Argon Compressibility And Viscosity At Clusterization Conditions

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Abstract. It is proposed to use the lattice gas model for analysis of effects of cluster formation in real dense gases. This model takes into account the own molecular volume and interactions between atoms with using of quasi-chemical approximation preserving the effects of direct correlation. Taking into account the compressibility of lattice structure and triple interactions the modified variant of model gives the good agreement with experimental data on concentration dependence of argon compressible factor and viscosity. It was carried out the comparison of calculated results with results based on cluster theory with using of virial decomposition equations and of the anharmonicity of vibrational excitation of argon clusters.

INTRODUCTION

The cluster formation and small particle processes accompany many technological processes in different regions of update industry. In the time of gas movement it is forming as short-living quasi-molecular formations as different steady stable clusters and small particles. The formation of this particles leads to change of gas dissipated coefficients particularly considerable in pressure and temperature region typical for industrial conditions.

In this paper it is suggested to use two update approaches: the simplest model of condense phase - the gas-lattice model and the cluster method of virial decomposition for analysis of equilibrium characters of real gases (for example of gaseous argon) [1-6].

The gas-lattice model takes into account the own atom and molecular volume and its interactions between themselves. Importance significance has the fact that only in the given model the self-consistent description of equilibrium and kinetic characteristics in concentration region with the help of uniform set of molecular parameters is provided [4].

The cluster method of virial decomposition takes into account anharmonicity of vibrational excitation of clusters.

Calculated results with the help of the gas-lattice model are compared with analogous calculations carried out on base of cluster gas-kinetic model [5,6].

GAS-LATTICE MODEL (M1)

According to gas-lattice model the researched volume of system \( V_s \) is divided on set of elementary volumes each from their approximatly equal to molecular volume \( v_0 \). The ratio \( V_s/v_0 = N \) defines number of clusters of lattice frame, which one is characterized by number of the proximate-neighbours \( z \). The most convenient variant of the lattice theory is the "holey" model accepting two busy condition of site: the site occupied in a molecule \( A \) or is free (occupied in vacancy \( V \) ). At usage of lattice models usually apply quasi-chemical approximation of pair interactions of particles taking into account effects of direct correlation. In the given paper the modified variants of the lattice theory is utilized with taking
into account pair interactions on arbitrary distances and triple interactions of the proximate particles and compressibility of lattice frame. We shall characterize concentration of a fluid with the help of the value $\theta = N_p / N$, where $N_p$ - number of molecules in a unit volume. Let's designate number of $r$ coordination or$r$ of a site through $z(r)$ $(z(1) = z)$. Distances between sites we shall measure in numbers of coordination orbs. Let's designate the energy parameter of interaction (describing an average energy of interaction) of particles at distance $r$ through $\varepsilon(r)$, $1 \leq r \leq R$, $R$ - radius of a potential of inter particle interaction. For molecules of a fluid we shall utilize a Lennard-Johnes potential. For compressible lattice the lattice constant $\lambda$ is defined from the condition of minimum of a free energy of the system [7]. The triple interactions were allowed by the way of concentration dependence of the pair potential for the proximate neighbours $\varepsilon (1/\theta) = \varepsilon (1)/(1 - D \theta)$, where $D$ - ratio of the contribution of triple interactions to the contribution of pair interactions of the proximate neighbours.

The equation of state in lattice model is written as [1,4]:

$$\beta P V_0 = -\ln(1 - \theta) - \frac{1}{2} \sum_{r=1}^{\infty} z(r) \ln[\theta_{\varepsilon(r)}(r) / \theta_r].$$  

where $\theta_r = 1 - \theta$, $\theta_{\varepsilon(r)} = 1 - 2\theta + \theta_{\varepsilon(r)}, \theta = \theta_r$, $\theta_{\varepsilon(r)}(r) = \theta(2(r))$, $\delta(r) = \{1 + 4\theta(1 - \theta)[\exp(\beta \varepsilon(r) - 1)]^{1/2}, \beta = 1/\theta$.

The factor of compressibility of a fluid is defined as $Z = \beta P V_0 / \theta$, and the link of a mole fraction, for example, of dimers $\alpha_{\text{dim}}$, with concentration of particles $\theta_r$ in the region of small concentrations is given by the equation:

$$\alpha_{\text{dim}} = n_{\text{dim}} / n = \{2 \theta \exp(\beta \varepsilon) \}^{1/2} + 1, \quad (2)$$

where $n = n_{\text{mon}} + n_{\text{dim}}$ $n$ - number of atoms as were monomers and dimers, in a unit volume, the index $i$ means monomers ($i = \text{mon}$) or dimers ($i = \text{dim}$). For calculation of coefficient of shift viscosity in a broad band of concentrations we shall take advantage of modified Eiring model [8]. The essence of modification is, that the initial Eiring model offered for the cellular model of a fluid phase (without presence of vacancies), is generalized on all region of concentrations of molecules within the framework of model of lattice gas (with allowance for of vacancies) by analogy with paper [9]. The final expression for shift viscosity $\eta$ can be presented by the way:

$$\eta = \eta_{0} \theta^{2} \epsilon_{\text{eff}}, \quad \epsilon_{\text{eff}} = U_{w}(\rho)/\theta,$$

where $\eta_{0} = (m kT/\pi\sigma^{2})(\pi \alpha^{2})$ - viscosity of a ideal dilute gas, $m$ - mass of molecule, $U_{w}(\rho)$ - average velocity of a jump of a particle on distance $\rho$ ($\rho$ - length of a jump of a particle $A$ in a vacant site), it expresses as [4,8]:

$$U_{f_k}^{\text{eff}}(\rho) = K_{f_k}^{\text{eff}}(\rho) V_{f_k}^{\text{eff}}(\rho), \quad V_{f_k}^{\text{eff}}(\rho) = \theta_{f_k}^{\text{eff}}(\rho) T_{k_f}^{\text{eff}}(\rho), \quad (4)$$

$$K_{f_k}^{\text{eff}}(\rho) = K_{f_k}^{\text{eff}}(\rho) \exp[-\beta E_{f_k}^{\text{eff}}(\rho)], \quad K_{f_k}^{\text{eff}}(\rho) = w/4\rho, \quad w = (8/\pi \alpha)^{1/2},$$

$$T_{k_f}^{\text{eff}}(\rho) = \sum_{r=1}^{\infty} \sum_{\alpha=1}^{\infty} S_{f_k}^{\text{eff}}(\alpha, \rho), \quad S_{f_k}^{\text{eff}}(\alpha, \rho) = \frac{\theta_{f_k}^{\text{eff}}(r) \theta_{f_k}^{\text{eff}}(r)}{\theta_{f_k}^{\text{eff}}(r) \theta_{f_k}^{\text{eff}}(r)} E_{f_k}^{\text{eff}}(\alpha),$$

$$E_{f_k}^{\text{eff}}(\alpha) = \exp[\delta_{f_k}^{\text{eff}}(r)], \quad (2)$$

At small density the viscosity varies linearly with changed $\theta$. It is necessary to mark the change of character of dependence of coefficient of shift viscosity from temperature for different density. At small density $\eta$ depends as $\theta^{1/2}$, and at major density we have an exponential temperature dependence, as well as in traditional Eiring model [8].

**GAS-KINETIC CLUSTER MODEL (M2)**

According to the experimental data the value of coefficient of shift viscosity depends not only on temperature, but also from pressure $\eta = \eta_{0}/(1 + \gamma \rho + ...).$ In paper [10] viscosity of gas, in which one there can be an elementary molecular association, i.e. formation of dimers and quasi-dimers, represented by the way $\eta = \eta_{0} + \eta_{\text{c}}$. The first term represents viscosity of mixture consisting of monomers and dimers, and it is featured through typical expressions for mixture of ideal gases. For example, utilizing the known formula Wilky $\eta_{c} = \eta_{0}(x_{i}, \eta_{i}^{0})$, where $x_{i}$ and $\eta_{i}^{0}$ - mole fractions and coefficients of viscosity of components of mixture. The second term $\eta_{\text{c}}$ stipulated by collisions of molecules, for model of hard spheres can be represented by the way [10]: $\eta = 7b n^{0} \eta^{0}/(40V)$, where the value $b = dTB(T)/dT$. Here $B(T)$ - second virial coefficient, which one can be represented by the way of three parts $B(T) = B_{0}(T) + B_{0}(T) + B_{0}(T)$, here first term $B_{0}$ features collision of free particles, the second term $B_{0}$ is bound to an equilibrium constant of the process of formation of bound dimers in
gas, the third term $B_m$ is bound to a constant of formation of metastable dimers. The value of the second virial coefficient $B_m \ll B_b$ at temperatures $\theta < \varepsilon/k$ (here $\varepsilon$ depth of potential pit). At major temperatures $B_m$ it is less or order of magnitude $B_b$. On the basis of these estimations and guessing, that the value $B_f$ can be approximated by constant value $b_\theta = \frac{2\pi N_A^m \sigma_m^2}{3}$, we shall receive \( B(T) = b_\theta(Ar) + B_b \). This expression for the summary value of the second virial coefficient well features experimental values for a lot of gases at appropriate adjustment of the value $\sigma$. Therefore according to \([11]\) expression for the second virial coefficient represented for mixture of monomers and dimers in the simplified sort: $B(T) = b_\theta - K(T)$, where the equilibrium constant $K(T) = -B_\theta$ for gas, in which one can happen response of dimer formation $A + A + M \rightarrow A_2 + M$, can be calculated with the help of the method, known from statistical mechanics \([1]\); here $\theta$ is $k_f / k_d$ ($k_f$ and $k_d$ - rate constant of generation and decay of dimer). $A$ - atoms and $M$ - molecule participating in triple collision. The equilibrium constant $K(T)$ is bound to change of a free energy of the Gibbs \([1]\): $\Delta G^0 = G^0 - 2G_0 = -2\ln K(T)$. According to \([12]\) the vibrational-rotational constants of dimer Ar$_2$ are: $\omega_v = 30.68 \text{ sm}^{-1}$; $\omega_v \chi_v = 2.42 \text{ sm}^{-1}$; $B_v = 0.059 \text{ sm}^{-1}$; $\alpha_v = 3.64 \times 10^{-3} \text{ sm}^{-1}$. $h_n = 586775 \times 10^{-16} \text{ g} \cdot \text{m}^2$. $D_0 = 109.8K$ - dissociation energy of argon dimer. At calculations the models of harmonic and anharmonic oscillators and rigid rotator were utilized.

**RESULTS**

In fig.1 the experimental and theoretical values of dependence of the factor of compressibility for an argon $Z = p/nkT$ from reduced numerical density $n^* = n \sigma^2$ are given, where $n$ - numerical density, $\sigma = 3.4051 \times 10^{-10}$ m at temperatures $T = 162K$ \([13]\) and $328K$ \([14]\) (curves 1 and 2). Also in this figure curves 3-5 calculated with using of the model of virial decomposition M2 (curve 3 - two terms of virial decomposition, 4 - three terms, 5 - four terms) are given. Obviously it is necessary to use as minimum five and more terms of virial decomposition to describe experimental data and to reach the agreement with the gas-lattice model M1 data.

![Figure 1](image-url)

In a fig.2 the dependence $Z(n^*)$ in a range $n^* < 0.05$ is reduced at $T=162K$. The curve 3 answers to model M1. The linear character of dependence testifies to sufficiency of usage in this region of concentrations the model M2 with only second virial coefficient. The comparison of mole fraction of bound dimers (curves 1 and 2) indicates the good consent between model M1 and M2 at taking into account the vibrational anharmonicity of dimer Ar$_2$. The discrepancies between curves 1 and 2 in region $n^* \approx 0.05$ and above bound with necessity of taking into account for virial decomposition of the third and higher virial coefficient.
In fig. 3 the curves 1 and 2 (models M1 and M2), corresponding to mole fractions of bound argon dimers in dependence on a gaseous pressure at stationary temperature value $T=500\mathrm{K}$. At small pressures these curves are close, but they differ approximately on 30% at pressure about 400 atm. The dependence of a coefficient of viscosity on pressure is given by curves 3 (model of lattice gas M1), 4 (taking into account of the second and third coefficients in virial decomposition of a coefficient of viscosity according to model M2) [10] and 5 (gas-kinetic model). The calculations under the formula for gas-kinetic model $\eta = \eta_0 + \eta_c$ (curve 5) coincide a curve 4 only at low values of the value of pressure (up to 10 atm). It answers the region, in which the mole fraction of bound dimers $\alpha_{\text{dim}}$ is close to the similar value for model of lattice gas M1. As 4 curves for M1 are visible from a figure is close to calculations on M2 of a coefficient of viscosity in a broad band of pressures, differing only it is non-significant.
In a fig. 4 the comparison of concentration dependence of the coefficient of viscosity calculated in model of lattice gas M1 at two temperatures with the experimental data reduced in [10,15] is carried out. Let's mark their satisfactory consent among themselves at the parameter value $e^* = 0.85e$, where the value $e$ mentioned above is found from the equilibrium data under the factor of compressibility and at calculation of coefficient of viscosity did not vary.

The carried out comparison of equilibrium and dissipated argon characteristics in a broad band of concentrations (from rarefied to dense, practically liquid, state) shows that lattice model M1 satisfactory describe as experimental data as calculated results with using of cluster gas-kinetic model M2. This allows to do the conclusion about of perspective of using of modify lattice model for quick and enough correct calculations of thermodynamic and kinetic parameters of different (dense or rarefied) gaseous systems.

REFERENCES