta) b_{01}^2(\beta) v \left[\frac{3}{2} j_{12} + (j_{11} + j_{02}) (F_{HS}^{(3)} - 16) \right], \\
f_{03}(R_{12}; \beta) &= b_{01}^3(\beta) v \left[\frac{3}{2} j_{03} + j_{02} (F_{HS}^{(3)} - 16) \right].
\end{aligned}$$

Here $v = 4\pi\sigma^3/3$, dimensionless i -, α -, j -integrals are determined by long-range effective interatomic interactions, for example,

$$\begin{aligned}
i_{20} &\equiv \int_2^\infty d\rho \rho^2 \{ \exp[-\beta U_{20}(\rho\sigma)] - 1 \}, \\
i_{11} &\equiv \int_2^\infty d\rho \rho^2 \left\{ \sum_{\lambda=1}^2 \exp[-\beta U_{11}^\lambda(\rho\sigma)] - 2 \right\}, \\
i_{02} &\equiv \int_2^\infty d\rho \rho^2 \{ \exp[-\beta U_{02}(\rho\sigma)] - 1 \}; \\
j_{20} &\equiv \exp[-\beta U_{20}(\rho_{12}\sigma)], \\
j_{11} &\equiv \sum_{\lambda=1}^2 \exp[-\beta U_{11}(\rho_{12}\sigma)], \\
j_{02} &\equiv \exp[-\beta U_{02}(\rho_{12}\sigma)];
\end{aligned}$$

explicit expressions for other integrals can be found in [22], $F_{HS}^{(3)} = 8 - 3R_{12}/\sigma + (R_{12}/\sigma)^3/16$ if $2\sigma \leq R_{12} < 4\sigma$ and $F_{HS}^{(3)} = 0$ if $4\sigma \leq R_{12}$. The obtained results (2), (3) permit to obtain second and third virial coefficients in the virial state equation

$$\begin{aligned}
p &= \frac{1}{\beta} \rho \left[1 + \rho B_2(\beta, c_0, c_1) + \rho^2 B_3(\beta, c_0, c_1) + \dots \right], \\
B_2(\beta, c_0, c_1) &= 4v - \frac{3}{2}v \left(c_0^2 i_{20} + c_0 c_1 i_{11} + c_1^2 i_{02} \right), \\
B_3(\beta, c_0, c_1) &= 10v^2 -
\end{aligned}$$

$$\begin{aligned}
& v^2 \left[c_0^3 \left(\frac{3}{2} i_{30} - 9i_{20}^2 + \frac{3}{2} \alpha_{20} \right) + \right. \\
& c_0^2 c_1 \left(\frac{3}{2} i_{21} - 9i_{20} i_{11} - \frac{9}{4} i_{11}^2 + \frac{3}{2} \alpha_{20} + \frac{3}{2} \alpha_{11} \right) + \\
& c_0 c_1^2 \left(\frac{3}{2} i_{12} - \frac{9}{4} i_{11}^2 - 9i_{11} i_{02} + \frac{3}{2} \alpha_{11} + \frac{3}{2} \alpha_{02} \right) + \\
& \left. c_1^3 \left(\frac{3}{2} i_{03} - 9i_{02}^2 + \frac{3}{2} \alpha_{02} \right) \right] \quad (4)
\end{aligned}$$

and two- and three-particle contributions to the series in degrees of density for canonical pair spatial distribution function

$$\begin{aligned}
& F_2(R_{12}; \beta, c_0, c_1, \rho) = \\
& F_2^{(2)}(R_{12}; \beta, c_0, c_1) + \rho F_2^{(3)}(R_{12}; \beta, c_0, c_1) + \dots, \text{ if } R_{12} \geq 2\sigma, \\
& F_2(R_{12}; \beta, c_0, c_1, \rho) = 0, \text{ if } R_{12} < 2\sigma, \\
& F_2^{(2)}(R_{12}; \beta, c_0, c_1) = c_0^2 j_{20} + c_0 c_1 j_{11} + c_1^2 j_{02}, \\
& F_2^{(3)}(R_{12}; \beta, c_0, c_1) = v \left\{ c_0^3 \left[\frac{3}{2} j_{30} + (F_{HS}^{(3)} - 6i_{20}) j_{20} \right] + \right. \\
& c_0^2 c_1 \left[\frac{3}{2} j_{21} + (F_{HS}^{(3)} - 3i_{11}) j_{20} + \left(F_{HS}^{(3)} - 3i_{20} - \frac{3}{2} i_{11} \right) j_{11} \right] + \\
& c_0 c_1^2 \left[\frac{3}{2} j_{12} + \left(F_{HS}^{(3)} - \frac{3}{2} i_{11} - 3i_{02} \right) j_{11} + \left(F_{HS}^{(3)} - 3i_{11} \right) j_{02} \right] + \\
& \left. c_1^3 \left[\frac{3}{2} j_{03} + (F_{HS}^{(3)} - 6i_{02}) j_{02} \right] \right\}. \quad (5)
\end{aligned}$$

It should be noted, that the results obtained are in agreement with the well known expressions for virial coefficients and the contributions to the expansion in the density of the pair spatial distribution function, and the developed approach may be viewed as a generalization of many-particle Mayer functions formalism [23] for the systems with quantum resonance interactions.

Let's discuss briefly the results of *numerical calculations that is the main purpose of the present paper*. Within the adopted approximations the atom is characterized by the mentioned already dimensionless parameter a . The dimensionless temperature, distance, pressure, density convenient for presentation of numerical results are determined by $\tau = 1/[\beta(E_1 - E_0)]$, $\rho_{12} = R_{12}/\sigma$, $\pi = pv/(E_1 - E_0)$, $\eta = \rho v$. In fig.1 the temperature dependences of the second and third virial coefficients for different cocentrations of excited atoms $c_1 = N_1/(N_0 + N_1)$ are depicted. In figs.2,3 two- and three-particle contributions to pair spatial distribution function at different concentrations of excited atoms and temperatures are shown. One can easily note that in high-temperature limit, when the mutual attraction of atoms becomes not essential, two- and three-particle contributions correspond to the values of these quantities for a gas of hard spheres: $B_2(\beta, c_0, c_1) \xrightarrow{\beta \rightarrow 0} 4v$, $B_3(\beta, c_0, c_1) \xrightarrow{\beta \rightarrow 0} 10v^2$, $F_2^{(2)}(R_{12}; \beta, c_0, c_1) \xrightarrow{\beta \rightarrow 0} 1$, $F_3^{(2)}(R_{12}; \beta, c_0, c_1) \xrightarrow{\beta \rightarrow 0} vF_{HS}^{(3)}$. While the temperature decreases the role of long-range interactions increases. Moreover, it is important what is the concentration of excited atoms. In the absence of excited atoms the long-range interaction contributions are caused by van der Waals interaction. In the presence of excited

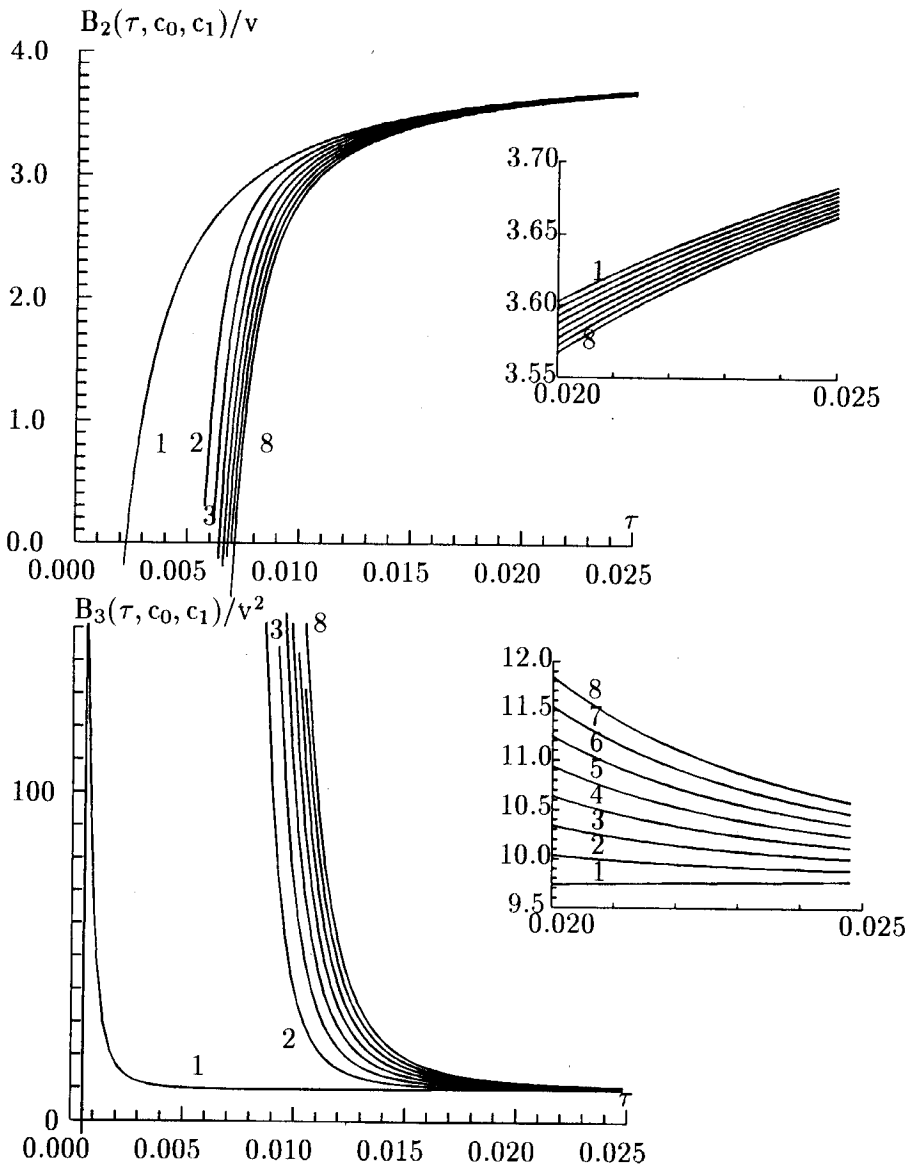


Figure 1. Temperature dependences of the second and third virial coefficients of PEG for different concentrations of excited atoms; $a = 0.5$; 1 - $c_1 = 0.00\%$, 2 - $c_1 = 0.01\%$, 3 - $c_1 = 0.02\%$, 4 - $c_1 = 0.03\%$, 5 - $c_1 = 0.04\%$, 6 - $c_1 = 0.05\%$, 7 - $c_1 = 0.06\%$, 8 - $c_1 = 0.07\%$.

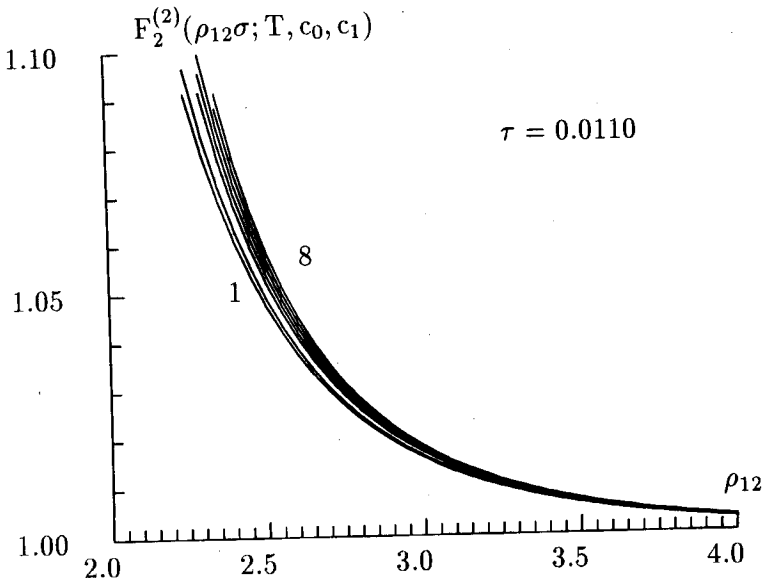
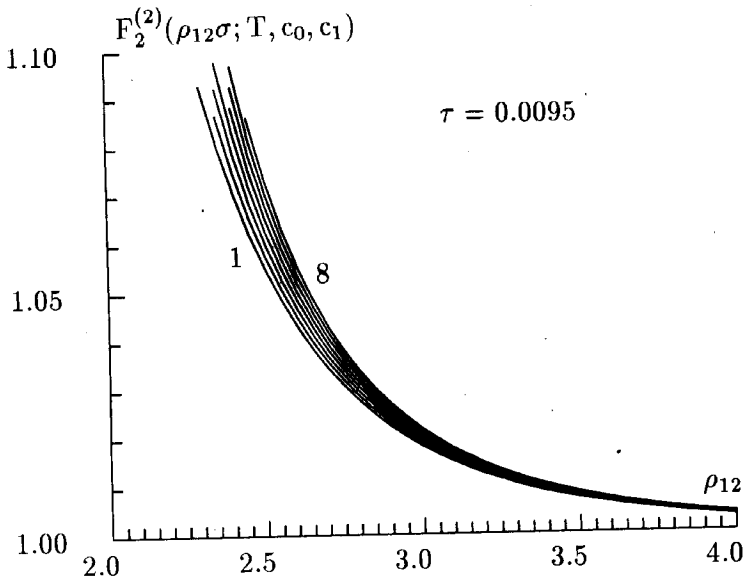


Figure 2. Two-particle contributions to canonical pair spatial distribution function of PEG for different concentrations of excited atoms and temperatures; $a = 0.5$; 1 - $c_1 = 0.00\%$, 2 - $c_1 = 0.01\%$, 3 - $c_1 = 0.02\%$, 4 - $c_1 = 0.03\%$, 5 - $c_1 = 0.04\%$, 6 - $c_1 = 0.05\%$, 7 - $c_1 = 0.06\%$, 8 - $c_1 = 0.07\%$.

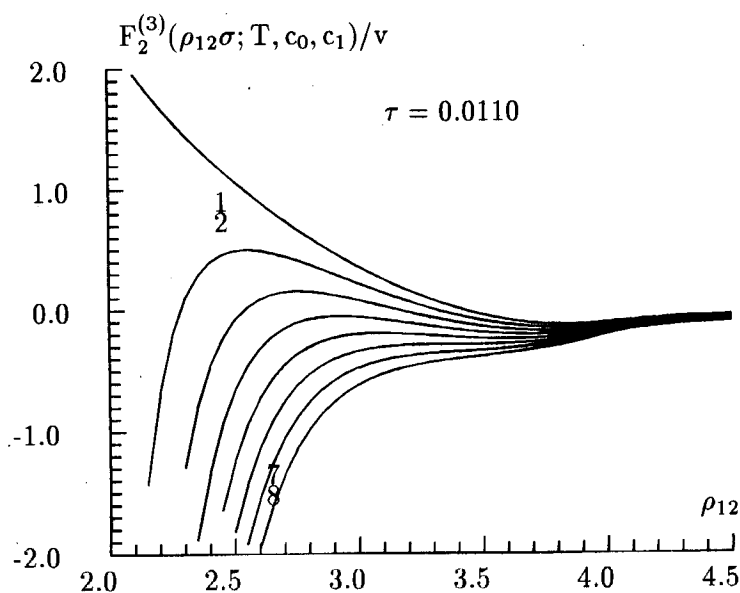
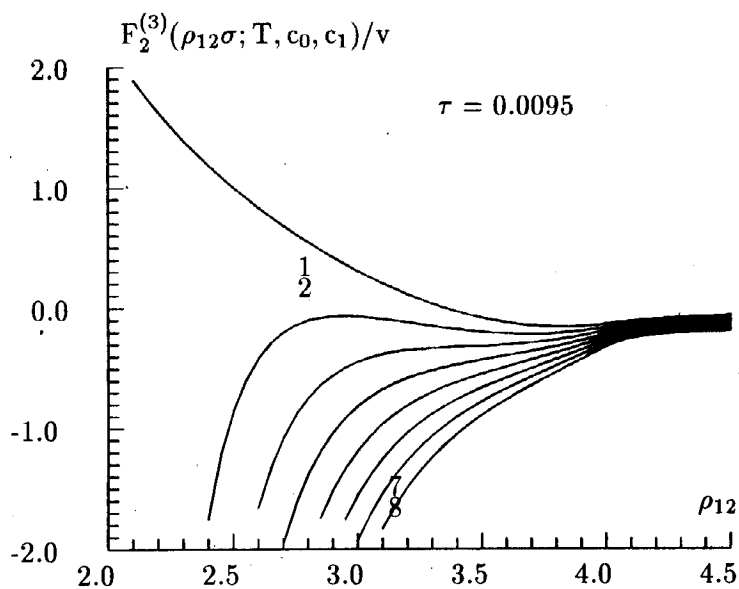


Figure 3. Three-particle contributions to canonical pair spatial distribution function of PEG for different concentrations of excited atoms and temperatures; $a = 0.5$; 1 - $c_1 = 0.00\%$, 2 - $c_1 = 0.01\%$; 3 - $c_1 = 0.02\%$, 4 - $c_1 = 0.03\%$, 5 - $c_1 = 0.04\%$, 6 - $c_1 = 0.05\%$, 7 - $c_1 = 0.06\%$, 8 - $c_1 = 0.07\%$.

atoms there appear the contributions of resonance dipole-dipole interaction; the concentrations of atoms in the ground and excited states control the contributions of different interactions. It can be shown that the sum of terms that are resonance interactions in the group of $l = l_0 + l_1$ atoms found in the first order of perturbation theory is equal to zero, $\sum_{\lambda} U_{l_0 l_1}^{\lambda}(\dots, R_{ij}, \dots) = 0$, and therefore the equilibrium properties do not contain a contribution that is linear in resonance interaction. Thus in dipole approximation one has the contributions caused by the square of resonance dipole-dipole interactions that are accompanied by a factor β^2 in contrast to the contributions from the van der Waals interactions which are accompanied by factor β (compare i_{20}, i_{02} and i_{11} , j_{20}, j_{02} and j_{11}). That is why the presence of excited atoms essentially influences the temperature dependences of second and third virial coefficients and two- and three-particle contributions to canonical pair spatial distribution function.

Due to described peculiarities the presence of excited atoms slightly influences the PEG isotherms at high temperatures and is significant at low temperatures. It is worthwhile to discuss the behaviour of the PEG isotherms with the decreasing of temperature. One can easily see from (4) and fig.1 that at the presence of excited atoms with decreasing of temperature the pressure is influenced by two factors: decreasing of $\frac{1}{\beta}$ in (4) and increasing of $\rho^2 B_3(\beta, c_0, c_1)$ (the latter essentially depends on c_1). Due to the latter factor it may happen so that for the fixed density the pressure will increase with decreasing of temperature. However, for smaller densities the role of the second factor decreases and the isotherms depend on temperature in a usual way: for fixed density with decreasing of temperature the pressure decreases.

Combining (5) and the results depicted in figs.2,3 one finds that canonical pair spatial distribution function in the absence of excited atoms weakly depends on temperature whereas in the presence of excited atoms due to the contributions of resonance dipole-dipole interaction the temperature dependence is very strong. It is known that short-range hard sphere repulsion leads to increase of $F_2^{(3)}(R_{12}; \beta, c_0, c_1)$ at the range of distances between 2σ and 4σ whereas the contributions of attraction leads to decrease of $F_2^{(3)}(R_{12}; \beta, c_0, c_1)$ [24]. Since the latter contribution in the presence of excited atoms strongly depends on temperature the presence of excited atoms is of great significance for structural properties.

The obtained results qualitatively agree with such results for systems with short-range repulsion and long-range attraction. They are most similar to the results for Stockmayer potential that is used for a gas of polar molecules [25].

On the base of obtained virial state equation one can construct in a standard way van der Waals type state equation

$$\beta p = \rho / (1 - \rho b) - \rho^2 \beta a(\beta), \quad b = 4v, \quad a(\beta) = a' + a''(\beta), \\ a' \equiv (c_0 - c_1) v a^2 (E_1 - E_0) / 32, \quad a''(\beta) \equiv c_0 c_1 v a^2 \beta (E_1 - E_0)^2 / 16. \quad (6)$$

It should be noted that the constant $a(\beta)$ that describes the change in pressure due to long-range interaction because of temperature dependence of the contribution to the second virial coefficient of the resonance dipole-dipole interaction depends on temperature. PEG state equation (6) together with Maxwell rule permits one to construct gas-liquid coexistence curves in the presence of excited atoms (fig.4) [26].

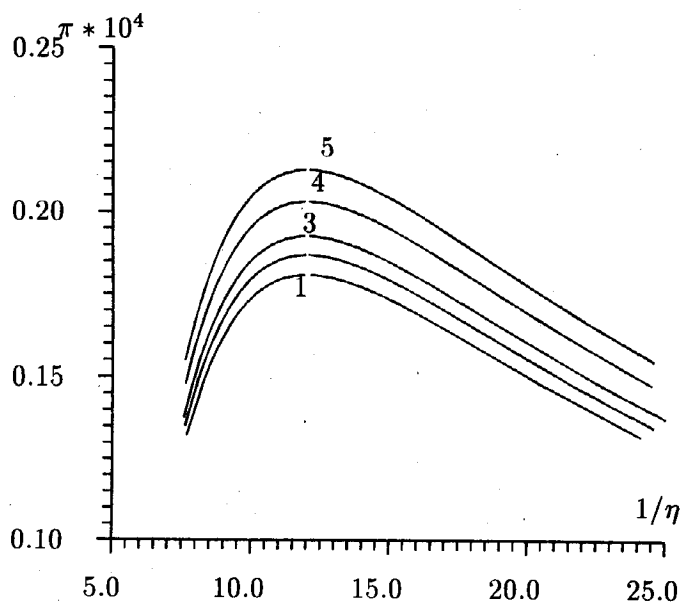


Figure 4. Gas-liquid coexistence curve for different concentrations of excited atoms; $a = 0.5$; 1 - $c_1 = 0.00\%$, 2 - $c_1 = 0.01\%$, 3 - $c_1 = 0.02\%$, 4 - $c_1 = 0.04\%$, 5 - $c_1 = 0.06\%$.

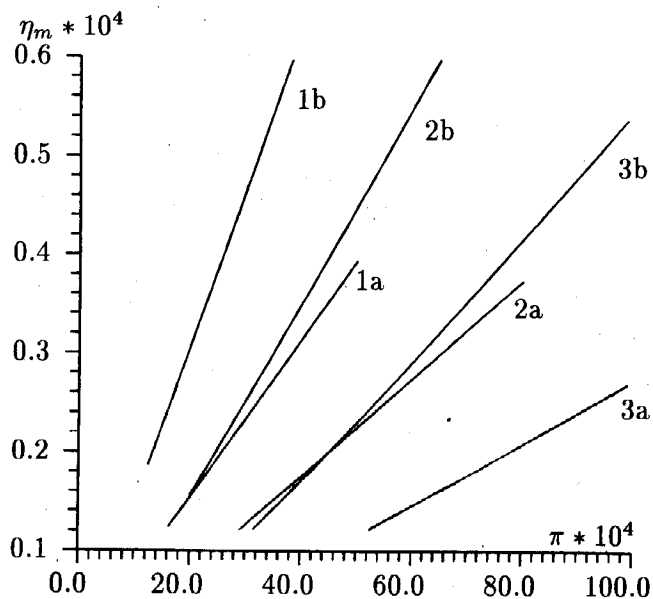


Figure 5. The dependence of eximer molecule density on pressure for different temperatures and concentrations of excited atoms; $a = 0.5$; 1 - $\tau = 0.0125$, 2 - $\tau = 0.02$, 3 - $\tau = 0.03$; a - $c_1 = 0.01\%$, b - $c_1 = 0.02\%$.

Another type of PEG state equations that was first pointed out in [15] permits to study excimer molecules formation in PEG [27]. Taking into account in (2) only two-particle contributions, neglecting by $b_{20}(\beta)$ and $b_{02}(\beta)$, and expressing z_0, z_1 via $\rho_0 = \rho c_0$ and $\rho_1 = \rho c_1$ one gets $\beta p = \rho_0 + \rho_1 - z_0 z_1 b_{11}(\beta)$, $z_1 = [\rho_0 - z_0 b_{10}(\beta)]/[z_0 b_{11}(\beta)]$, $z_0 = (\rho_0 - \rho_1 - b_{10}(\beta) \times b_{01}(\beta)/b_{11}(\beta) \pm \{[\rho_1 - \rho_0 + b_{10}(\beta)b_{01}(\beta)/b_{11}(\beta)]^2 + 4\rho_0 b_{10}(\beta)b_{01}(\beta)/b_{11}(\beta)\}^{1/2})/[2b_{10}(\beta)]$, $z_0 z_1 b_{11}(\beta) = (\rho + b_{10}(\beta)b_{01}(\beta)/b_{11}(\beta) \mp \{[\rho_1 - \rho_0 + b_{10}(\beta)b_{01}(\beta)/b_{11}(\beta)]^2 + 4\rho_0 b_{10}(\beta)b_{01}(\beta)/b_{11}(\beta)\}^{1/2})/2$ and therefore

$$\beta p = \frac{\rho}{2} - \frac{b_{10}(\beta)b_{01}(\beta)}{2b_{11}(\beta)} \pm \frac{b_{10}(\beta)b_{01}(\beta)}{2b_{11}(\beta)} \sqrt{\left[1 + \frac{(\rho_1 - \rho_0)b_{11}(\beta)}{b_{10}(\beta)b_{01}(\beta)}\right]^2 + 4\rho_0 \frac{b_{11}(\beta)}{b_{10}(\beta)b_{01}(\beta)}}. \quad (7)$$

The upper sign should be taken in (7) since such a choice leads to ideal state equation for small densities ρ . Rewriting r.h.s. of equation (7) as $(\bar{N}_0 + \bar{N}_1 + N_m)/V$, where $\bar{N}_0 = N_0 - N_m$, $\bar{N}_1 = N_1 - N_m$ are the numbers of free atoms in the ground and excited states, and N_m is the number of pairs non-excited atom - excited atom, that are identified with excimer molecules, one finds for excimer molecules density $\rho_m \equiv N_m/V$ that

$$\rho_m = \frac{\rho}{2} + \frac{b_{10}(\beta)b_{01}(\beta)}{2b_{11}(\beta)} - \frac{b_{10}(\beta)b_{01}(\beta)}{2b_{11}(\beta)} \sqrt{\left[1 + \frac{(\rho_1 - \rho_0)b_{11}(\beta)}{b_{10}(\beta)b_{01}(\beta)}\right]^2 + 4\rho_0 \frac{b_{11}(\beta)}{b_{10}(\beta)b_{01}(\beta)}}.$$

In fig.5 the dependences of excimer molecules density on pressure for several temperatures and concentrations of excited atoms are depicted. The increasing of excimer molecule density with the increasing of pressure seems quite natural and does not contradict to experimental data on the dependence of radiation intensity of excimer laser on the gas pressure [28].

To summarize, we present results of equilibrium statistical properties investigation of a gas with excited atoms within cluster expansion method with the accuracy up to three-atom groups contributions. Thermodynamical and structural properties are strongly influenced by resonance interactions the contributions of which to equilibrium statistical properties have special temperature dependence. The obtained results may be developed in different directions. In particular, they permit to study the influence of excited atoms on gas-liquid phase transition and to estimate a number of excimer molecules that form in the gas with excited atoms.

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РІВНОВАЖНІ ВЛАСТИВОСТІ ГАЗУ АТОМІВ, ЧАСТИНА З КОТРИХ ЗБУДЖЕНА, У МЕЖАХ МЕТОДУ ГРУПОВИХ РОЗВИНЕНЬ

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Розглядається газ атомів, частина з яких перебуває у збудженому електронному стані. Оскільки час життя у збудженому стані є набагато більшим за час, необхідний для встановлення рівноваги за поступальними ступенями вільності, система володіє рівноважними властивостями. Вони істотно визначаються багаточастинковими резонансними взаємодіями, що виникають у системі тотожних різнозбуджених атомів. Дана робота містить результати числових розрахунків, пов'язаних з дослідженням віріального рівняння стану і розвинення за степенями густини канонічної парної просторової функції розподілу системи, що розглядається, з точністю до внесків від тричастинкових груп. Отримані результати дозволяють вивчити вплив збуджених атомів на фазовий перехід газ-рідина та утворення ексимерних молекул у газі зі збудженими атомами.