REVIEWS OF TOPICAL PROBLEMS

Theoretical and computational approaches to predicting the viscosity of liquids

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Abstract. Predictive models for the shear viscosity of liquids and gases along with exact equations of state are of great practical importance for hydrodynamic modeling of processes occurring in nature, industrial plants, and machinery. We consider currently proposed theoretical, including atomistic modeling, and semi-empirical approaches to predicting the viscosity of liquids, gases, and their mixtures in a wide range of thermodynamic conditions. Viscosity models of homogeneous liquids in a thermodynamically stable state are described. The dynamics of supercooled and vitrescent liquids and dispersed systems (colloids, emulsions) remain beyond the scope of this review. We discuss the area of applicability of correlation methods for predicting viscosity and the accuracy of various methods in the pressure range up to 1 GPa. Application examples of various approaches for hydrocarbons-model oil and gas, fuel, and lubrication systems — are given.

Keywords: shear viscosity, liquids, theoretical models, empirical models, molecular modeling, atomistic modeling

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1. Introduction

An accurate description of the shear viscosity of liquids and gases along with exact equations of state are of great practical importance for hydrodynamic modeling of processes occurring in nature, industrial plants, and machinery. Transport coefficients determine the key properties necessary for multiscale modeling of physical processes, complementing the experimental approach.

The aim of the present review is to consider the currently proposed approaches to predicting the viscosity of liquids, gases, and their mixtures in a wide range of thermodynamic conditions.

The methods of predicting the transport coefficients proposed in the literature can be divided into several categories: those based on theoretical correlation models, empirical correlations, and simulative numerical modeling of a liquid. A number of models imply a relation between the thermodynamic and transport properties of a liquid and extend the thermodynamic similarity method over the transport coefficients. In other theoretical models (reduction to a system of hard spheres, free volume theory), the correlation formulas are derived from assumptions about the form of intermolecular interactions responsible for the viscous friction, rather than from a direct relation between thermodynamics and transport properties.

Purely empirical correlations do not assume rigorous theoretical substantiation of the functional form, which is chosen based on the experience of good agreement with a large array of experimental data. The advantage of such relationships is that they are not related to a specific form of the equation of state and express viscosity as a function of directly measured quantities—temperature, pressure, and density. The extension of correlation models over mixtures is commonly implemented using mixing rules, i.e., by calculating the correlation parameters for mixtures from the mixture composition and the parameters of individual components.

Finally, simulative numerical modeling, most frequently implemented using the method of molecular dynamics (MD), allows direct calculation of viscosity and other properties based on a detailed model of molecular interaction. Among the methods of calculating the transport properties, it is possible to distinguish two conceptually different groups, namely, the equilibrium and nonequilibrium molecular dynamics. Studies in recent years demonstrate a good agreement between the calculated viscosity and experimental data for various liquids. However, there are peculiarities that limit the applicability of both equilibrium and nonequilibrium approaches.

The present review analyzes the applicability and accuracy of the described methods and approaches for pure substances and mixtures within the range of viscosity coefficients up to 1 Pa s. The issue of model accuracy in the pressure range up to 1 GPa is considered. The review of methods is restricted to homogeneous thermodynamically stable liquids. Disperse systems, such as colloids and emulsions are beyond the scope of discussion, as are the issues of viscosity in strongly overcooled liquids approaching a vitrification state.

2. Viscosity of liquids

Let us consider some semi-theoretical and empirical relationships describing the viscosity of liquids and dense gases. Note that, in contrast to the gas viscosity theory, no complete theory has been constructed for the viscosity of liquids; therefore, models are usually applicable only to a certain class of substances with limitations imposed on the range of thermodynamic parameters.

2.1 Batchinski's relation

One of the first relationships that offered a prediction of viscosity depending on thermodynamic parameters was the Batchinski's equation for fluids [1]:

$$\eta = \frac{C}{v_{\rm m} - b} \,, \tag{1}$$

where η is the viscosity, $v_{\rm m}$ is the molar volume of the liquid and *C* and *b* are empirical parameters depending on the substance. Batchinski discovered that *b* has the meaning of the excluded volume in the liquid, commonly close to the excluded volume in the van der Waals equation, equal to $v_{\rm c}/3$, where $v_{\rm c}$ is the critical volume of the liquid.

In spite of its simple form, Eqn (1) under pressures of the order of 1 kbar can describe the viscosity behavior of a number of liquids: hydrocarbons [2, 3], halogenated hydrocarbons, and mercury [4]. Clearly, the area of applicability of Eqn (1) is limited. The Batchinski's relation becomes invalid at high densities, when $v_m \approx b$ and accurate consideration of the pressure dependence of the excluded volume is necessary. For such densities, it is also typical that the isochoric viscosity substantially depends on temperature, i.e., it is necessary to introduce the temperature dependence of the coefficient *C*. On the other hand, in the low-density limit, Eqn (1) does not yield an expression for the viscosity of a rarefied gas, i.e.,

cannot be used in the entire range of densities between a liquid and a gas. Nevertheless, the idea that the viscosity of a liquid is mainly determined by the free volume turns out to be fruitful in more advanced theories, too. The free volume concept also explains the extremely strong sensitivity of viscosity to the density changes, since the quantity $v_{\rm m} - b$ in a liquid is usually small compared to $v_{\rm m}$.

2.2 Theory of corresponding states

One of the approaches to a unified description of viscosity in liquids and dense gases is the theory of corresponding states, widely used to describe oil and gas mixtures, hydrocarbon fuels, refrigerants, etc. Finding the unknown viscosity of a substance or mixture at temperature T, pressure P, and density ρ reduces to finding the viscosity of the substance chosen for reference at temperature T_{ref} , pressure P_{ref} , and density ρ_{ref} , followed by using the scaling relations. The values of T_{ref} , P_{ref} , and ρ_{ref} are determined by the thermodynamic similarity relations.

Usually, the similarity relations are expressed either in the form

$$\eta = \eta_{\rm ref} \, {\rm scale} \tag{2}$$

or in the form

$$\eta = \eta_0(T) + \Delta \eta_{\text{ref}} \text{ scale} \,, \tag{3}$$

where η_0 is the viscosity of the substance at a given temperature in a rarefied gas state, η_{ref} and $\Delta \eta_{ref}$ are the total and excess viscosity of the reference substance, and scale is the scaling factor that depends on density, pressure and temperature.

2.3 Method of corresponding states based on density and temperature

The method of corresponding states [5] is based on an assumption that the intermolecular potentials in both the studied and the reference substance can be presented in the form of an effective pair potential with the parameters of characteristic size σ and characteristic energy ϵ :

$$U(r) = \epsilon f\left(\frac{r}{\sigma}\right),\tag{4}$$

where f is a certain function. For example, for the Lennard-Jones potential, $f_{LJ}(r^*) = 4(r^{*-12} - r^{*-6})$. The reference and the studied substance thus differ only in the values of the parameters, namely, ϵ_{ref} and σ_{ref} for the reference substance, and ϵ_x and σ_x for the substance of interest.

From the method of dimensions, it is possible to introduce the reduced viscosity

$$\eta^* = \eta \sigma^2 (m\epsilon)^{-1/2} \,, \tag{5}$$

where *m* is the mass of a molecule.

Equating the reduced viscosities for the considered substance and the reference one, we arrive at the expression

$$\eta_{\rm x}[v_{\rm x}, T_{\rm x}] = \eta_{\rm ref} \left[\left(\frac{\sigma_{\rm ref}}{\sigma_{\rm x}} \right)^3 v_{\rm x}, \frac{\epsilon_{\rm ref}}{\epsilon_{\rm x}} T_{\rm x} \right] \\ \times \left(\frac{M_{\rm x}}{M_{\rm ref}} \right)^{1/2} \left(\frac{\sigma_{\rm ref}}{\sigma_{\rm x}} \right)^2 \left(\frac{\epsilon_{\rm x}}{\epsilon_{\rm ref}} \right)^{1/2}, \tag{6}$$

where v is the molar volume, M is the molecular mass of the compound, T is the absolute temperature, the quantities with the subscript x refer to the considered substance, and the quantities with the subscript ref indicate to the reference substance.

Since the critical temperature T_c and volume v_c are related to the parameters of the potential as $T_c \sim \epsilon/k_B$ (where k_B is the Boltzmann constant) and $v_c \sim \sigma^3$, the similarity relation can be presented in the form

$$\eta_{\rm x}[v_{\rm x}, T_{\rm x}] = \eta_{\rm ref} \left[v_{\rm x} \, \frac{v_{\rm c, ref}}{v_{\rm c, x}}, T_{\rm x} \, \frac{T_{\rm c, ref}}{T_{\rm c, x}} \right] \\ \times \left(\frac{M_{\rm x}}{M_{\rm ref}} \right)^{1/2} \left(\frac{v_{\rm c, ref}}{v_{\rm c, x}} \right)^{2/3} \left(\frac{T_{\rm c, x}}{T_{\rm c, ref}} \right)^{1/2}.$$
(7)

Such a scaling, reflecting the principle of the corresponding state, however, will be exact only when the function $f(r/\sigma)$ is the same in the reference substance and the substance of interest. For real substances, the two-parameter representation of the 'universal' potential is insufficient. The next approximation is the introduction of scaling factors for temperature and volume:

$$f_{\rm x} = \theta_{\rm x} \, \frac{T_{\rm c,\,x}}{T_{\rm c,\,ref}} \,, \quad h_{\rm x} = \phi_{\rm x} \, \frac{v_{\rm c,\,x}}{v_{\rm c,\,ref}} \,, \tag{8}$$

where ϕ and θ are the 'shape factors' [6–8], which transform the reference substance equation of state into that of the substance of interest. Exact values of ϕ and θ are found from the nonlinear system of equations [6, 7]:

$$\begin{cases} F_{x}^{ex}(v,T) = f_{x}F_{ref}^{ex}\left(\frac{v}{h_{x}},\frac{T}{f_{x}}\right) - RT\ln h_{x},\\ Z_{x}(v,T) = Z_{ref}\left(\frac{v}{h_{x}},\frac{T}{f_{x}}\right), \end{cases}$$
(9)

where $F^{\text{ex}}(v, T) = F(v, T) - F^{\text{id}}(v, T)$ is the excess Helmholtz energy (the difference in energy between the substance and the ideal gas at equal densities and temperatures), *R* is the universal gas constant, and Z = Pv/(RT) is the supercompressibility coefficient.

Expression (7) for the viscosity coefficient takes the form

$$\eta_{\rm x}[v_{\rm x}, T_{\rm x}] = \eta_{\rm ref} \left[\frac{v_{\rm x}}{h_{\rm x}}, \frac{T_{\rm x}}{f_{\rm x}} \right] \left(\frac{M_{\rm x}}{M_{\rm ref}} \right)^{1/2} h_{\rm x}^{-2/3} f_{\rm x}^{-1/2} \,. \tag{10}$$

Expressing the viscosity in such a form is called the principle of extended corresponding states (ECS).

Since the solution of the system of Eqns (9) requires an iteration method and the known equation of state, for practical use of the ECS method it is more convenient to use analytical approximations for the factors f_x and h_x as functions of thermodynamic states. For a number of hydrocarbons and freons, using the calculated exact solutions, the approximations for factors θ and ϕ chosen in an explicit form as functions of the reduced temperature T/T_c , reduces specific volume v/v_c and acentric Pitzer factor ω [7, 9, 10].

In the original version of ECS correlation, gaseous methane was chosen as a reference substance [5, 7], and the viscosity–density dependence was taken in the form proposed in [11]. These correlations for methane are valid only at temperatures beyond the triple point, $T > T_{\rm tr} = 0.48T_{\rm c}$. In higher hydrocarbons, the reduced temperature of the triple point is usually lower than in methane; therefore, they can be

at $T/T_c < 0.48$ even under normal conditions. Thus, in Ref. [7], the equation of state and the correlation for the viscosity of methane are reparametrized to correspond to the data for other hydrocarbons at low reduced temperatures. The final model with methane as a reference substance, called TRAPP (TRAnsport Properties Prediction) [8], was used as an etalon model in the database of the National Institute of Standards and Technology (NIST, USA) [10]. In subsequent versions of the ECS model, methane as a reference substance for the family of hydrocarbons was replaced with propane [10, 12], which has a minimum reduced temperature of the triple point in the family of n-alkanes. Empirical corrections are also introduced, which can take into account the experimental data on the transport coefficients under the standard conditions.

A similar approach was later proposed for freons [13, 14] based on the equation of state and reference data on the viscosity for 1,1,1,2-tetrafluoroethane (R134a). In Ref. [14], it was found that, for freons and their mixtures, two scaling parameters f_x and h_x (8) are not sufficient; therefore, an additional density-dependent shape factor for the viscosity is introduced. The predictions of freon viscosity based on the method of corresponding states without the additional shape factor demonstrate a discrepancy from the experimental data from 7% to 45% for different substances. The viscosities of hydrocarbons based on the R134a equation of state without introducing the additional shape factor are predicted with an error of 66–168% [14]. Thus, although the model based on the principle of corresponding states is a predictive method, it demonstrates high accuracy only for the family of n-alkanes. For accurate (within 20%) reproduction of viscosity of a substance from other families, it is usually required to introduce substantial empirical corrections into the model.

Mixing rules. Within the ECS, the viscosity of mixtures is described by Eqn (10), where factors f_{mix} and h_{mix} are introduced for a mixture. Based on thermodynamic similarity considerations, Ref. [7] proposes the following mixing rules:

$$h_{\text{mix}} = \sum_{i,j} x_i x_j h_{ij},$$

$$f_{\text{mix}} h_{\text{mix}} = \sum_{i,j} x_i x_j f_{ij} h_{ij},$$
(11)

where x_i is the molar fraction of the *i*th component in the mixture,

$$f_{ij} = \xi_{ij} (f_i f_j)^{1/2}, \quad h_{ij} = \psi_{ij} \, \frac{\left(h_i^{1/3} + h_j^{1/3}\right)^3}{8},$$
(12)

and ψ_{ij} and ξ_{ij} are correction coefficients, which by default are equal to one but can be corrected in the presence of experimental data on the viscosity of mixtures,

$$\eta_{\rm mix}[v,T] = \eta_{\rm ref} \left[\frac{v}{h_{\rm mix}}, \frac{T}{f_{\rm mix}} \right] \left(\frac{M_{\rm mix}}{M_{\rm ref}} \right)^{1/2} h_{\rm mix}^{-2/3} f_{\rm mix}^{1/2} \,. \tag{13}$$

The similarity relations employed also lead to the following mixing rule for the effective molecular mass [7]:

$$M_{\rm mix}^{1/2} f_{\rm mix}^{1/2} h_{\rm mix}^{4/3} = \sum_{i,j} x_i x_j M_{ij}^{1/2} f_{ij}^{1/2} h_{ij}^{4/3},$$

$$M_{ij} = \frac{2M_i M_j}{M_i + M_j}.$$
(14)

2.4 Method of corresponding states based on pressure and temperature

The extended principle of corresponding states can also be applied when there are no data on the viscosity, but the liquid pressure is known [7]. Then, the unknown density is obtained from the solution of the equation

$$P_{\rm ref}\left(\frac{v_x}{h_x}, \frac{T_x}{f_x}\right) = \frac{P_x h_x}{f_x} , \qquad (15)$$

where P_x is the pressure of the mixture, and $P_{ref}(v_{ref}, T_{ref})$ is the state equation for the reference substance. Equation (15) is solved by the simple iteration method: the values $\phi = \theta = 1$ are taken for the first approximation, then, from Eqn (15), the next approximation for the quantity v_x is found, for which new values of ϕ and θ are calculated, and the procedure is repeated until convergence is achieved. In TRAPP models, the dependence $P_{ref}(v, T)$ is represented by a multiparametric equation of state, parameterized for methane in [15] and for propane in [16].

Using the pressure as the main variable instead of density offers some advantages for modeling oil and gas mixtures, since the cubic equations of state widely used to describe them do not always reproduce their density well enough.

In Refs [17, 18], an alternative model is proposed, in which the principle of corresponding states is directly expressed in terms of temperature and pressure:

$$\eta_{\rm mix}(P,T) = \eta_{\rm ref}(P_0,T_0) \left(\frac{T_{\rm c,\,mix}}{T_{\rm c,\,ref}}\right)^{-1/6} \left(\frac{P_{\rm c,\,mix}}{P_{\rm c,\,ref}}\right)^{2/3} \\ \times \left(\frac{M_{\rm mix}}{M_{\rm ref}}\right)^{1/2} \frac{\alpha_{\rm mix}}{\alpha_{\rm ref}} , \qquad (16)$$

where α_{mix} and α_{ref} are 'shape factors' for the mixture of interest and the reference substance. The temperature T_0 and pressure P_0 are calculated as

$$T_0 = \frac{\alpha_{\rm ref} T_{\rm c, ref}}{\alpha_{\rm mix} T_{\rm c, mix}} T, \qquad P_0 = \frac{\alpha_{\rm ref} P_{\rm c, ref}}{\alpha_{\rm mix} P_{\rm c, mix}} P.$$
(17)

Therefore, one factor, $\alpha_{ref}/\alpha_{mix}$, instead of the two shape parameters ϕ and θ is used to scale both temperature and pressure.

In Ref. [17], methane is taken as a reference substance. Its density $\rho_{ref}(P_0, T_0)$ and viscosity $\eta_{ref}(\rho_0, T_0)$ are calculated from the same equations of state [15] and correlation [11] as in the TRAPP model. The authors of Ref. [18] extend the correlations for viscosity to the region of reduced temperatures below the triple point of methane. The explicit form of the pressure dependence of factor α corresponds to the solution of Eqn (15) obtained after the first iteration. Therefore, the model proposed in Refs [17, 18] is a simplification of the TRAPP model for practical calculations.

2.5 Reduction to a system of hard spheres

The reference system for the method of corresponding states should not necessarily be a real substance. Alternatively, an idealized model system, whose properties can be obtained by numerical modeling with any desired accuracy, can be taken for reference.

The authors of Ref. [19] proposed to reduce the transport coefficients of real liquids to those of a system of hard spheres, the properties of which are determined with high accuracy within the frameworks of molecular dynamics (see [20]). For the viscosity coefficient of a liquid of hard spheres, a universal relation holds:

$$\frac{\eta(v,T)}{\eta_0(T)} \left(\frac{v}{v_0}\right)^{2/3} = \eta^*(v^*)\,,\tag{18}$$

where $v^* = v/v_0$, v is the molar volume of the system, $v_0 = N_A d^3/\sqrt{2}$ is the molar volume of densely packed hard spheres with diameter d, N_A is Avogadro's number, and $\eta_0(T)$ is the system viscosity in the low-density limit (see Section 5.1). Thus, we may write

$$\eta = \eta^* \left(\frac{v}{v_0}\right) \frac{5}{16} \sqrt{\frac{MRT}{\pi}} v^{-2/3} (2N_{\rm A})^{-1/3}, \qquad (19)$$

where M is the molar mass of the liquid.

Therefore, to determine the viscosity of a real liquid, the effective diameter of hard spheres should be known for the specified thermodynamic conditions. In Refs [19, 21], the roughness factor R_{η} of the molecules is additionally introduced into Eqn (19) to consider the contribution of intermolecular angular momentum transfer to the transport coefficients. It is assumed that for a given substance the effective volume v_0 of hard spheres depends only on temperature. The equation for the viscosity takes the form

$$\eta = R_{\eta} \eta^* \frac{5}{16} \sqrt{\frac{MRT}{\pi}} (2v_{\rm m}^2 N_{\rm A})^{-1/3} \,. \tag{20}$$

In Ref. [21], the function $\eta^*(v^*)$ is proposed in the form

$$\log_{10} \eta^* = \sum_{k=0}^7 \frac{a_k}{(v^*)^k} \, .$$

For a number of saturated hydrocarbons, from methane to hexadecane, correlations for the dependence of v_0 on temperature and chain length and for the dependence of R_{η} on the chain length are proposed.

The correlation proposed in [21] is valid for values of v^* from 1.5 to 5, i.e., only for liquids at moderate degrees of compression. Therefore, a drawback is that there is no smooth transition from a dense fluid to a gas, which can occur in transcritical flows. To remove this drawback, in Ref. [22] it is proposed to extend the correlation as

$$\eta = \eta_0 + R_\eta \Delta \eta^* \, \frac{5}{16} \, \sqrt{\frac{MRT}{\pi}} (2v_{\rm m}^2 N_{\rm A})^{-1/3} \,, \tag{21}$$

where $\Delta \eta^*(v^*)$ is a universal function for the excess viscosity, which possesses the property $\Delta \eta^* \to 0$ at $v^* \to \infty$ upon transition to an ideal gas.

By analogy with the original viscosity–density correlation for a system of hard spheres, $\Delta \eta^*(v^*)$ is introduced in the form

$$\log_{10} (1 + \Delta \eta^*) = \sum_{k=1}^{7} \frac{a_k}{(v^*)^k} ,$$

which demonstrates the correct asymptotic behavior $\Delta \eta \rightarrow 0$ when moving to an ideal gas. The values of coefficients a_k , presented in Ref. [22], are chosen such that, in the region $1.5 \leq v^* \leq 2.5$, the results of calculations using both the updated and the initial correlation [21] coincide, the new correlation being applicable to describe both high-density states and gases in the supercritical region, with a continuous transition between the gas-like and liquid-like states. The authors of Ref. [22] called the updated form of the correlation between viscosity and density the extended hard sphere (EHS) correlation.

The effective values of v_0 for n-alkanes in [21, 22] are approximated by polynomials of $T^{1/2}$ and the chain length, while the values of roughness R_η are considered independent of temperature and are taken in the form of a quadratic polynomial of the chain length. Reference [23] proposes the values of parameters v_0 and R_η for alkyl benzenes and cycloalkanes. The presented correlations are intended for use in the temperature range from 110 to 400 K. The proposed values of parameters reproduce experimental data on the density dependence of viscosity in hydrocarbons in the pressure range to 75 MPa, with the mean absolute deviation within 5% and the maximum deviation less than 10%.

A similar model is considered in Ref. [24] for melted salts. In [24], instead of the effective volume v_0 of densely packed spheres, the salt volume v_s at the melting line was taken, which allowed using only one fitting parameter in the model, namely, the roughness coefficient R_η . The constructed correlation reproduces the viscosity values for a number of halogenides and nitrates of metals with a mean-root-square error less than 3%.

Mixing rules. In Refs [21, 22], simple rules of linear mixing of v_0 and R_η values for components with weights equal to molar fractions are proposed. Further, these rules, together with model [22], will be referred to as EHS. The mixing rules introduced in this way allow a high-accuracy prediction of the viscosity–density dependence, even for rather asymmetric mixtures, e.g., methane–n-decane [25].

The authors of [26] proposed another approach (1c-EHS) for mixtures of homologous compounds: the mean molecular mass and carbon chain length are calculated for the mixture and the parameters v_0 and R_η are then determined using the EHS formulas for one component. The proposed expressions for the effective molecular mass and chain length take into account that, for an accurate prediction of the viscosity, the effective chain length in an asymmetric mixture should be shifted towards the chain length of the heaviest component. This approach was checked in Ref. [26] for mixtures of n-alkanes with a chain length from 1 to 60 at pressures up to 500 MPa. For strongly asymmetric mixtures containing heavy hydrocarbons (e.g., $C_{10} + C_{22} + C_{60}$), the usual EHS mixing rules lead to an underestimation of viscosity by 30-40%. In 1c-EHS, thanks to the correction introduced in the mixing rules shifting the effective molecular mass towards the heaviest component, the viscosity of such mixtures is predicted more accurately.

Reference [23] extends the 1c-EHS method over the mixtures of substances of three classes: n-alkanes and cyclic and aromatic hydrocarbons, and also compared the 1c-EHS model with the original EHS version, in which the parameters v_0 and R_n for the mixture components are linearly mixed. The presented results demonstrate good agreement of the basic EHS model with experimental data in mixtures of 2-4 components, even in cases where the mixture components belong to different homologous series. The mean deviations from the experimental data are from < 1% to 12% for different mixtures, with the maximum deviation of 16.1% found in a mixture of cyclooctane, benzene, toluene, and ethylbenzene. Reference [27] checks the accuracy of models based on the reduction to the viscosity of the liquid of hard spheres for several synthetic multicomponent hydrocarbon mixtures with a large number of components. It is noted that,

for mixtures of n-alkanes, the EGS model reproduces viscosities within the experimental error; for mixtures with cyclic compounds, the prediction accuracy deteriorates, but remains within 20%.

Thus, the EHS model is a correlation model for pure substances (since it requires data on the viscosity to determine the parameters v_0 and R_η for the substance), but for mixtures it can be considered a predictive model, since the application of simple rules yields a rather accurate result for the dependence of the mixture viscosity on density.

A certain EHS drawback, inherent in all density-based correlations, is the need to have high-precision data on the liquid density. An uncertainty in the density values of 0.5-1% can lead to an uncertainty in viscosity of about 10% [23]. In practical applications, the dependence of viscosity on pressure and the equations of state used do not always ensure an acceptable accuracy of reproducing the viscosity.

2.6 Reduction to other model systems

Scaling relationships for reducing to other classical model systems, such as liquids with Morse or Lennard-Jones potentials, exist but are less elaborated than the models considered in Sections 2.3–2.5. Reference [28] considers a reduction to the viscosity of the Lennard-Jones system. To calculate the viscosity η_x , the formula

$$\eta_{\rm x}(\rho_{\rm x},T) = \eta_{0,{\rm x}}(T) + \Delta \eta^*(\rho^*,T^*) \, \frac{\sqrt{m_{\rm x} \varepsilon_{\rm x}}}{\sigma_{\rm x}^2} \tag{22}$$

is proposed, where ρ and T are the density (in particles per unit volume) and the temperature, $\eta_0(T)$ is the rarefied gas viscosity at temperature T, $m_x = M_x/N_A$ is the mass of a substance molecule, ε_x and σ_x are the effective parameters of the Lennard-Jones potential for the substance considered, $\rho^* = \rho \sigma_x^3/N_A$, $T^* = k_B T/\varepsilon_x$ are the reduced density and temperature, respectively, and $\Delta \eta^*(\rho^*, T^*)$ is the excess viscosity of the Lennard-Jones system with the unit parameters ε and σ .

The advantage of Eqn (22) is that, for nonpolar molecules with a near-spherical shape, it can be considered fully predictive, since the parameters of the Lennard-Jones potential are evaluated from the relations of thermodynamic similarity through the critical temperature and density:

$$\varepsilon_{\rm x} = \frac{k_{\rm B} T_{\rm c,x}}{1.2593} , \qquad (23)$$
$$\sigma_{\rm x} = \left(\frac{0.302 N_{\rm A}}{\rho_{\rm c,x}}\right)^{1/3} .$$

Evaluating the parameters ε_x and σ_x from the critical parameters of the substance yields an estimate of the Lennard-Jones liquid viscosity and an estimate of viscosity for lower hydrocarbons (methane, ethane, propane) [28] at temperatures from the triple point to $\sim 2T_{\rm c}$ and pressures from 0.1 to 100 MPa with a mean absolute deviation of less than 5%. The maximal deviation from experimental data amounts to 8.8% for methane, 11.3% for ethane, and 15.62% for propane. For heavier compounds, toluene and n-decane, it was found in [28] that the estimate of parameter σ_x through the critical density is insufficient to accurately reproduce the density in the liquid phase: for decane, the mean absolute deviation from the experimental data amounts to 37% and the maximum to 50.9% in the pressure range from 0.1 to 140 MPa. In this connection, for large molecules, it is proposed to consider σ_x to be a fitting parameter.

For mixtures, Ref. [28] proposes to use the model of quasisingle-component fluid, for which the parameters ε and σ are determined by the Lorentz–Berthelot rules. Such an approach for mixtures of light hydrocarbons yields nearly the same accuracy as for pure components. However, for asymmetric mixtures of methane + toluene with a molar fraction of methane from 0.25 to 0.95, an average absolute deviation of 19.2% and a maximum deviation of 36% from the experimental data were demonstrated [29].

Reference [30] considers the reduction to systems of Mietype potentials

$$U(r) = C\varepsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6 \right]$$

with the parameter n from 10 to 20 and of the exp-6 type

$$U(r) = \varepsilon \left[A \exp\left(-n\left(\frac{r}{\sigma} - 1\right)\right) - C\left(\frac{\sigma}{r}\right)^{6} \right]$$

with the parameter *n* from 12 to 22. For methane, ethane, argon, oxygen, and nitrogen, the parameters ε and σ are chosen for all potentials that minimize the error of viscosity reproduction for six states: a liquid, two states on the critical isotherm, and three supercritical states. For all values of *n*, the optimal parameters ensure the reproduction of viscosity through the reduction to the model system within 10–12% of the reference values. (By reference values, the values calculated using the formulas recommended by NIST are meant here.) An interesting result is that the minimum error in estimating the viscosity has been obtained for the classical Lennard-Jones potential with n = 12, although initially such a value of *n* was proposed exclusively for the convenience of calculations rather than based on theoretical considerations.

2.7 Correlation between transport coefficients and excess entropy

With the progress in atomistic modeling, it was found in model systems that the dependence of a number of liquid properties on the state parameters could be reduced to a unique dependence on a single parameter, the excess entropy. Rosenfeld [31] studied the behavior of the viscosity and self-diffusion coefficients in systems of hard spheres, soft spheres with the potential $U(r) \sim r^{-12}$, the Lennard-Jones system, and model single-component plasma. It was shown that, in these systems, upon the appropriate choice of scaling factors for the transport coefficients, the dependences $\ln D^*(s^*)$ and $\ln \eta^*(s^*)$ (where $s^* = S_{res}/(Nk_B)$ is the excess entropy reduced to the dimensionless form) can be presented by straight lines, i.e., the relation $D^* = A \exp(-\beta s^*)$ holds.

Later, the simple scaling proposed by Rosenfeld in the form $D^* = A_D \exp(-\beta_D s^*)$, $\eta^* = A_\eta \exp(\beta_\eta s^*)$ was refined in more complex models. Dzugutov [32] proposed a predictive model

$$D^* = 0.049 \exp(S_2),$$
 (24)

where S_2 is the contribution to the entropy from pair interaction, determined from the radial function of pair distribution g(r) by the expression

$$S_2 = -2\pi\rho \int_0^\infty \left[g(r) \ln g(r) - \left(g(r) - 1 \right) \right] r^2 \,\mathrm{d}r \,. \tag{25}$$

Since in many liquids the diffusion and viscosity coefficients are related by the Stokes-Einstein expression $D = k_{\rm B}T/(6\pi\eta r_{\rm eff})$, the Dzugutov relation can also be used to estimate viscosity.

Reference [33] shows that, for many organic compounds, the dependence $\ln \eta^*(s^*)$ can be considered universal, but the linear approximation is too rough to apply in accurate predictive models. To construct a model that allows predicting the transport coefficients with an accuracy of 5–10%, a functional form is proposed taking the nonlinearity of $\ln \eta^*(s^*)$ into account. A cubic polynomial is chosen for a nonlinear function:

$$\ln \eta_x^* = A_x + B_x s^* + C_x s^{*2} + D_x s^{*3}, \qquad (26)$$

where the reduced viscosity η^* equals the ratio of the viscosity to the viscosity of a system of hard spheres in the Chapman-Enskog theory, $s^* = s_{res}/(k_B m_{gc,x})$ is the reduced entropy, and $m_{gc,x}$ is the number of segments in a molecule in the perturbed chain polar-statistical associating fluid theory (PCP–SAFT) model. The coefficients A_x , B_x , C_x , and D_x are determined through the contributions of the various functional groups of which the molecule consists. The choice of viscosity scaling coefficients based on the data for n-alkanes, from butane to nonane, allowed predicting the data for nalkanes with a chain length of 10-36 with the average absolute deviation from experimental data within 10%. Analogous results were obtained for amines, for which the optimization of parameters was performed based on the data on four compounds. In Ref. [33], the parameters for the contributions to the coefficients A_x , B_x , C_x were obtained for a total of 19 functional groups, including the hydroxyl groups of alcohols and carbonyl groups of aldehydes and ketones, as well as individual coefficients for methane, methanol, and water.

Thus, a model is proposed for predicting the viscosity in a wide class of organic compounds. Within this model, no difference between the positions of functional groups in isomers is taken into account, due to which the accuracy of predicting the viscosity of isomers can differ by a few times (Ref. [33] presents the data on a mean absolute deviation of 7.21% for 3-methylpentane and 29.81% for 2-methylpentane). Probably, the accuracy of the approach can be increased by taking into account thermodynamic parameters, such as the critical and triple point positions, in addition to the group contributions, in the expressions for the coefficients $A_x - D_x$ for Eqn (26).

In Ref. [34], the method of entropy scaling is checked for describing the viscosity coefficient of metals and alloys based on *ab initio* molecular dynamic calculations. The presence of a universal linear dependence of $\ln \eta^*$ on S_2 is demonstrated for Al, Cu, Ni, and Zn.

The theoretical substantiation of the universal entropy scaling is possible for some simple models. In a liquid with the potential of soft spheres $U(r) \sim r^{-n}$, the lines $\rho^{n/3}T = \text{const}$ correspond to a dynamic invariant in reduced units, i.e., the reduced excess entropy should also be constant along these lines [35]. On the other hand, the invariance of dynamics implies the constancy of the reduced transport coefficients as well.

Rosenfeld [31], who used the relationship between the reduced excess entropy and the density of packing in a liquid of soft spheres according the Carnahan–Starling equation [36], proposed another explanation for entropy scaling. From this relation, it follows that the density of packing is a singlevalued function of the excess entropy. The reduced transport coefficients for a system of hard spheres are universal functions of the packing density (see [19, 21]). Thus, the reduced excess entropy characterizes the effective packing density of a liquid in the approximation of hard spheres.

The validity of entropy scaling in real liquids can be interpreted as a consequence of the fact that the dynamics of particles in a condensed medium is mainly determined by the repulsive part of the interaction potential.

Substances are also known in which the universal entropy scaling of the transport coefficients is not confirmed [35, 37]. For the model systems in Ref. [38], the behavior of the selfdiffusion coefficient is thoroughly studied in liquids with potentials limited at $r \rightarrow 0$ and the potential having a repulsive shoulder. The dynamics of these systems is fundamentally different from the dynamics of the liquid of hard spheres and for them the abnormal behavior of transport coefficients is known. It is shown that the universal entropy scaling for such systems holds in the limit of high temperatures; however, abnormalities in the diffusion coefficient correspond to different values of the reduced entropy at different temperatures. Entropy scaling is impossible in substances possessing a region of negative thermal expansion, such as water, in the zone of abnormal properties $(\partial s_{\rm res}/\partial \rho)_T > 0$ [39]. However, even in this case, the nonmonotonicity of the dependence of the excess entropy on density is quantitatively reflected in the nonmonotonicity of the density dependence of transport coefficients in the above region. At temperatures above the abnormality temperature, the entropy scaling of the transport coefficients can be applied to water, too.

The presence of universal scaling allows extrapolating data on the transport coefficients obtained at moderate temperatures and pressures to more extreme conditions. Thus, it becomes possible to estimate the viscosity at high temperatures or pressures based only on PVT data, without the necessity to attract experimental data on the viscosity in this region. The limitation is only the requirement of the state equation, for which the excess entropy can be calculated. From this point of view, the most convenient means are the equations of state, for which the dependence F(V, T) or G(P, T) is known in analytical form, where F and G are the Helmholtz and Gibbs free energies. For organic liquids and nonpolar gases, the widely used cubic equations of state [40-42] are reduced to such a form. In this form, the equations of state are initially formulated in the statistical association fluid theory (SAFT) [43-45], as are the fundamental multiconstant equations of state [46, 47]. For liquid metals, the equation of state based on the model of soft spheres has such a form [48].

Entropy scaling at high pressures. The approach based on entropy scaling seems promising for constructing predictive correlations of liquid viscosity at high pressures. Reference [49] shows that the entropy scaling with the nonlinear dependence $\ln \eta^*(S_{res}^*)$ proposed in [33] for hydrocarbons makes it possible to predict the viscosity with an accuracy of about 10–20% at pressures up to 350 MPa, which is much better than the accuracy of other predictive models, e.g., TRAPP. Two other methods discussed in Ref. [49] describing well the experimental data are considered correlation methods, i.e., the coefficients were chosen to ensure the best description of each substance, while the entropy scaling method was tested as predictive, i.e., no additional corrections to correlation [33] were introduced. Nevertheless, for long branched hydrocarbons and some aromatic compounds, the mean absolute error of the predicted viscosity exceeds 25%, which is also noted in Ref. [33]. References [50, 51] develop approaches of applying the entropy scaling method to liquid mixtures at high pressures. An interesting result of Ref. [50] is a decrease in the error of predicting the viscosity of mixtures with the growth of pressure, whereas in most correlation models, on the contrary, at higher pressures the agreement with experiment deteriorates.

There are also experimental confirmations of the universal scaling of the reduced viscosity with the reduced entropy at higher pressures. References [52–55] present experimental data on the viscosity of nitrogen, carbon dioxide, and argon at supercritical temperatures and pressures up to 10 GPa. It is shown that, for these substances, the linear dependence of the logarithm of the reduced viscosity on the reduced excess entropy is preserved, even at pressures of the order of 10 GPa.

In the review by Bell [56], experimental data on the viscosity of argon, methane, sulfur hexafluoride, carbon dioxide, methanol, water, and R-134a and R-125 freons are analyzed. For each of the substances, it is confirmed that the complex dependence of viscosity on temperature and pressure practically lies on the same curve in the reduced viscosityreduced excess entropy coordinates. However, the curves for different substances do not necessarily coincide. For argon and methane, the dependences are closest to the initial Rosenfeld correlation, since these liquids are close in their properties to the model Lennard-Jones fluid, for which it has been derived. For other compounds, except methanol and water, a practically linear dependence $\ln \eta^*(s^*)$ is demonstrated. For methanol and water, liquids to whose properties hydrogen bonds make a substantial contribution, the dependence strongly differs from linear, but can be presented as quasi-universal. It was shown that the approximation of quasi-universal dependence $\ln \eta^*(s^*)$ describes the viscosity of six non-associated liquids with an error of less than 10% and the viscosity of water and methanol with an error of less than 40% at $s^* < -0.5$ in the entire range of pressures for which the analysis was performed.

2.8 Friction theory (f-theory)

One of the new approaches is the friction theory or f-theory [57], in which the viscosity is associated with the friction between the adjacent layers of the liquid. The friction force between two layers with thickness δh is considered a function of the normal interaction force and the relative velocity:

$$F_{\tau} = f(F_{\rm n}, v) \,. \tag{27}$$

Since the friction and normal interaction forces are expressed as $F_{\tau} = A\tau$ and $F_{n} = A\sigma$, respectively, where A is the area of layers gliding with respect to each other, and τ and σ are the shear and normal stresses, it is possible to write

$$\tau = f(\sigma, v) \,. \tag{28}$$

According to the f-theory, viscosity consists of the contribution of an ideal gas and the contribution of interparticle interaction. In turn, the interaction includes components of attraction and repulsion. In the presence of a velocity gradient, one can distinguish in the shear stress the ideal gas contribution τ_0 and the contributions of interparticle attrac-

tion τ_a and repulsion τ_r . Since f-theory is based on the hypothesis that attractive and repulsive forces are independent of each other, one can establish a one-to-one correspondence between τ_a and σ_a , as well as between τ_r and σ_r :

$$\tau = \tau_0 + \tau_a(\sigma_a) + \tau_r(\sigma_r) \,. \tag{29}$$

Since the Newton formula relates the shear stress and the shear velocity as $\tau = \eta \, du/dh$, the dependence of viscosity on pressure can be presented as

$$\eta = \eta_0 + \frac{\tau_a(\sigma_a) + \tau_r(\sigma_r)}{du/dh} \,. \tag{30}$$

In the linear f-theory, it is assumed that

$$\frac{\tau_{\rm a}}{{\rm d}u/{\rm d}h} = \kappa_{\rm a} , \qquad \frac{\tau_{\rm r}}{{\rm d}u/{\rm d}h} = \kappa_{\rm r} ,$$

and the values of κ_a and κ_r depend on temperature but not on the shear velocity. Then, the part of viscosity related to intermolecular interaction is expressed as

$$\Delta \eta = \kappa_a \sigma_a + \kappa_r \sigma_r \,. \tag{31}$$

However, in the high-pressure limit, the linear model must yield the dependence $\eta \approx \kappa_r \sigma$, since in a compressed liquid the pressure is mainly determined by the repulsive forces. In real liquids, the viscosity increases with growing pressure faster than linearly; therefore, at least in the function $\tau_r(\sigma_r)$, nonlinear terms should be taken into account. References [57–60] consider only the quadratic approximation:

$$\Delta \eta = \kappa_{\rm a} \sigma_{\rm a} + \kappa_{\rm aa} \sigma_{\rm a}^2 + \kappa_{\rm r} \sigma_{\rm r} + \kappa_{\rm rr} \sigma_{\rm r}^2 \,. \tag{32}$$

In Ref. [58], the model is parameterized for pure hydrocarbons with cubic equations of state [40, 41]. For these equations of state, it is possible to cope with the linear approximation with respect to the attraction forces and the quadratic approximation with respect to the repulsion forces. Correlations are also proposed for the coefficients of f-theory with the multiparametric simplified boiling water reactor (SBWR) equation of state [59] and the equations of state belonging to the perturbed chain SAFT (PC-SAFT) class [60]. Since the representation of attraction and repulsion forces in these equations of state differs from that in cubic equations of state, it is required that the quadratic approximation be introduced for both the attraction and the repulsion forces.

A limitation of the f-theory is the impossibility of transferring the introduced coefficients between the equations of state. In addition, underestimation should probably be expected in the prediction of viscosity at high pressures, since the quadratic f-theory (32) in the limit yields the dependence $\eta \sim P^2$, and the empirical viscosity of liquids depends on pressure rather as $\ln \eta \sim P$ [61, 62]. The problem of fluid viscosity underestimation at high pressures in the f-theory quadratic approximation was noted in the analysis in [49], where the f-theory is considered a correlation model, and the coefficients are chosen for several hydrocarbons in order to best describe the experimental data array. At the same time, in spite of not very high mean absolute deviation (7%), an increase in the systematic error with the growth of temperature and pressure is noted. For most substances, the functional forms of correlation proposed in Ref. [57] can be considered reliable only at pressures below 100 MPa.

2.9 Free volume theory

The idea that viscosity is determined by the free volume fraction in a liquid developed in the theory of free volume. It is assumed that the excess viscosity of a liquid is expressed as

$$\Delta \eta = A \exp \frac{B}{f_{\rm v}},\tag{33}$$

where f_v is the free volume fraction, and A and B are certain parameters, possibly depending on temperature.

According to the theory of [63], the free volume $v_{\rm f}$ is determined by the interaction of a molecule with a quasihomogeneous medium and is expressed as $v_{\rm f} = (4k_{\rm B}T/k_{\rm a})^{3/2}$ according to the fluctuation–dissipation theorem. Assuming that the medium hardness $k_{\rm a}$ is related to the energy *E* of interaction of the molecule with neighbors as $k_{\rm a} \propto E/v^{2/3}$ (where *v* is the volume per molecule),

$$f_{\rm v} = \frac{v_{\rm f}}{v} \propto \left(\frac{RT}{E}\right)^{3/2}.$$
(34)

The value of $E = E_0 + Pv$ is taken as the interaction energy, where E_0 is the diffusion activation energy, and Pv is considered the energy necessary to form a free volume in a liquid for molecule diffusion.

The ultimate expression for the viscosity takes the form

$$\Delta \eta = \frac{\rho l \left(\alpha \rho + PM/\rho\right)}{\sqrt{3RTM}} \exp\left[B\left(\frac{\alpha \rho + PM/\rho}{RT}\right)^{3/2}\right].$$
 (35)

Therefore, the viscosity dependence on thermodynamic parameters for each substance is determined by three adjustable parameters, l, α , and B. Parameter α characterizes the dependence of the diffusion activation energy on the density, l is the characteristic length scale, and B is the overlap degree of free volumes of different molecules. Formula (35) can be applied both for direct approximation of experimental data [63] and together with the equations of state [64–66]. In Refs [64, 66], correlations of parameters l, α , and B with the molecular mass of a substance are proposed for the family of n-alkanes. Therefore, for n-alkanes, the theory of free volume can be considered a predictive model.

Reference [66] analyzes the applicability of the free volume theory to hydrocarbons, ionic liquids, phthalates, haloid substituted hydrocarbons, and liquid mixtures of substances belonging either to one class or to different classes. The presented results testify to the best prediction of the viscosity of mixtures when using the following mixing rules for the parameters of the free volume theory:

$$\alpha_{\text{mix}} = \sum_{i} x_{i} \alpha_{i} ,$$

$$l_{\text{mix}} = \sum_{i} x_{i} l_{i} ,$$

$$B_{\text{mix}}^{-1} = \sum_{i} x_{i} B_{i}^{-1} .$$
(36)

The free volume theory is noted to yield satisfactory viscosity predictions for mixtures of n-alkanes; however, as to mixtures of substances belonging to different families (n-alkanes and aromatic compounds, n-alkanes and branched hydrocarbons, etc.), the accuracy of predicting viscosity is unstable.

2.10 Expanded fluid model

The expanded fluid (EF) correlation model proposed in Ref. [67] develops the ideas of Batchinski [1] and Hildebrand [4, 68] about the dependence of liquid fluidity on free volume. The functional form of this dependence, in contrast to that in the free volume theory [63], is considered exclusively to be a correlation, without theoretical substantiation. The viscosity of liquids and gases is described in a unique way:

$$\eta = \eta_0 + \Delta \eta(\rho, P), \qquad (37)$$

where $\eta_0(T)$ is the viscosity of a rarefied gas at the given temperature, and the excess viscosity $\Delta \eta(\rho, P)$ is proposed to be expressed as

$$\Delta \eta = c_1 \left[\exp\left(c_2 \beta\right) - 1 \right],$$

$$\beta = \left\{ \exp\left[\left(\frac{\rho_s^*}{\rho} \right)^n - 1 \right] - 1 \right\}^{-1},$$
(38)

where ρ is the liquid density, and ρ_s^* is the pressure-dependent compressed state density, $\rho_s^* = \rho_s^0 \exp(c_3 P)$. Due to the sharp dependence $\rho_s^*(P)$, the authors of Ref. [63] recommend not to use the EF model at pressures above 10 MPa. Indeed, at a constant coefficient c_3 , at high pressures, the 'compressed' state has a compressibility higher than the fluid as such with the additional free volume, which makes no physical sense.

For a complete description of the dependence of viscosity on density and pressure in the expanded fluid model, it is necessary to specify the parameters c_1 , c_2 , c_3 , the exponent n, and the density of the compressed state at normal pressure ρ_8^0 .

In Ref. [69], the described approach has been completed by the mixing rules for the coefficients c_1 , c_2 , c_3 in multicomponent systems, based on the mass fractions of the components, whereas, in most other models, the mixing rules are based on molar fractions. The use of mass fractions in the mixing rules allows applying them to mixtures whose components themselves are mixtures with not exactly known compositions and molar masses. Such a situation often arises in the analysis of natural and technical liquid mixtures.

The expanded fluid model was further developed by Polishuk [66, 70, 71] to be applied with the state equations of the SAFT family [44, 45]. Reference [70] introduces the extended form of the correlation. In particular, in the improved modified Yarranton–Satyro (MYS) model, the 'compressibility' of the liquid dense state is not constant, but is related to the compressibility of the liquid. In Ref. [71], within the critical point-based revision of PC-SAFT (CP-PC-SAFT), parameters c_2 and ρ_s^* are related to the equation of state parameters, namely, the effective chain length, and the width and depth of the potential well for monomers. In the final version of correlation [66], the following relation is introduced:

$$c_{2} = \gamma_{1}\sqrt{m} + \ln\left(1 + \frac{M^{4}}{\gamma_{2}v^{4}m^{3}}\right) \ln\frac{T}{T_{\text{tr}} + 120},$$

$$\frac{1}{v_{s}^{*}} = 1.04 \exp\left(\frac{\gamma_{3}P}{\varepsilon/k_{\text{B}}\sqrt{-(\partial P/\partial v)_{T}\sqrt{mv}}}\right) (N_{\text{A}}m\sigma^{*3})^{-1},$$
(39)

where $v_s^* = M/\rho_s^*$ is the molar volume corresponding to the density of the extremely compressed state in the EF model, *m*, ε , and σ are the number of segments and the segment parameters in the CP-PC-SAFT model, T_{tr} is the triple point temperature of the substance [K], *v* is the molar volume [l mol⁻¹], *T* is the temperature [K], *P* is the pressure [atm],

and M is the molar mass of the substance [g mol⁻¹]. The viscosity is calculated as

$$\eta = 0.1 \left\{ \exp\left[\frac{c_{2,\text{MYS}}}{\exp\left(v/v_{s,\text{MYS}}^*\right) - 1}\right] - 1 \right\} \text{ [mPa s]}.$$
(40)

For hydrocarbons, Ref. [71] proposes universal values of the constants: $\gamma_1 = 0.27$, $\gamma_2 = 2.5 \times 10^{11}$, $\gamma_3 = 2.1$. Parameters *m*, ϵ , and σ for the CP-PC-SAFT equation of state, in turn, are obtained by solving a system of equations, for which only the parameters of the critical and triple points of the substance should be known [45]. The CP-PC-SAFT+MYS model with the fixed coefficients $\gamma_1 - \gamma_3$, is, therefore, predictive, since it does not require data on the viscosity at some point.

The MYS model with the PC-SAFT+cubic equation of state was compared to the free volume theory in a number of pure substances and mixtures [66]. It was demonstrated that, although the free volume theory in many cases yields more accurate results, the maximum deviations from the known experimental data are smaller in the MYS model, because the result of the latter is more stable. In particular, a good predictive capability is shown for the MYS model applied to hydrocarbons and their mixtures, inert gases and nitrogen, carbon dioxide, acetone, and ionic liquids. In Ref. [72], the testing of the free volume theory, f-theory, and the MYS model was carried out for the viscosity of ionic liquids based on imidazole at pressures up to 1 kbar. It was demonstrated that, of these three models, MYS most accurately predicts the dependence of viscosity of ionic liquids on pressure and temperature, while the predictions of f-theory are the most inaccurate. In Ref. [73], the predictions of the CP-PC-SAFT + MYS model are compared with the recent experimental data for 1-iodoalkanes. Good agreement is obtained for iodoethane and 1-iodopropane. For the rest of the sequence of 1-iodoalkanes, agreement between the prediction and the experimental data is obtained with the fact taken into account that, as of the writing of this paper, the values of critical parameters for iodoalkanes were not known accurately enough and probably require correction.

3. Comparison of some models for hydrocarbon liquids

The properties of hydrocarbons in a wide range of states are important for optimizing their production, transportation, and application. In this connection, a large amount of experimental data has been obtained for hydrocarbons to construct and test correlation models.

Figure 1 presents the results of predicting the viscosity using various models and experimental data on the viscosity of n-pentane and n-decane at pressures up to 250 MPa. The results of the TRAPP model are seen to diverge from those of experiments at high pressures, the discrepancy beginning at lower pressures for a longer hydrocarbon (decane). This is probably due to the fact that the correlations of viscosity and density for methane are constructed using the data for $\rho/\rho_c < 3$ [7], while for decane, under the conditions presented in Fig. 1, $\rho/\rho_c \gtrsim 5$. The propane-based TRAPP model shows better results; however, a systematic underestimation of viscosity upon an increase in pressure is characteristic of it, too.

The best agreement with the experimental data for pentane and decane are shown by the expanded fluid model [67] and the EHS model [22]. In this case, the coefficients for



Figure 1. Calculated and experimental values of the viscosity of n-pentane and n-decane. Experimental data are taken from Refs [74, 75]. In the viscosity calculations, values of liquid densities from Refs [74, 75] are used.

the expanded fluid model were chosen individually for each substance, whereas for the model of a system of hard spheres a universal reduced viscosity function is used. At high pressures, both these models are extremely sensitive to the accuracy of density determination. For example, if the density of decane at a pressure of 230 MPa is underestimated by only 1%, the deviation from the experimental viscosity values is increased from 6% to 20% for the EHS model and from 8% to 30 % for the model of expanded fluid.

Figure 2 shows the results of predicting the viscosity within the same models for a mixture of octane and dodecane (moderately asymmetric mixture) and a mixture of methane and decane (asymmetric mixture). These examples demonstrate that, to predict the viscosity of hydrocarbon mixtures depending on the density, the reduction to a system of hard spheres shows much better results than in the remaining cases. The discrepancy between the predictions and the experiment for the methane-based TRAPP model reaches 20% at a pressure of about 90 MPa, and for the propane-based TRAPP model, at a pressure of 200 MPa. The EF model for these systems yields accurate (within 6%) predictions at pressures up to 250 MPa, but further it predicts an inflection in the viscosity-density dependence not observed in experiment. As noted in Section 2.10, such an inflection is due to the choice of the functional form for the density of the compressed state $\rho_s^* = \rho_s^0 \exp(c_3 P)$. As is seen from the example, due to this fact, the correlation possesses poor extrapolation capabilities, namely, if the coefficients have been chosen for the description at pressures up to 250 MPa, then beyond this range the correlation results may be incorrect, even at a qualitative level. For the methanedecane mixture, both modifications of the TRAPP method underestimate the viscosity values, and the EF model greatly overestimates them. This is explained by the fact that the mixing rules for methane-containing mixtures yield a small coefficient c_3 , and the effective density of the compressed state



Figure 2. Calculated and experimental values of the viscosity of binary mixtures 0.5n-C₈H₁₈ + 0.5n-C₁₂H₂₆ and 0.6n-CH₄ + 0.4n-C₁₀H₂₂. Experimental data are taken from Refs [76, 77]. Viscosity calculations use the values of liquid densities from these papers. Viscosity of the methane–decane mixture in the figure is increased 10-fold.

turns out to be overestimated. As is seen from Fig. 2, the EHS model predicts for both mixtures viscosities coinciding with the experimental values within 7%, in spite of using simple mixing rules and the absence of special coefficients of pair interaction.

4. Viscosity of metallic melts

Melts of metals, on the one hand, can be considered simple liquids, since they consist of individual atoms rather than molecules. On the other hand, in metals, especially in alloys, at temperatures close to the solidus temperature, the formation of associates is possible, which affect the transport properties. Experimental studies of the properties of liquid metals are also complicated by the necessity of hightemperature measurements, in connection with which the data on metals are fewer than for organic liquids. Thus, the accuracy of predictions using various models can be estimated only rather roughly.

The widely used model for metals is the Andrade theory predicting the following relation for liquid viscosity at the melting temperature:

$$\eta_{\rm m} = C_{\rm A} \, \frac{\sqrt{MT}}{v^{2/3}} \,, \tag{41}$$

where $\eta_{\rm m}$ is the metal viscosity at temperature T on the melting line, $C_{\rm A}$ is the empirically determined coefficient, M is the metal atomic mass, and v is the molar volume of the liquid phase.

Upon exceeding the melting temperature, for most metals and alloys, an Arrhenius-type equation is satisfactory [78]:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right),\tag{42}$$

where E_{η} is the viscous flow activation energy. It is known empirically that the activation energy is proportional to the melting temperature $T_{\rm m}$ of metals. Kaptay [79] proposed that the Andrade equation be combined with the Arrhenius dependence in the form

$$\eta = A \, \frac{\sqrt{MT}}{v^{2/3}} \exp\left(B \, \frac{T_{\rm m}}{T}\right),\tag{43}$$

where A and B are semiempirical coefficients. Kaptay has shown in [79] that a similar functional form can be obtained from Eqn (41) based on the free volume concept.

Based on 101 points for 15 'simple' metals, Kaptay obtained the values of the parameters $A = (1,80 \pm 0,39) \times 10^{-8} (J \text{ K}^{-1} \text{ mol}^{1/3})^{1/2}$, $B = 2.34 \pm 0.20$. Correlation (43) with these values of the parameters has been checked for 14 metals not used in the correlation, and, for nine of them, Eqn (43) reproduced the viscosity at the melting temperature with an accuracy within 20%. Large differences were observed for Hf, Mn, Pd, Pu, and V.

Based on the concept of viscous flow activation energy, Kaptay proposed an equation taking into account the enthalpy of mixing and the alloy composition:

$$\eta = \frac{hN_{\rm A}}{\sum_i x_i v_i + \Delta v^{\rm mix}} \times \exp\left(\frac{\sum_i x_i \Delta G_i^* - (0.155 \pm 0.015)\Delta H^{\rm mix}}{RT}\right), \quad (44)$$

where *h* is the Planck constant, Δv^{mix} and ΔH^{mix} are the volume excess and the mixing enthalpy, and ΔG_i^* is the viscous flow activation energy in pure components, expressed in terms of the viscosities of pure elements η_i as

$$\Delta G_i^* = RT \ln \frac{\eta_i v_i}{h N_{\rm A}} \,. \tag{45}$$

In Refs [80, 81], where various forms of correlations for binary alloys were tested, it was shown that Eqn (44) corresponds to the known experimental data with an accuracy of 20–30%. However, for nonideal alloys with a eutectic, this correlation incorrectly reproduces the qualitative behavior of the viscosity concentration dependence — the positions and in many cases even the presence of extrema are not reproduced. As is shown in Refs [81–83], many more correct qualitative results for the viscosity of alloys can be obtained from the Kozlov–Romanov–Petrov correlation [84]

$$\ln \eta = \sum_{i} x_i \eta_i - \frac{\Delta H^{\text{mix}}}{3RT} \,. \tag{46}$$

5. Viscosity of rarefied gases

In this section, we consider some approaches to calculating the viscosity of a rarefied gas, since it enters expressions for some of the correlations for liquids considered in Section 2. It should be noted that, for most liquids far from the critical point, the contribution to viscosity caused by the rarefied gas amounts to only a few percent, whereas the main contribution is due to interparticle interaction in a liquid. Therefore, in practice, it is sufficient to predict the value of the viscosity of a rarefied gas in order to apply in a liquid viscosity models with an accuracy of a few tens of percent. For high-viscosity liquids, the contribution of the rarefied gas viscosity is often less than 1%, i.e., it can be merely ignored.

5.1 Chapman–Enskog theory

In the Chapman–Enskog theory, the viscosity is found from the exact solution of the Boltzmann kinetic equation for a rarefied gas. For a system of hard elastic spheres with diameter d in this case, the result is the following (see, e.g., [85, Ch. 1.2]):

$$\eta = 1.016 \, \frac{5}{16d^2} \, \sqrt{\frac{mk_{\rm B}T}{\pi}}.\tag{47}$$

The dependence of real gas viscosity on the temperature, strictly speaking, differs from dependence (47). For a gas of particles interacting via the Lennard-Jones potential, the relation [86]

$$\eta = \frac{5/8f_{\eta}}{\sigma^2 \Omega^{(2,2)}(T^*)} \sqrt{\frac{mk_B T}{\pi}}$$
(48)

is obtained, where $\Omega^{(2,2)}(T^*)$ is the collision integral, $T^* = k_{\rm B}T/\varepsilon$, and f_{η} is a function weakly depending on temperature (it is practically always possible to assume that $f_{\eta} = 1$ [87]). The parameters σ and ε for the Lennard-Jones potential can be determined from the experimental values of gas viscosity at two temperatures. For function $\Omega^{(2,2)}(T^*)$, Hirschfelder, Curtiss, and Bird [86] published the tabulated values and proposed analytical approximations [88]. Parameters σ and ε for a number of gases can be found in the literature [85] or evaluated through the critical parameters of the substance using Eqns (23). For polyatomic molecules, corrections to Eqn (48) are proposed to allow for the asphericity parameter, dipole moment, and hydrogen bonds [89]:

$$\eta = \frac{5(1 - 0.2756\omega + 0.059035\mu^{*4} + \kappa)}{8\sigma^2 \Omega^{(2,2)}(T^*)} \sqrt{\frac{mk_{\rm B}T}{\pi}}, \quad (49)$$

where ω is the Pitzer acentric factor, $\mu^* = \mu/\sqrt{\epsilon\sigma^3}$ is the dipole moment reduced to a dimensionless form, and κ is the correction for molecular association for compounds forming hydrogen bonds (first of all, water and alcohols).

5.2 Gas mixture viscosity

To calculate the viscosity of a mixture of gases, it is common to use mixing formulas. The Wilke rule is widely used [90]:

$$\eta_{\rm mix} = \sum_{i=1}^{N} \frac{x_i \, \eta_i}{\sum_{j=1}^{N} x_j \, \varphi_{i,j}} \,, \tag{50}$$

where

$$\varphi_{i,j} = \frac{\left[1 + \sqrt{\eta_i \sqrt{M_j} / (\eta_j \sqrt{M_i})}\right]^2}{\left[8(1 + M_i / M_j)\right]^{1/2}}$$

and x_i and M_i are the molar fraction and molecular mass of the *i*th component of the mixture.

Other mixing rules are also possible [91]. For not too high temperatures (within 1000 K), different mixing rules yield close results. Therefore, in practice, instead of the Wilke rule, it is possible to take the simpler Herning–Zipperer mixing rule [92]

$$\eta_{\rm mix} = \frac{\sum_{i=1}^{N} x_i \eta_i \sqrt{M_i}}{\sum_{i=1}^{N} x_i \sqrt{M_i}} \,. \tag{51}$$

Reference [93] proposes the following mixing rule:

$$\eta_{\rm mix}^{-1} = \sum_{i,j=1}^{N} \frac{y_i y_j}{\sqrt{\eta_i \eta_j}} \left(\frac{2\sqrt{M_i M_j}}{M_i + M_j}\right)^{1/3},\tag{52}$$

where $y_i = x_i \sqrt{M_i} / \sum_{j=1}^{N} (x_j \sqrt{M_j})$ is the momentum fraction transferred by the *i*th component.

Equation (52) was tested for 40 pairs of nonpolar gases; a root-mean-square error from 0.11% (methane–ethane system) to 5.82% (neon–carbon dioxide system) was obtained, smaller than when using Eqns (50) and (51).

6. Atomistic modeling

As was mentioned in Sections 2–5, there are systems for which the description of transport coefficients by theoretical models faces difficulties. These are highly nonideal mixtures and alloys, liquids at high densities, and associating liquids (e.g., water and alcohols). The authors of this review are unaware of purely theoretical methods capable of satisfactorily predicting the transport coefficients in all the cases mentioned. Sometimes, it is possible to introduce an ad hoc correction for particular mixtures; however, a general theory should, apparently, take into account numerous factors related to the structure of liquid molecules and the details of interaction between particles, which determines the complexity of its creation.

As the most general approach, which automatically takes into account all the details of the interaction in a liquid, one can consider modeling by the method of molecular dynamics (MD), i.e., the numerical solution of the equations of motion of a system of atoms [94–96]. At present, due to the relatively high availability of computing resources, the role of MD modeling as a universal method of predicting a wide range of thermophysical properties of matter increases. The predictive ability of the MD method is largely determined by the choice of the interatomic interaction potential [97–102].

Methods for calculating viscosity in dense gases and liquids up to 10^3 MPa can be divided into two conceptually different classes: equilibrium methods, in which the simulated substance is not subjected to external perturbations, and nonequilibrium methods, in which the viscosity coefficient is obtained from the reaction of the substance to shear stress.

Section 6.1 presents a review of models for describing interactions in liquids in classical MD and Section 6.2 briefly discusses ab initio approaches. Section 6.3 thoroughly presents information on equilibrium methods, as well as examples of their applications. Nonequilibrium approaches are described in Section 6.4. The dependence of viscosity on shear velocity is considered in Section 6.5.

6.1 Interatomic interaction potentials

Interatomic interaction potentials for classical MD differ in form and complexity, depending on the substance under consideration. In this review, we consider several models of interparticle interaction. A detailed comparison of MD potentials in terms of their predictive ability is presented, e.g., in [97–100, 102].

6.1.1 Pair potentials. To model the properties of noble gases, liquids of nonpolar diatomic molecules (nitrogen, oxygen), and some substances with relatively simple quasispherical molecules (methane), spherically symmetric pair potentials of interaction are widely used, among which the most popular

are the Lennard-Jones and Buckingham potentials, respectively:

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$
(53)

$$U(r) = A \exp\left(-\frac{r}{r_0}\right) - \frac{C}{r^6}.$$
(54)

In the potentials (53), (54), the term $\sim 1/r^6$, responsible for the attraction, is determined by the dipole–dipole interaction ($\sim 1/r^3 1/r^3$), the form of repulsion in the Lennard-Jones potential is chosen for convenience (it is obtained by squaring the dipole–dipole part), and, in the Buckingham potential, it is chosen for general physical considerations.

Since information on the internal degrees of freedom and the energy and momentum exchange between them is lost when describing a molecule by a single unstructured particle, the effective pair potential parameters for molecular compounds, ensuring the best agreement of the model and real substance thermodynamic properties, usually lead to inaccurate predictions of transport coefficients. In this regard, the prediction of a liquid viscosity with an accuracy of 10-20% in a model with pair potential is possible only for liquids of small nonpolar molecules. Reference [103] shows that, when deriving the effective parameters ε and σ of the Lennard-Jones model from the critical temperature and pressure of a substance, the mean deviation from the experimental data in the liquid viscosity is less than 10% only for methane and oxygen. For heavier hydrocarbons, it reaches 30%, and even for noble gases, it amounts to about 20%. According to the data in Ref. [28], the predicted viscosity substantially declines from the experimental values at densities $\rho \gtrsim 0.7 \sigma^{-3}$. Apparently, at higher densities, the influence of the repulsive branch of the interaction potential is too strong, and in the Lennard-Jones potential just this branch poorly corresponds to repulsion in real substances. Also, with increasing density, the influence of the molecule nonsphericity and the transfer of not only momentum but also the angular momentum during collisions should increase. Due to these factors, at high densities, the viscosity predictions via the reduction to the Lennard-Jones system underestimate the real values of viscosity. As noted by Brazhkin in review [104], the Lennard-Jones model satisfactorily describes the viscosity of glycerol at near-critical temperatures and densities, but the use of the same parameters of a Lennard-Jones fluid ε and σ to estimate the viscosity at the triple point predicts a viscosity value a few orders of magnitude lower than the real one.

An important class of substances, to which it is possible to apply pair potentials, is melts of salts. For them, long-range electrostatic interactions are added to the short-range forces:

$$U_{ij}(r) = \frac{q_i \, q_j}{r} + U_{\text{SR}, \, ij}(r) \,, \tag{55}$$

where U_{ij} is the energy of interaction between atoms *i* and *j*, *r* is the distance between these atoms, q_i and q_j are the effective charges of the atoms, and $U_{\text{SR},ij}$ is the short-range part of the interaction.

In Ref. [105], using the MD method, the viscosity and heat conductivity are calculated for $NaF + AlF_3$ melts of various concentrations. The Buckingham potential is taken for shortrange interactions. The partial charges on atoms and the parameters of the Buckingham potential for atoms of different sorts were chosen based on quantum mechanical calculations of forces in a crystal system and did not rely on the experimental data on the transport coefficients. Good agreement is demonstrated between MD calculations and experimental dependences of the melt viscosity on the fraction of NaF at a temperature of 1305 K.

References [106, 107] study the viscosity of NaCl and KCl melts. Using in Eqn (55) the short-range potential in the form

$$U_{\text{SR},ij}(r) = A_{ij} \exp\left[B(r_{0,ij} - r)\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8}, \qquad (56)$$

agreement within 10–15% with the etalon NIST correlations is obtained for the viscosity of salt melts [108] in the range of temperatures of 1050–1300 K.

Models based on pair potentials seem to be applicable for estimating the viscosity of salt solutions and its qualitative behavior in a wide range of conditions. Judging by the available comparison with experimental data, models that are more sophisticated are required for accurate prediction of the viscosity of salts. At the same time, due to the high melting temperature of salts, there is much less experimental data on their viscosity than for substances liquid under normal conditions. Therefore, even estimates with an accuracy of up to an order of magnitude based on relatively simple MD models are valuable.

6.1.2 Potentials for modeling metals. The approximation of a pair potential independent of the external conditions is good for noble gases and some simple molecular compounds: nitrogen, oxygen, methane, in which van der Waals and electrostatic forces play the main role in the intermolecular interaction. Since the interatomic coupling in metals is implemented via common electrons and the interaction essentially depends on the electronic density, to model metals, effective density-dependent pair potentials (for a review of methods for constructing such potentials, see [109]) or multiparticle potentials, in which the metallic bond specific features are allowed for by multiparticle terms, are needed. The most popular ones are multiparticle potentials for metals and alloys within the framework of the embedded atom model (EAM) [110, 111] and its extensions.

For a number of metals, the viscosity is calculated based on the model of a density-dependent pair potential or the EAM model. For alkali metals lithium, sodium, and rubidium, good agreement is shown between the viscosity calculated by MD modeling with an effective pair potential and the experimental data on the viscosity [112-114]. For sodium and aluminum, good agreement of viscosity within the EAM models with the experimental data is also obtained [115, 116]. For some EAM models, in particular, for lithium [115] and nickel [117], the published results of MD modeling differ from the experimental ones by nearly two times. However, review [118] shows that different models of potential for one substance yield substantially different values of viscosity, and in Ref. [119] it is noted that the EAM potentials parameterized relying only on the crystal phase properties often describe the liquid phase with a large error. Therefore, the viscosity prediction is not a principle limitation of EAM. The prediction of transport coefficients in melts will be more accurate, when using potentials parameterized to reproduce thermodynamic and structural properties of the liquid [119] or based on so-called force matching to quantum mechanical calculations [120].

It is difficult to describe the concentration dependence of viscosity in melts, even when using the embedded atom



Figure 3. n-Triacontane molecule $(C_{30}H_{62})$ with examples of all intermolecular interactions. Covalent bonds are shown in red, angular ones in blue, torsion ones in green, Lennard-Jones and Coulomb ones in violet and black, respectively. 1, 4, 6 are the numbers of atoms, 1.0 and 0.5 are the scaling coefficients to calculate forces between the appropriate pairs of atoms. Partial charges on the hydrogen and carbon atoms are also presented.

potential; therefore, at present, more sophisticated models are under development based on quantum mechanical calculations and machine learning (see Section 6.2).

6.1.3 Molecular models ('force fields'). For molecular compounds, more detailed models are introduced that take into account the structure of molecules. The most advanced approach consists in specifying molecules with a fixed topology of valence bonds and separating the interactions into intra- and intermolecular. The intermolecular part describes the interactions among atoms in one molecule (Fig. 3):

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{improper}} + E_{\text{vdW}} + E_{\text{Coul}},$$
(57)

where E_{bond} , E_{angle} , E_{dihedral} , E_{improper} are the valence interactions (nearest neighbor coupling, angular, torsional), and E_{vdW} and E_{Coul} are the nonvalence interactions (van der Waals and Coulomb). The intermolecular part describing the forces that act between the atoms of different molecules consists of van der Waals and Coulomb forces. The Coulomb interaction is presented in the form $E_{\text{Coul}} = \sum_{i < j} q_i q_j / r_{ij}$, where q_i and q_j are the effective charges of atoms of ions, and r_{ij} is the distance between particles. Van der Waals forces in MD are considered to include short-range nonvalence interactions between both charged and uncharged atoms.

The most widespread models are those in which the effective charges of atoms are constant and coincide with their centers of mass, while the van der Waals interaction has the form of the Lennard-Jones potential (53). There are also other approaches to the description of Coulomb and van der Waals interactions of atoms in the system. In relatively recent paper [121], the necessity of using softer forms of repulsion to satisfy the equation of state of liquids at high pressures is demonstrated. In the widespread family of TIP4P models for water [122–124], the partial charge is shifted from the oxygen atom. For ionic compounds, core–shell-type potentials [125] are also used to describe polarizability.

The set of functional forms for the contributions E_{bond} , E_{angle} , E_{dihedral} , E_{improper} , E_{vdW} , and E_{Coul} , when describing a certain class of substances (usually a wide range of organic compounds) and the set of coefficients for particular types of atoms, valence bonds, functional groups, etc., is often referred to as the *force field* in the literature.

The form of equations characterizing intramolecular interactions determines the complexity of the model. Sections 6.1.4 and 6.1.5 contain a brief review of the main features of model potentials and two subclasses of these models. A thorough review can be found, for example, in Ref. [126] and references therein.

6.1.4 Class I models. Class I models include potentials in which the vibrational energy of bond lengths and bond angles is described by the potential of a harmonic oscillator

$$E_{\text{bond}} = \frac{1}{2} K_{\text{bond}} (r - r_{\text{eq}})^2 ,$$

$$E_{\text{angle}} = \frac{1}{2} K_{\text{angle}} (\theta - \theta_{\text{eq}})^2 ,$$
(58)

where r and θ are the current values of the bond length and valence angle, r_{eq} and θ_{eq} are the appropriate equilibrium values, and K_{bond} and K_{angle} are the energy constants. The torsion energy is usually considered in the form of variations in the Fourier series expansion. The Lennard-Jones potential most often describes nonvalence interactions.

Models of class I, in turn, can be divided into all-atom, united atom, and coarse-grained models.

The widely used all-atom models are Amber (also General Amber Force Field, GAFF) [127], CHARMM (Chemistry at HARvard using Molecular Mechanics) [128], and OPLS-AA (Optimized Potential for Liquid Simulations–All Atom) [129]. The first two potentials are mainly aimed at modeling biological molecules and, therefore, are optimized to reproduce the properties of macromolecules under conditions close to normal. The last potential was intended to model the properties of various organic liquids in a wide range of temperatures and thus is the most interesting from the point of view of predicting the viscosity under various conditions.

Soon after the presentation of the OPLS-AA potential, Allen carried out calculations of the etalon lubricant liquid [130]. In Ref. [131], with a potential similar to OPLS-AA but a different parameterization, the diffusion, viscosity, and heat conduction coefficient are calculated for ionic liquids. A detailed comparison of OPLS-AA with other models by predictive ability can be found in Ref. [97].

In 2012, a modification of the OPLS-AA potential for long-chain hydrocarbons (L-OPLS-AA) was proposed [132], which reproduces the properties of alkanes and alkenes with a chain length of five and more with higher accuracy than the original OPLS-AA model. In Ref. [133] of 2017, the possibility of abandoning similar particle charges for atoms of each type in the OPLS-AA was studied, using instead the CM1A technique to determine the partial charge for each atom in the molecule individually, based on quantum mechanical calculations. The use of the CM1A technique improves the density of liquid reproduction in the OPLS-AA model. A more accurate reproduction of the pressure dependence of density should also improve the prediction of density-sensitive properties of liquids, such as diffusion and viscosity coefficients.

In the united atom models (sometimes the term 'extended atoms' is also used), for the simplicity of calculations, functional groups are considered to be single particles. Usually, one or a few hydrogen atoms are joined to the heavy atom, to which they are attached, since the hydrogen atoms are the lightest and the R-H bonds have a maximum

frequency of vibration in a molecule. The vibration frequencies determine the acceptable time step in the MD method; therefore, uniting a hydrogen atom with other atoms not only reduces the number of particles but also allows modeling with a longer time step. One of the popular potentials in this class is the TraPPE-UA (Transferable Potential for Phase Equilibria–United Atom) model [134]. Although TraPPE-UA was developed for calculating mainly the phase equilibrium, it and its modifications are also being applied to calculate the transport coefficients for isomers of C_{30} hydrocarbons [135].

Many of the widely used united atom models predict an overestimated diffusion coefficient and underestimated coefficient of viscosity [136]. Although, as it seems from general considerations, the overestimation of mobility occurs due to 'smoothing' the molecular shape upon roughened consideration of interactions, the authors of [137] substantiate an alternative assumption. In the parameterization of most models, no transport properties are considered, and the attention is focused on the energy of conformations and thermodynamic properties: evaporation curves, thermal expansion coefficients, etc. These properties are rather insensitive to intramolecular interactions, whereas the transport coefficients are sensitive to the energy parameters of rotation about bonds [136]. Based on this observation, the authors of [137] proposed an optimized form of the rotation barrier in n-alkanes for the AUA4 potential [138], which does not really change the calculated thermodynamic properties, but considerably improves the prediction of transport properties: the deviation from experimental data on viscosity decreases from 30% with the initial AUA4 to 10-15% after the modification. In Ref. [139], such an optimized model applied to a synthetic petrol mixture demonstrated agreement with the experimental density and viscosity values.

6.1.5 Class II models. In contrast to models of class I, described in Section 6.1.4, class II models consider the anharmonicity of vibrations of valence bonds and angles. For example, the vibrational energy of a bond is presented in the form

$$E_{\text{bond}} = K_2 (r - r_{\text{eq}})^2 + K_3 (r - r_{\text{eq}})^3 + K_4 (r - r_{\text{eq}})^4$$
. (59)

In addition, in class II models, there is an exchange of energy between different degrees of freedom. For example, the bonds react to the angle change as follows:

$$E_{\text{bond-angle}} = M(r - r_{\text{eq}})(\theta - \theta_{\text{eq}}).$$
(60)

Considering the anharmonicity and cross terms allows a better description of molecular structure, conformation properties, vibrational spectra, and heat of formation than in class I models.

One of the class II models is that of condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [140]—the result of combining several potentials used in industry, which was carried out in 1998. One more difference from class I models is the representation of van der Waals forces by the 6–9 Mie potential

$$E_{\rm vdW} = \varepsilon \left[2 \left(\frac{\sigma}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma}{r_{ij}} \right)^6 \right].$$
(61)

The softer form of repulsion allows a realistic description of the behavior of liquids at high pressures. COMPASS has complex parameterization, since it takes more constants to specify all types of interaction than in class I models.

We use this potential to calculate equations of state and transport coefficients in alkanes [62, 141, 142], aromatic compounds [62, 142, 143], as well as binary mixtures of hydrocarbons [62].

6.2 Ab initio calculations

Under extreme conditions (superhigh temperatures, high compression ratios), classical approaches to the parameterization of interaction potentials go beyond the scope of their applicability. For example, the assumption of a fixed molecular composition and geometry of valence bonds is valid only in the limit of high (compared to $k_B T$) barriers for the occurrence of chemical reactions. A partial solution to this problem for modeling at high temperatures is given by the reaction potentials of interaction based on the empirical bond order [144]. However, this approach becomes inapplicable at high pressures, when the electrons of the inner shells begin to participate in the formation of a chemical bond.

The most general approach for MD modeling is to find the effective interaction potential based on quantum mechanical calculations (so-called ab initio calculations) and the dynamics of atoms in the Born-Oppenheimer approximation or combining the dynamics of electronic and nuclear motion within the framework of the Car-Parrinello approach [145] (ab initio molecular dynamics). At present, the most widespread approach is based on the theory of the electron density functional and the Kohn-Sham formalism [146]. Even approximate quantum mechanical calculations are much more complicated than calculations with effective interatomic potentials. Therefore, the inner electrons are usually replaced with an effective pseudopotential, and direct calculations are carried out only for the density of outer ('valence') electrons, the number of which can be chosen so as to be different, depending on the complexity of the model. In particular, modeling at superhigh pressures requires increasing the number of valence electrons, when the inner electron shells of atoms begin to overlap [147]. Even with these approximations, the complexity of ab initio modeling is 5-6 orders of magnitude higher than for modeling with empirical analytically expressed potentials; therefore, the size of modeled systems amounts to 100-1000 atoms.

In spite of the computational complexity of quantum mechanical calculations, there are examples of ab initio calculations of viscosity in the literature [148-151]. In such studies, the method of evaluating through diffusion is most frequently used (see Section 6.3.2), and the values of viscosity are restricted to an order of 1 mPa s due to the impossibility of going beyond the limit modeling time of a few tens of picoseconds. It is important that *ab initio* MD calculations are practically the only theoretical way to predict the anomalous behavior of the transfer coefficients in melts of compounds with covalent bonds, e.g., the change in the diffusion coefficient with pressure in liquid carbon during the liquid-liquid transition [152], or an increase in the diffusion coefficient and a decrease in viscosity coefficient with increasing pressure in boron oxide [153], arsenic sulfide [154], zinc chloride [155], and selenium during metallization [156].

Also noted should be the rapidly progressing field of developing potentials for single-component (nickel [157]) and multicomponent (Al-Cu-Ni melt [158], potential [159])

systems using deep learning methods (see, e.g., [160, 161]). According to complexity, calculations with such potentials are between those with classical potentials and *ab initio* calculations; however, they allow predicting the transport coefficients with an accuracy comparable to that of *ab initio* modeling.

6.3 Equilibrium methods of viscosity calculation

Equilibrium methods of viscosity calculation are based on the interrelation of the dimensional effect in the diffusion coefficient with the viscosity under periodic boundary conditions [162], the Stokes–Einstein formula, and the Green–Kubo [163, 164] and Einstein–Helfand [165] approaches. The advantage of these methods is that they allow obtaining the 'zero shear' viscosity, observed experimentally.

6.3.1 Dimensional effect for the self-diffusion coefficient. The Einstein–Smoluchowski (ES) formula relates the root-mean-square displacement of particles $\langle \Delta r^2 \rangle$ with time *t*:

$$\langle \Delta \mathbf{r}^2 \rangle(t) = 6Dt + \text{const}, \qquad (62)$$

where *D* is the self-diffusion coefficient, and the angular brackets mean averaging over both the time and the ensemble. Formula (62) is valid at consideration times deliberately greater than the characteristic travel times in a gas or liquid. Therefore, by calculating the time dependence of the mean-square displacement of molecular centers of mass in MD, it is possible to find the self-diffusion coefficient as $D = \langle \Delta \mathbf{r}^2 \rangle / (6t), t \to \infty$.

The presence of the dimensional effect for the diffusion coefficient is based on the presence of collective flows reported in the pioneering paper by Alder and Wainwright [166] for a system of hard spheres. Because of the finite size of the computational cell in the MD method, the collective flows are reproduced incorrectly (see, e.g., [167, 168]). For the periodic boundary conditions used in the MD, Yeh and Hummer theoretically derived a correction taking into account the finite cell size for the self-diffusion coefficient [162] of spherical particles and demonstrated the applicability of the formula for a liquid with the Lennard-Jones potential and water:

$$D_{\infty} = D_{\rm PBC}(L) + \frac{k_{\rm B}T\xi}{6\pi\eta L}, \qquad (63)$$

where D_{∞} and $D_{\text{PBC}}(L)$ are the self-diffusion coefficients in the thermodynamic limit and for the finite size L of a computation cell, respectively, η is the shear viscosity of the system, and ξ is a dimensionless constant approximately equal to 2.837297. System size correction for diffusion coefficients is used in Refs [98, 169–171].

The shear viscosity can be obtained from the linear slope coefficient in Eqn (63) by calculating the dependence of the self-diffusion coefficient $D_{PBC}(L)$ on the reciprocal cell size L[171]. Reference [172] demonstrates agreement between the values of the viscosity coefficient obtained using the dimension effect and by the Green–Kubo method for liquid water. The authors of Ref. [171] extended this method and analyzed the optimal cell dimension L and the number of statistically independent runs of MD trajectories for Lennard-Jones liquids, water, and the [Bmim][Tf₂N] ionic liquid. In recent paper [157], using this method, the temperature dependence



Figure 4. Example of a computation cell containing ~ 1300 molecules for the liquid n-pentane at a temperature of 330 K and density of 0.601 g cm⁻³. Carbon atoms are shown in blue, hydrogen atoms in red. Visualization was performed in the Visual Molecular Dynamics (VMD) software package [173].

of the viscosity coefficient of a nickel melt is calculated for a model trained on *ab initio* calculations.

For clarity, in this review we present the calculation of the viscosity coefficient of n-pentane by the considered method at a temperature of 330 K and density of 0.601 g cm⁻³. An example of the computation cell is shown in Fig. 4. Under the specified conditions, according to the experimental results [174], n-pentane is in a liquid state, which is also confirmed by MD modeling. The self-diffusion coefficient was calculated using the ES method (see Eqn (62)) with the OPLS-AA potential for 125, 512, 1300, and 35,000 molecules in a computation cell [129]. Figure 5 illustrates the dependence of self-diffusion coefficient $D_{PBC}(L)$ on the reciprocal finite size L of the system.

The shear viscosity of n-pentane is determined from the slope coefficient of dependence (63) to be equal to $(220 \pm 10) \times 10^{-3}$ cP (mPa s), the experimental value being 190×10^{-3} cP [174].

6.3.2 Stokes–Einstein formula. For the steady-state motion of a particle in a medium, the magnitude of the acting force is equal to the medium drag force. Assuming that the shape of the particles is close to spherical and the drag force is determined by viscous friction, we arrive at the Stokes–Einstein formula relating the coefficients of viscosity and diffusion

$$\eta = \frac{k_{\rm B}T}{6\pi Dr} \,. \tag{64}$$

If the diffusion coefficient is known, then by estimating the particle hydrodynamic radius we can get the viscosity coefficient. Since in practice the diffusion coefficient is simpler to calculate than the viscosity, Eqn (64) has been used in *ab initio* MD calculations to estimate the viscosity of $Al_{80}Cu_{20}$ melt [149], chalcogenide GeTe in a liquid state [150], and NaCl-CaCl₂ salt melt [151]. The characteristic values of viscosity in the mentioned papers are of the order of 1 mPa s (1 cP). In Ref. [175], the viscosity coefficient is evaluated from the diffusion of atoms in an iron crystal both using the *ab*



Figure 5. Dependence of the self-diffusion coefficient of liquid n-pentane on the reciprocal computational cell size 1/L at a temperature of 330 K and a density of 0.601 g cm⁻³.

initio MD and within the classical MD using the EAM potential. According to Ref. [176], in an Mg_2SiO_4 melt, the Stokes–Einstein formula is valid for magnesium atoms at pressures up to 35 GPa and temperatures of 2500–3000 K.

Gordon demonstrated in [177] the validity of the Stokes– Einstein relation for classical MD calculations of diffusion and viscosity coefficients in isoparaffins, from C₆ to C₁₆, at various temperatures and pressures up to 10,000 atm with the molecule nonsphericity taken into account by means of the radius of inertia of molecules. This approach sometimes allows performing MD calculations of the diffusion coefficient with lower computational costs, and then using them to determine the values of viscosity of a liquid. Such estimates are carried out in Ref. [178] for the liquid n-pentane.

In Ref. [142], the relation between the coefficients of diffusion D and viscosity η for model lubricant liquids (isooctane C_8H_{18} and 1,1-diphenyletane $C_{14}H_{14}$) at pressures up to 4 kbar is studied. The gyration radius is used as a molecule's characteristic size. Figure 6 presents the results of calculating D and $1/\eta$ with potentials of interatomic interaction possessing different degrees of detailing: TraPPE-UA, OPLS-AA, and COMPASS. The lower the points, the higher the pressure. A remarkable fact is that the results for isooctane lie on a universal curve corresponding to the Stokes-Einstein equation for all models. At higher pressures, the deviation from the Stokes-Einstein relation for isooctane in the COMPASS and OPLS-AA models is due to the heterogeneous nature of diffusion upon reaching a high viscosity [179]. The universal curve $D(1/\eta)$ for several force field models allows a more efficient estimation of the pressure dependence of viscosity in complex COMPASS-type force fields. Since the MD calculation of the diffusion coefficient is computationally cheaper than the viscosity calculation, such an approach ultimately reduces the cost of calculation for the curve of the viscosity dependence on pressure.

Recent paper [180] shows a correlation similar to (64) between viscosity and thermal conductivity for the Lennard-Jones and Coulomb potential models, hard spheres, and simple molecular liquids.



Figure 6. Dependence of diffusion coefficient *D* on the reciprocal viscosity $1/\eta$ for isooctane in TraPPE-UA, OPLS-AA, and COMPASS potentials, as well as for 1,1-diphenyletane. The lower the points in the plot, the higher the pressure.

6.3.3 Einstein–Helfand formula. In 1960, in the theoretical paper [165], Eugene Helfand derived analogs of the Einstein–Smoluchowski relation (62) for the expression of shear viscosity and heat conductivity coefficients as limit values of the time dependence slope of a square of some microscopic properties ('moments'). For the viscosity, the Helfand formula has the form

$$\eta = \lim_{N, V, t \to \infty} \frac{1}{2k_{\rm B}TVt} \left\langle \left[G^{(\eta)}(t) - G^{(\eta)}(0) \right]^2 \right\rangle,\tag{65}$$

where $G^{(\eta)}(t) = \sum_{a=1}^{N} p_{xa}(t) y_a(t)$ is the Helfand moment, and summation is performed over the appropriate projection of the coordinates and momenta of particles.

Subsequent studies provide evidence in favor of updating this approach for systems considered under periodic boundary conditions [181, 182]. To avoid an incorrect growth of the discrepancy (65) under periodic boundary conditions, the authors of [181] reasonably introduce additional terms in the expressions for $G^{(\eta)}(t)$, which ensures the convergence of the results obtained by the Einstein–Helfand and Green–Kubo methods for a Lennard-Jones liquid. However, the form of corrections is derived only for the case of pair potential of interparticle interaction, and, even in this case, the use of the Helfand formula turns out to be less practically convenient than the use of the Green–Kubo formula, which will be considered in Section 6.3.4.

6.3.4 Green–Kubo formula. The Green–Kubo (GK) formula for calculating shear viscosity $\eta_{\alpha\beta}$ in plane $\alpha\beta$ has the following form [163, 164]:

$$\eta_{\alpha\beta} = \lim_{t' \to \infty} \frac{V}{k_{\rm B}T} \int_0^{t'} C_{\sigma}(t) \,\mathrm{d}t \,, \tag{66}$$

where $C_{\sigma}(t) = \langle \sigma_{\alpha\beta}(0)\sigma_{\alpha\beta}(t) \rangle$ is the autocorrelation function of nondiagonal elements of the viscous stress tensor $\sigma_{\alpha\beta}$, and

V and *T* are the volume and temperature of the system. Practically, the integral in (66) is calculated to a certain temporal limit t', so that C_{σ} tends to zero with an accuracy to the computation error. The viscosity η of a homogeneous liquid is calculated as an average of η_{xy} , η_{xz} , and η_{yz} , since the three shear planes are equivalent.

In the case of atomic and simple molecular liquids, in the classical MD it is possible to reach the convergence of the GK integral within the computational error [172, 183–188]. Using the GK method, the authors of Ref. [148] managed to calculate the viscosity of a helium–hydrogen mixture for the Jupiter adiabat ($\eta \sim 1$ mPa s) even using the *ab initio* MD.

In the case of liquids with higher viscosity coefficients $(\eta > 10 \text{ mPa s})$, the convergence of integral (66) becomes a serious problem because of long-term correlations in the autocorrelation function $C_{\sigma}(t)$. Maginn's team [189, 190] proposed a method of temporal decomposition that allows extrapolating the integral at $t \to \infty$. The essence of the method is approximating the GK integral by a function of the form [191, 192]

$$\eta(t) = A\alpha\tau_1 \left[1 - \exp\left(-\frac{t}{\tau_1}\right) \right] + A(1-\alpha)\tau_2 \left[1 - \exp\left(-\frac{t}{\tau_2}\right) \right],$$
(67)

where A, α , τ_1 , and τ_2 are the approximation parameters. The values of the autocorrelator integral $C_{\sigma}(t)$ at long times are taken into account with the weight $1/\sigma^{0.5}$ during the procedure of choosing the approximation parameters (because of computing errors). An attempt to relate the approximation parameters τ_1 and τ_2 to the characteristic times of correlation decay in liquid n-alkanes was recently made by Kondratyuk in [193].

The authors of the method successfully use the temporal decomposition method to calculate the viscosity of ionic liquids [189, 194]. This approach is also used in other papers for n-alkanes [169], branched alkanes [141, 195, 196], aromatic compounds [62, 143], linear ethers [197], as well as binary mixtures of hydrocarbons [62].

A new method based on the probabilistic distributions of fluctuations for the Green–Kubo method is proposed in Refs [198, 199]. For a Lennard-Jones liquid, the possibility of calculating the transport coefficients along one MD trajectory is demonstrated.

We also present an example of viscosity calculation for npentane at a temperature of 330 K and density of 0.601 g cm⁻³ by the Green–Kubo method. For 30 statistically independent MD trajectories, calculated in a canonical ensemble, the autocorrelators of nondiagonal elements $\sigma_{\alpha\beta}$ were obtained. The Green–Kubo integrals were calculated for each data set and then averaged. The mean values of the Green–Kubo integral and their errors are shown in Fig. 7. Since the divergence of the integral is observed in the considered time window, there is no need to use function (67) for approximation. The ultimate viscosity value of $(220 \pm 10) \times 10^{-3}$ cP agrees with the value obtained from the dimension effect of the diffusion coefficient (see Section 6.3.1).

6.4 Nonequilibrium calculation methods

The family of nonequilibrium MD (NEMD) methods allows avoiding the convergence problems inherent in equilibrium methods in the case of viscous liquids. The setting of the computational problem is maximally close to the conditions



Figure 7. Dependence of the Green–Kubo integral (Eqn (66)) on the upper limit of integration for n-pentane at T = 330 K and $\rho = 0.601$ g cm⁻³. Black line corresponds to the final value.

of real experiments: the viscosity coefficient appears as a reaction of the substance to a shear stress. In the applied sense, in the MD the artificial creation of both a momentum flux (Müller-Plathe method) and a shear stress (SLLOD method) is possible.

6.4.1 Müller-Plathe method. In the Müller-Plathe implementation [200, 201], so-called reverse nonequilibrium molecular dynamics (RNEMD), a momentum flux is created in the computing cell. First, the cell is divided into a certain number of layers. The momentum flux is implemented through the exchange of velocities differing by directions between identical atoms in the bottom and the middle layers of the cell (Fig. 8). The magnitude of the momentum flux density is proportional to the velocity gradient $\partial v_x/\partial z$ with the shear viscosity coefficient

$$\eta = -\frac{j_z(p_x)}{\partial v_x / \partial z} \,, \tag{68}$$

where $j_z(p_x)$ is the density of the momentum *x*-component flux along the *z*-axis.

This method was applied in Ref. [141] to calculate the viscosity of isooctane and isononane in a wide range of pressures. The agreement of viscosities obtained at small shear velocities with the equilibrium values from the Green–Kubo method is also demonstrated (see Section 6.3.4).

For clarity, we present the results of the viscosity calculation using the Müller-Plathe method for the liquid n-pentane at T = 330 K and $\rho = 0.601$ g cm⁻³. The computation cell is divided into 50 layers in the z direction. Velocity exchanges between atoms of hydrogen of n-pentane molecules in layers 1 and 25 are executed every 10 fs, which creates an artificial flux of momentum along the z-axis. The velocities for exchange are chosen close to 100 m s⁻¹. Such a procedure creates a momentum flux density of the order of 10⁸ Pa.

Velocity profiles for various momentum flux densities are shown in Fig. 9. The viscosity is calculated as the ratio of the momentum flux density to the slope of the velocity profile.



Figure 8. Schematic diagram of Müller-Plathe calculation [200, 201]. Velocity exchanges are performed in the bottom and middle layer for identical particles.



Figure 9. Velocity profiles for the liquid n-pentane at T = 330 K and $\rho = 0.601$ g cm⁻³, produced along the *x*-axis at various values of the momentum flux density $j_z(p_x)$. Symbols show the mean values of velocity in layers. Trajectory length required for one dependence is 5 ns with an integration step of 1 fs.

The error in the viscosity, corresponding to the error in determining the profile slope, is not greater than 5%.

The values of viscosity coefficients depending on the created momentum flux density $j_z(p_x)$, as well as the corresponding values of velocity gradients $\partial v_x/\partial z$, are presented in the table. The presented data allow the conclusion that the

Table. Values of shear viscosity η obtained by the Müller-Plathe method for various values of the momentum flux density $j_z(p_x)$ in the computing cell.

$j_z(p_x), 10^8 \text{ Pa}$	$\partial v_x/\partial z$, 10^{12} s ⁻¹	η , 10^{-3} cP
4.36	2.13	205
10.60	5.25	202
21.75	11.5	189
33.0	18.9	174

viscosity tends to the value of 220×10^{-3} cP, which corresponds to the Newton flow.

6.4.2 SLLOD method. The shear stress in the MD method can be produced by adding special terms to the equations of particle motion. This method was called SLLOD [202]. Later, Tuckerman et al. proposed a modification of the approach called g-SLLOD [203], describing the process of stretching the liquid by introducing an additional term $-m_i \mathbf{r}_i \nabla \mathbf{u} \nabla \mathbf{u}$ in the equation for the particle momentum:

$$\dot{\mathbf{r}}_{i} = \frac{\mathbf{p}_{i}}{m_{i}} + \mathbf{r}_{i} \nabla \mathbf{u} ,$$

$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i}^{\phi} - \mathbf{p}_{i} \nabla \mathbf{u} - m_{i} \mathbf{r}_{i} \nabla \mathbf{u} \nabla \mathbf{u} ,$$
(69)

where \mathbf{F}_i^{ϕ} are the forces of interatomic interaction determined by the potential, and $\nabla \mathbf{u}$ is the flow velocity gradient. This algorithm requires a thermostat, since, due to the friction, heating of the system occurs. Daivis and Todd [204] have theoretically shown the equivalence of SLLOD and g-SLLOD methods.

The algorithm produces a Couette flow with the shear velocity $\dot{\gamma} = \partial u_x / \partial y$ in the calculation cell. By analogy with the Müller-Plathe method, the shear viscosity coefficient is found from the relation

$$\eta = -\frac{\langle \sigma_{xy} \rangle}{\dot{\gamma}} \,, \tag{70}$$

where $\langle \sigma_{xy} \rangle$ is the mean shear stress.

Review [205] from 2021 includes examples of using the SLLOD for calculating the viscosities of model lubricant liquids. Worth mentioning is the paper by McCabe et al. [206] from 2001, devoted to calculating the viscosity in 9-oxyheptadecane at high pressures using the nonequilibrium MD, which qualitatively described the experimental dependence of viscosity on pressure. In 2002, Bair et al. calculated the viscosity of the liquid squalane (C₃₀H₆₂) and compared the result with the experimental data. Robbins et al. have studied the flow regimes and the lubricate morphology under shear, and calculated the viscosity coefficients of squalane in a wide range of pressures [207, 208]. In the paper by Liu et al. [209], the viscosity coefficients are found using NEMD at shear velocities $\dot{\gamma} \approx 10^8 - 10^{10} \text{ s}^{-1}$, and then the viscosity coefficient is extrapolated to the region of experimental values $\dot{\gamma}$ using the Carreau model [210]. Worth noting is the recent study carried out together with British Petroleum, in which both experimental and theoretical investigations of squalane were performed at pressures up to 50 thousand atmospheres [211]. The viscosity was calculated by the SLLOD method, while the extrapolation of the values to the Newton domain was carried out.

6.5 Dependence of viscosity on shear velocity

As was mentions in Section 6.3.4, one of the problems of using the Green–Kubo formula is the convergence of integral (66). The problem is particularly urgent in molecular liquids due to the slow decay of correlations and the numerical 'noise' at the tails of autocorrelation functions in real calculations. In this regard, it seems attractive to use NEMD methods, which are in some sense more direct (the relationship between shear stress and shear velocity is directly studied) and usually converge faster. However, worth attention is the fact that the shear velocities in the NEMD can reach values of

Figure 10. Values of the viscosity coefficient for liquid n-pentane at T = 330 K and $\rho = 0.601$ g cm⁻³, obtained by the Müller-Plathe method at various shear velocities $\dot{\gamma}$. Highlighted in red is the viscosity obtained by the equilibrium Green–Kubo method.

 $10^9 - 10^{12}$ s⁻¹. At such velocities, the viscous friction regime is often non-Newtonian, i.e., the viscosity depends on the shear velocity (Fig. 10). For non-associated liquids, 'shear thinning' most often manifests itself, i.e., the viscosity decreases with a decrease in the shear velocity.

In the coupled mode theory (CMT), the dependence of viscosity η on shear velocity $\dot{\gamma}$ in the limit $\dot{\gamma} \rightarrow 0$ has the form

$$\eta = \eta_0 - A \dot{\gamma}^{1/2} \,. \tag{71}$$

Formula (71) has been widely used for extrapolating the dependence $\eta(\dot{\gamma})$ to zero in the early ages of nonequilibrium MD development [212, 213]. In [213], it was shown that the dependence of the form $\eta(\dot{\gamma}^{1/2})$ in a wide range of shear velocities looks like a combination of crossing straight lines rather than a single straight line, and the coefficient *A* of the linear approximation for low velocities is a few times greater than for high velocities. As a consequence, the extrapolation using Eqn (71) with the data at shear velocities above the crossover will overestimate the values of η_0 compared to the true value of the Newton viscosity. At present, the approximation using the Carreau model [210],

$$\eta = \eta_0 \left[1 + (A\dot{\gamma})^2 \right]^{-p}, \tag{72}$$

is considered more accurate. Equation (72) automatically predicts an increase in the shear thinning effect with an increase in the shear velocity. In Ref. [107], the extrapolation by the Carreau formula is directly compared with the CMT extrapolation and the conclusion of Ref. [213] that the CMT extrapolation overestimates the Newtonian viscosity is confirmed.

While the aim of MD modeling is to obtain the Newton viscosity, the use of nonequilibrium methods requires either modeling with small share velocities, at which the shear thinning effect is insignificant, or carrying out a series of calculations with different shear velocities and extrapolation. As shown by the practical experience of the authors of the present review, an accurate approximation of the dependence $\eta(\dot{\gamma})$ with the Carreau formula is possible only in the presence of several points in the region of small shear velocity (see our paper [141] and the dependences $\eta(\dot{\gamma})$ in Refs [107, 214, 215], used to carry out the approximation). The shear velocity can be considered small if the condition $\dot{\gamma} \sim \tau^{-1}$ is satisfied, where τ is determined by the maximum time of rotational relaxation in the studied liquid [216]. Chen et al. in the 2009 paper [217],



appropriately titled "Are pressure fluctuation-based equilibrium methods really worse than nonequilibrium methods for calculating viscosities?", show that, regarding computation expenses, the statistical set of MD trajectories sufficient to ensure GK integral convergence is nearly equal to that of nonequilibrium MD calculations to average the velocity profiles at low velocities and to extrapolate the function $\eta(\dot{\gamma})$. The experience of the authors of the present review confirms this conclusion. However, NEMD turns out to be an indispensable method if the purpose of modeling is to reveal the dependence of viscosity on shear rate. GK formulas are also inapplicable for calculating the viscosity of constrained liquids, since they are derived assuming the molecules of the liquid interact only with other molecules of the liquid. To introduce interaction with a wall, one has to apply other methods of viscosity calculations, using either the NEMD or self-diffusion coefficient scaling, in correspondence with the size of the calculation cell [218].

7. Predictive atomistic modeling

Below are examples of problems for which theoretical and empirical approaches do not allow accurate prediction of the viscosity of liquids in the range of $10^1 - 10^3$ mPa s, and atomistic modeling can be a full-fledged alternative to experiment. For the molecular liquids mentioned below, we are not aware of papers on the experimental studies of phase diagrams. Based on the measured viscosity coefficients, it is possible to conclude that the molecular liquids are in a liquid phase.

When compressing a liquid, on approaching the melting line, the viscosity can increase faster than exponentially with the growth of pressure (see, e.g., [219–221]). The nature of this phenomenon is related to the transition of the liquid to the supercooled state and further amorphization by pressure [179, 222]. The dependence of liquid viscosity on pressure $\eta(P)$ for these regimes is of practical significance, since the pressures produced in diesel engines upon fuel injection can reach 3 thousand atmospheres, and the pressure acting on the lubricant liquid in the transmission elements can be greater than 10 thousand atmospheres.

The experimental measurement of viscosity at such high pressures is a rather complex and labor-consuming process. Therefore, to assess the practical significance of molecular modeling, industry leaders in the USA (Army Research Lab, Dow Chemical, NIST, etc.) have for 20 years been conducting the Industrial Fluid Properties Simulation Challenge [223]. Within the competition, the possibility of predicting the properties of liquids using molecular modeling methods is evaluated. In 2018 and 2019, the competitions were aimed at predicting the shear viscosity of model lubricant liquids: isononane (2,2,4-trimethylhexane) (C_9H_{20}) and 1,1-diphenyl-ethane ($C_{14}H_{14}$). Of additional interest is the construction of interrelations between the microscopic structure of matter and the liquid properties [224] at high pressures.

Within the framework of the competitions of 2018 [141] and 2019 [143], the authors of the present review carried out shear viscosity calculations in the region of high pressures. As an interaction model, the COMPASS potential [140] was chosen. To verify the model for 2,2,4-trimethylhexane, both the equilibrium Green–Kubo method [163, 164] and the nonequilibrium Müller-Plathe method [200, 201] were used. For 1,1-diphenylethane, only the calculations using the equilibrium method were performed. Figure 11 presents the



Figure 11. Dependence of shear viscosity of 2,2,4-trimethylhexane (C_9H_{20}) and 1,1-diphenylethane $(C_{14}H_{14})$ on pressure at T = 298 and 311 K, respectively. Colored circles show the result of MD calculations; black squares show the experimental data.

results of predicting the viscosity by the MD method, as well as the experimental results [226] by S Bair published later.

The dependence $\eta(P)$ predicted in MD for 2,2,4-trimethylhexane (red circles in Fig. 11) agrees with Bair's experimental results (black circles) at pressures up to 5 thousand atmospheres and a temperature of 298 K. As the pressure increases, the MD results sink lower and lower compared to the experimental ones. This deviation of the calculated points from the experimental ones, in our opinion, is associated with insufficient sampling of the phase space of the system in the MD calculations. For 1,1-diphenylethane, the calculation technique was improved, which ensured agreement with experiment up to pressures of 2500 atm at high viscosities and qualitatively reproduced the transition to the superexponential regime in $\eta(P)$.

8. Conclusion

The analysis of theoretical models has shown that, at present, the theory of the viscosity in liquids is far from complete. Models based on thermodynamic similarity, ideally, allow predicting viscosity and other transport coefficients based only on the data on thermodynamics: the critical parameters, the evaporation curve shape, or, possibly, the parameters of the state equation. In the practically used models, the similarity method works well enough only within a homologous series. Such models are most advanced for the series of n-alkanes. However, applying such models even to substances from close families, e.g., to branched or cyclic hydrocarbons, yields predictions that strongly differ from the experimental data. This applies to both early models such as TRAPP [7] and newer models based on excess entropy scaling [49].

Among the thermodynamic similarity methods, the correlations between the viscosity and the excess entropy seem promising, because, using a small number of adjustable parameters that can be determined from the equation of state, it turns out to be possible to describe rather well the viscosity of a number of organic liquids at pressures up to 300 MPa. However, this scaling is not applicable to all substances;

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moreover, it seems to fail at high compression ratios or low temperatures due to association effects.

Theoretical models with empirically determined coefficients, such as the reduction to a system of hard spheres [21, 22] or the free volume theory [63], allow a more accurate description of the viscosity than do completely predictive models, due to the presence of free parameters, determined based on the experimental viscosity data. In this case, a theoretically substantiated functional form allows extrapolating the dependence to a wider domain of pressures and temperatures than used for the initial choice of parameters.

Finally, purely correlation models are the least substantiated theoretically, but can yield the most reliable results upon interpolation of experimental data. For some correlation models, a relation of adjustable parameters with the thermodynamics is also proposed [66, 71, 79], in which case the model becomes predictive.

Calculating the viscosity of liquid mixtures and alloys is a more complex problem. Simple mixing rules for the parameters of theoretical and correlation models for various substances yield satisfactory results in mixtures of substances close in structure, but for asymmetric mixtures the viscosity can be predicted with significant errors [25, 83].

The complexity of constructing and applying theoretical models for the viscosity consists in the extremely high sensitivity of viscosity to density. A difference in density of less than 1% in different equations of state can lead to a difference of 10% in viscosity values [26]. An accurate prediction of viscosity at high pressures requires either a general model of viscosity and a high-accuracy equation of state or the initial fitting of the correlation parameters to a particular equation of state. In the latter case, the chosen viscosity–density correlations may not appear to be transferable between different equations of state.

A reliable method of predicting the viscosity in liquids up to 1 Pa s, as well as a wide range of other properties, is modeling by the method of molecular dynamics, which requires substantial computation resources [227, 228]. The range of temperatures and pressures in which MD predictions can be considered reliable is determined by the choice of interaction potential for the substance. When using potentials that correctly describe the interaction features, the MD method reproduces the effects of association, such as the transition to a superexponential dependence of viscosity on pressure [62, 215]. For organic compounds, so-called force fields of class I and class II are widely used. The former are less costly computationally, but have a narrower field of application for a fixed set of parameters. Class II potentials can be used to predict the viscosity with an accuracy of the order of 10–20% at pressures of at least 0.5–1 GPa, as shown in Refs [62, 141, 143]. The advantage of the MD method is also the possibility of studying the dependence of viscosity on the shear stress, which is relevant for predicting friction in machinery.

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