A unified low-parametrical equation used to calculate the viscosity coefficient of liquid, gas, and fluid. Argon. Xenon

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Abstract. A simple unified low-parametric equation has been obtained for describing the coefficient of argon and xenon viscosity in a wide range of state parameters. It is shown that the proposed low-parametric equation for calculating the viscosity coefficient of liquid and gas allows reliable extrapolation beyond the studied region.

1. Introduction
Viscosity is the most important physicochemical and technical characteristic of a liquid or gaseous material and one of the most complex parameters in high-precision experiments, especially at low and high temperatures and pressures. However, there are no theoretically justified ab initio simple equations for calculating and describing experimental data, as well as for extrapolation to little-studied and hard-to-reach measurement regions, except for the molecular theory of viscosity of dilute and medium-density gases. Concerning the molecular theory of viscosity of liquids and dense gases (see, for example, [1, 2]), the obtained calculation formulas are so complex and inconvenient that they cannot be used for practical calculations.

It is known that, in rigorous kinetic theory [1], dynamic viscosity can be represented as the sum, where the first term is caused by momentum transfer at particle “collisions”, while the second makes a contribution to the momentum transfer due to intermolecular interaction; at low densities \( \eta = \eta_{\text{kin}} + \eta_{\phi} \). \( \eta_{\text{kin}} \) tends towards dilute-gas viscosity \( \eta_0(T) \). However, modern kinetic theory (see, for example, [2]) does not assume obtaining relatively simple equations for describing the viscosity coefficient with a small number of fitting coefficients in a fairly wide range of the state parameters. In this context, model theories and empirical equations are widely used to describe fluid viscosity.

Various versions of equations for calculating the viscosity allow us to describe the experimental data in a wide range of the state parameters. However, they include a large number of coefficients. This number increases significantly when trying to describe simultaneously the viscosity of gas and liquid.

It was shown earlier in [3] that the excess viscosity \( \delta \eta \) in a wide range of state parameters is described by equations:

\[
\delta \eta = A \exp \left( \alpha \frac{x_0}{(x_0 - x)} \right) \\
\eta(T, P) = \eta_\text{en} + \delta \eta,
\]

(1)

(2)
here $P$, $V$, and $T$ are pressure, specific volume, and temperature of the system, $\eta (T, P)$ is the viscosity of the system in the given state, $\mu$ Pa·s; $\delta \eta = \eta (P, T) - \eta_{\text{eq}} (T, \rho)$ is the excess viscosity, $\eta_{\text{eq}} (T, \rho) = \eta_0 (T) \Psi (\rho)$ is the viscosity of the system of solid spheres by Enskog, $\eta_0 (T)$ is the rarefied gas viscosity, $\mu$ Pa·s, calculated as:

$$\eta_0 (T) = A (M \cdot T)^{1/2} \exp \left( \sum_{i=0}^{4} b_i \left( \ln \left( \frac{T}{\varepsilon} \right) \right)^i \right)^{-1}, \quad (3)$$

where $M$ is the molecular mass of the material; $a, b_i$ are the empirical coefficients for each substance; and $\varepsilon$ is the depth of a potential pit for Lennard–Jones potential;

$$\Psi (y) = \frac{1}{g} \left( 1 + 0.8 y g + 0.761 y^2 g^2 \right), \quad (4)$$

where $y = \rho b$, $\rho = 1/V$ is the substance density, $b$ is the adjustable parameter with dimensionality of a volume, $x = \Delta U/V$ is the density of interaction energy, $\Delta U = U_{\text{ig}} (T) - U(P, T)$ is the energy of interaction, $U_{\text{ig}} (T)$ is the internal energy of ideal gas, $U(P, T)$ is the internal energy of the system in the given state; $x_0 = H^0_0 / V_0$, $V_0 = \lim_{T \rightarrow 0, P \rightarrow 0} (V(T, P))$ is the hypothetical volume supercooled to absolute zero of liquid, $H^0_0 = U_{\text{ig}} (0) - U(0, 0)$ is the enthalpy of evaporation at absolute zero temperature and zero pressure; and $A$, $\alpha$, the $b$ are the individual constants of substance to be determined from the data on viscosity coefficient. According to (1), excess viscosity $\delta \eta$ is an univocal function of interaction energy density $x = \Delta U/V$ (figure 1).

The close-to-optimal description of experimental data can be achieved at $b = V_0$. For well-studied materials, physical parameters $V_0$ and $H^0_0$ are generally given in tables of thermodynamic properties of materials. In this case, equations for viscosity (1) and (2) contain only two empirical constants: $A$ and $\alpha$ (as well as the known Arrhenius equation). In the case of the absence of data on $V_0$ and $H^0_0$, the number of empirical coefficients in equations (1) and (2), which are found from the data on viscosity, increases to 4: $A$, $\alpha$, $V_0$, and $x_0$. Equations (1) and (2) describe the dependence of the liquid and gas viscosity for a wide range of materials within the experimental (table) error in the entire considered range of state parameters [3]. It was shown in [4] that some known equations for describing viscosity (Eyring, Frenkel, Andrade, etc.) are particular cases of equations (1) and (2).

![Figure 1](image-url)

**Figure 1.** Dependence of the excess viscosity $\Delta \eta$ on the internal-energy density $x = \Delta U/V$: (1) argon, (2) xenon.
According to analysis (see [3, 5-6]), equations (1) and (2) describe satisfactorily the experimental and tabular data on viscosity of liquid, gas, and fluid in a wide range of state parameters (excluding the region of small and moderate densities) basically within the error of the initial data. We should emphasize that in order to use equations (1) and (2) for calculating the viscosity coefficient, it is necessary to have sufficiently accurate and simple thermal and caloric equations of state to calculate the thermal and caloric properties of the substance.

### 2. Equation for calculating the viscosity in a wide range parameters

The detailed analysis of equation (1) has revealed that the maximal systematic deviations of the calculated values of viscosity from the initial tabulated data are in the region corresponding to transition from rarefied to moderately dense gas [7]. It can be assumed that in the transition region, where it is necessary to take into account the dependence of viscosity coefficient on density, both mechanisms of momentum transfer are involved: via collisions and intermolecular interaction (the “field” mechanism). The field mechanism becomes the predominant mechanism of momentum transfer with increasing the density of interaction energy $\Delta U/V$.

For further analysis, let us distinguish the contribution to the excess viscosity caused by the mixed mechanism of momentum transfer: the collision (by Enskog) and the field one. To do this, from the initial data on excess viscosity, where $\delta\eta_{\text{tab}} = \eta(T, P) - \eta_{\text{en}}$, and $\eta(T, P)$ is the calculation by equations (3) and (4), we will subtract the values of $\delta\eta$ found by approximation of these initial data by equation (1), whose coefficients are calculated by the least-squares method. We assume that the obtained difference $\delta\eta_1 = \delta\eta_{\text{tab}} - \delta\eta$ is caused by the mixed (collision and field) mechanism of interaction. Since with increasing internal energy density the field mechanism of momentum transfer becomes predominant, and the mixed mechanism of momentum transfer can be neglected, the equation describing the viscosity of the mixed mechanism should be supplemented by a certain crossover function that must ensure the transition from one mechanism of momentum transfer in the shear flow to another. To estimate the total collision and field contribution to momentum transfer in the viscosity coefficient, the authors used the well-known approach and described the total contribution to viscosity by these mechanisms as the mean geometric value of both contributions. As a result of these specifications, the excess viscosity in the transition region from the collision to the field mechanism of momentum transfer in the shear flow can be written in the form

$$\delta\eta = \delta\eta_{\text{tab}} - \delta\eta = \left(\frac{\delta\eta_{\text{tab}}}{\delta\eta_{\text{en}}}ight)^{1/2} \exp(-\beta x/ x_0) = \left(\frac{x}{x_0}\right)^{1/2} \exp(-\beta x/ x_0),$$

(5)

Here it is taken into account that in the range of relatively low densities, viscosity does not depend on density, but it depends on temperature, proportionally to $T$ (contribution to momentum transfer due to elastic collisions). At low densities of internal energy $\Delta U/V$, one can restrict oneself to the linear approximation in the field mechanism of momentum transfer; multiplier $\exp(-\beta x/ x_0)$ is the crossover function, which ensures the transition to calculation of the viscosity coefficient by the field mechanism (equation (1)); and $T_c$ is the temperature at the critical point.

Thus, equation for calculating the viscosity coefficient in a wide range of the state parameters is written as

$$\eta_{\text{ad}}(T, P) = \eta_{\text{en}} + \delta\eta + \delta\eta_1.$$  

(6)

Substituting $\delta\eta_1$ from (5) in equation (6), we obtain the expression for the viscosity coefficient in the form:

$$\eta_{\text{ad}}(T, P) = A\exp\left(\alpha - \frac{x_0}{x_0 - x}\right) + B\left(\frac{T}{T_c}\right)^{1/4} \left(\frac{x}{x_0}\right)^{1/2} \exp(-\beta x/ x_0) + \eta_{\text{en}}.$$

(7)
3. Calculating the viscosity coefficient for argon and xenon

Below there are the results of calculating the viscosity coefficients of liquid, gas, and fluid by equation (7) for argon, xenon. A single low-parametric equation of state, required for calculating the density and internal energy in a wide range of parameters for the given temperature and pressure is given in [7]. Literature data [8-9] were used to calculate the viscosity \( \eta_0 \) of a rarefied gas. The calculation was carried out in the following ranges of parameters: for argon, temperatures of up to 700 K and pressures of up to 25 MPa, for xenon, temperatures of up to 500 K and pressures of up to 20 MPa, and density from 0 to density at the triple point \( \rho_\text{tr} \). As the initial data for calculating coefficients \( A, B \) and \( \alpha, \beta \) in equation (7), we used the calculated (averaged experimental) data for argon from [8], for xenon [9]. In calculations, we used the values of \( H_0^0 \) and \( V_0 \) obtained in [8-10]. The results of calculating the viscosity are shown in table 1 and in figures 2-4. The physical parameters of argon, xenon (parameters of characteristic points) and values of coefficients \( A, B, \alpha, \beta, H_0^0, V_0, \) and \( x_0 \), required for calculating the viscosity by equations (1), (2), and (7), ranges of description parameters as well as rms-average \( \sigma, \% = 100 \left( \frac{1}{N} \sum (\eta_\text{cal} - \eta_\text{tab})^2 / (N - 4) \right)^{1/2} \) and weighted average \( \text{AAD}, \% = 100 \frac{\sum (\eta_\text{cal} - \eta_\text{tab})}{(N - 4)} \) – deviations of calculated viscosities from the tabular values for argon [8], for xenon [9] are given in the table 1.

Table 1. Physical parameters of argon and xenon; coefficients \( A, \alpha, B, \beta, H_0^0 \) and \( V_0 \) in equations (1), (2), and (7) for calculation of viscosity; ranges of description parameters: by temperature \( \Delta T \), pressure \( \Delta P \); mean-square \( \sigma \) and weighted-mean \( \text{AAD} \) deviations of calculated viscosity values from initial data.

| Parameters                  | Argon   | Xenon   |
|-----------------------------|---------|---------|
| \( T_C \), K                | 150.687 | 289.73  |
| \( P_C \), MPa              | 4.863   | 5.842   |
| \( \rho_C \), kg/m\(^3\)    | 535.6   | 1102.9  |
| \( T_{tr} \), K             | 83.806  | 161.36  |
| \( \rho_{tr} \), kg/m\(^3\) | 1416.7  | 2966.2  |
| \( A, 10^{12} \) s          | 0.182468| 0.29139 |
| \( \alpha \)                | 0.8076  | 0.808   |
| \( B \)                      | 15.78   | 33.3    |
| \( \beta \)                 | 12.52   | 23.5    |
| \( x_0 = H_0^0 / V_0 \) MPa | 341.32  | 453.03  |
| \( H_0^0 \), J/g            | 192.675 | 119.6   |
| \( b = V_0 \), cm\(^3\)/g   | 0.5645  | 0.264   |
| \( \Delta T \), K           | 83.81...700 | 161.36......500 |
| \( \Delta P \), MPa         | 0.1...25 | 0.1...20 |
| \( \sigma, \% \)            | 0.68    | 0.9     |
| \( \text{AAD}, \% \)        | 0.47    | 0.57    |

Let us dwell in more detail only on the results of calculation of viscosity coefficient of xenon. The values of viscosity coefficient calculated by formula (7) are shown in figure 2 as a function of temperature and pressure on isobars in comparison with the tabular data of [9]. Deviation of the xenon viscosities calculated by (7) from the tabular data of [9-10] is shown in figure 3. According to analysis, the discrepancies between the values calculated by (7) and tabular (averaged experimental) values of viscosity from [9] do not exceed approximately 1.5–2.0 \( \% \), and do not exceed the discrepancies between the experimental data of other authors on viscosity. As can be seen from figure 3, a noticeable increase in the discrepancy between the values calculated by (7) and tabular values of

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[9] (up to 4–5 %) occurs both in the region of critical temperatures and pressures, and in the range of low temperatures (near the melting point of xenon) and high pressures. However, experimental and tabular data obtained by other authors differ considerably in this range. Thus, in particular, according to figure 3 it can be seen that the tabular values of xenon viscosity at high densities and pressures from [9] diverge from the tabular viscosity data from [10] by four or more percents.

It is interesting to estimate the extrapolation potential of equation (7) for calculating the viscosity coefficient in a poorly studied or unexplored domain of states. Experimental data on argon viscosity from [11], which are among the most reliable, are compared in figure 4 with the viscosity values calculated by relationship (7), whose coefficients are determined from tabular data of [9] in the pressure range up to 20 MPa. Comparison of viscosities calculated by (7) with experimental values of [11] was carried out in the pressure range up to 200 MPa, i.e., the extrapolation interval was 10 times higher than the size of the “reference” range of pressure. As can be seen from figure 4, the agreement

Figure 2. Comparison of xenon viscosities (lines), calculated by formulae (7) with tabular data of [9] (symbols) on isobars. 0.1 MPa (1), MPa 0.5 MPa (2), 1 MPa (3), 2 MPa (4), 4 MPa (5), 6 MPa (6), 8 MPa (7), 10 MPa (8), 15 MPa (9), 20 MPa (10).

Figure 3. Deviation of tabular data on viscosity of [9, 10] from the values calculated by formula (7). Data of [9, 10]: 1 MPa (1, 8), 2 MPa (2, 9), 4 MPa (3, 10), 6 MPa (4, 11), 8 MPa (5, 12), 10 MPa (6, 13), 20 MPa (7, 14).
between the calculated and experimental data should be considered quite satisfactory, excluding the discrepancies between the calculated extrapolated and experimental data of [11] on some isochors at high pressures.

4. Conclusion
The low-parametric unified equation has been obtained to calculate the viscosity coefficient of argon and xenon in the liquid and gaseous states. This equation includes four individual empirical coefficients, which should be found from the experimental or tabular data on viscosity.

It is shown that the viscosity values calculated by equation (7) agree with the experimental and tabulated data within the experimental errors, except the above-mentioned “outliers” (anomalously high deviations) near the triple and critical points. The root-mean-square deviation of the values of argon and xenon viscosity obtained by equation (7) from the standard tabular data [8], [9] is \( \sigma = 0.7\% \) (0.9 % xenon), and the weighted average deviation is AAD = 0.5% (0.57% xenon). The proposed equation (7) allows extrapolating the viscosity coefficient far beyond the reference region, where the coefficients of the given equation are found, with satisfactory accuracy.

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