AN ELEMENTARY DERIVATION OF THE COEFFICIENT OF DYNAMIC VISCOSITY BASED ON THE PRINCIPLES OF STATISTICAL MECHANICS

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ABSTRACT:
VISCOSITY IS A PHENOMENON WHICH IS OF GREAT IMPORTANCE TO THE THEORY OF FLUID MECHANICS AND KEY TO UNDERSTANDING MANY PHENOMENA IN NATURE. USING THE FORMALISM AND METHODS OF STATISTICAL MECHANICS, WE HAVE COMPLETED AN INTUITIVE DERIVATION OF VISCOUS SHEAR STRESS IN A FLUID BY CONSIDERING MOMENTUM TRANSPORT OF PARTICLES CONSTITUTING SAID FLUID AND OBTAINED AN EXPRESSION FOR DYNAMIC VISCOSITY WHICH DEPENDS ON PARTICLE PROPERTIES AND STATE VARIABLES. WE COMPARE THEORETICAL PREDICTIONS MADE BY THE MODEL WITH EXPERIMENTAL DATA.

KEY WORDS: VISCOSITY, INTERMOLECULAR FORCE, MEAN FREE PATH, PROBABILITY DENSITY FUNCTION

1. INTRODUCTION

A common method of understanding phenomena happening in complex systems is by considering the behavior of its individual constituents and then adding up their contributions into a whole which represents the system. With this mechanistic approach we can explain various properties pertaining to fluids, as well as numerous phenomena which show up in fluid dynamics, e.g. viscosity.

The purpose of this article is to analytically derive an expression for the coefficient of dynamic viscosity by utilizing the formalisms of classical and statistical mechanics. We derive said expression on the basis of a model, which predicts the exchange of linear momentum through binary particle collisions and takes into account all of the parameters which describe the properties associated with constituent particles.

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2. METHODOLOGY AND THEORETICAL ASPECTS

2.1. THEORY OF BINARY PARTICLE COLLISIONS

Particles, such as molecules, experience various forces, which arise as a consequence of particle interaction potential. Forces between molecules are either classical, i.e. electromagnetic, or quantum mechanical in origin. We can separate these interactions into long and short-range interactions. A comprehensive overview of the theory describing intermolecular forces can be found in ref.[3,4]. Because analytical expressions for inter-particle forces usually have quite complicated forms, we often use simpler mathematical models for the purposes of calculation, which can be a good enough approximation of analytical models and have a basis in reality. One such commonly used model is the Lennard-Jones model, which describes the potential energy field pertaining to a pair of atoms or molecules and takes the following form:

$$U = \varepsilon\left(\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6}\right). \qquad (1)$$

Here r represents the particle separation, ε the depth of the potential well and δ the distance of zero potential energy and is in essence equal to the diameter of a particle. This model combines the aspects of an attractive long range interaction, which becomes stronger as the particle separation decreases, and a highly repulsive short range interaction which is similar to a hard sphere model.

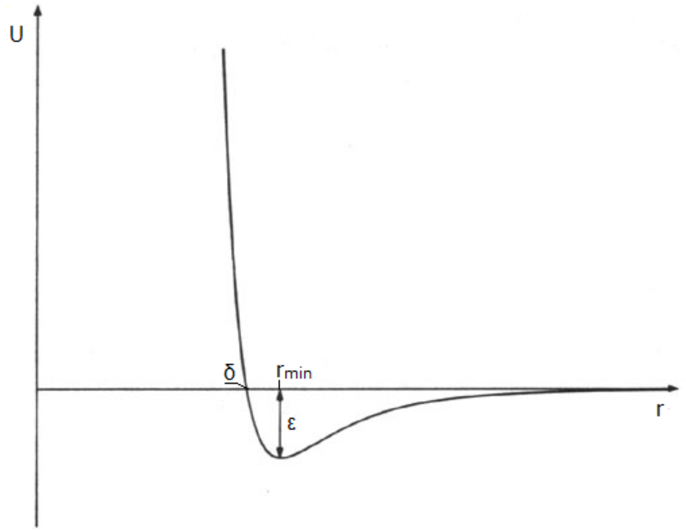

Fig. 1: Potential energy field of interparticle interaction according to the Lennard-Jones model.

Figure 1 displays a diagram which shows the potential energy of interaction as a function of particle separation according to the Lennard-Jones model. Parameter $r_{\min}$ denotes the

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[3] Stone, Anthony; The Theory of Intermolecular Forces, Second Edition. Oxford: Oxford University press, 2013.

[4] Buckingham, David; Utting, D.B.; Intermolecular forces, Annual Review of Physical Chemistry, no. 21 (1970), p. 287-316.

interparticle separation value where the interaction force due to potential energy of interaction is at its lowest value.

Forces between particles exert significant influence on various thermodynamic properties, such as the mean free path, which represents the average distance a particle travels between two separate collisions. The mean free path is equal to the following expression:

$$l_{mfp} = \frac{1}{\sqrt{2}\pi n d^2}, \tag{2}$$

where *d* is the particle collision diameter and *n* is the number density, defined as the number of particles per unit volume. The collision diameter is equal to the minimal lateral distance between the centers of pair particles, at which the two particles collide. A derivation of the expression above can be found in ref.[5].

For a non-interacting particle, such as a particle approximated with a hard sphere, its collision diameter is exactly the same to its actual diameter. However, in most physical cases, the collision diameter also depends on the particle interaction potential. For example, an attractive force between two particles will cause them to alter their trajectories and start approaching each other until they collide. We can expect the attractive force to exert more influence and cause collisions to be more likely if the two particles travel at lower velocities.

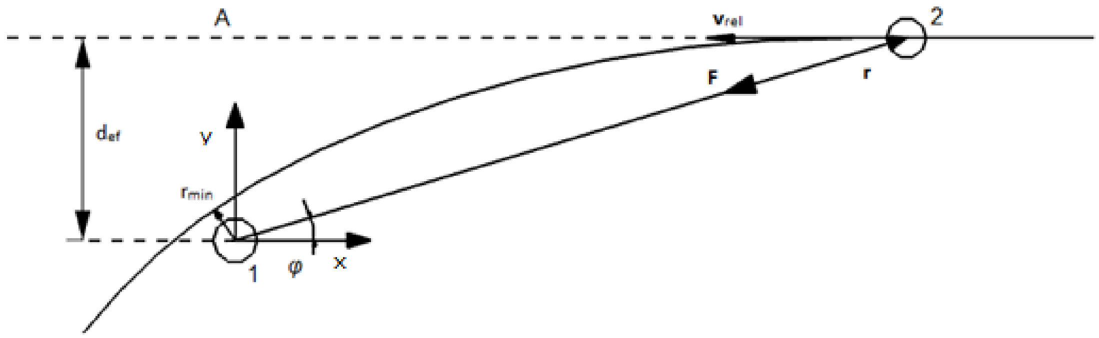

Fig. 2: Graphical representation of the effective collision diameter.

Figure 2 located above shows the motion of two particles in a plane, where the centre of the frame of reference is located at the centre of one of the particles, which means that the particle in question stands still for the purposes of this analysis. Furthermore, d_{ef} represents the effective collision diameter, $\mathbf{v}_{rel}$ represents the average relative velocity and r_{min} represents the distance of the closest approach (not to be confused with the distance defined in figure 1). The force acts on the particle in radial direction only, so we can describe the dynamics of one particle relative to another in polar coordinates with the following expression:

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[5] Serway, Raymond; Physics for Scientists and Engineers, Third Edition, Saunders College Publishing, 1990.

$$\boldsymbol{F}(\boldsymbol{r}) = m(\ddot{r} - r\dot{\varphi}^2)\boldsymbol{e_r}. \tag{3}$$

We then introduce an expression for angular momentum of particle 2 about particle 1, which takes the form $L = mr^2\dot{\varphi}$. The angular momentum of the particle is constant, because the force exerted on the particle has no tangential component and there is no torque exerted on the particle. For the purposes of the derivation we use an expression for specific angular momentum, i.e. angular momentum per unit mass: $\sigma = r^2\dot{\varphi}$.

To establish a link between relative velocity and effective collision diameter, we integrate the differential equation over the variable r, with the lower limit being equivalent to particle diameter d, as it is twice the particle radius, and the upper limit approach infinity. Since we simultaneously also integrate over velocity, with the lower limit being zero and upper limit being average relative velocity. In this manner, we arrive at the following expression:

$$\int_0^{v_{rel,a}} m\dot{r}d\dot{r} = \int_d^{\infty} \left(F(r) - \frac{\sigma^2}{r^3}\right) dr. \tag{4}$$

When we solve the integral, we make use of the fact that specific angular momentum is equivalent to the product of average relative velocity and the effective collision diameter: $\sigma = v_{rel,a} \cdot d_{ef}$. We understand the latter as the minimal lateral distance between a pair of particles, at which the two begin to move towards one another due to attractive forces. From this, it is possible to arrive at the following expression:

$$d_{ef} = d\sqrt{1 - \frac{2}{m{v_{rel,a}}^2}\int_d^{\infty} F(r)dr}. \tag{5}$$

A formal derivation of the expression above is given by ref.[6][7]. Interparticle force, which appears in the integral above, is equal to the gradient of Lennard-Jones potential, shown by equation 1. When solving the integral we leave out the first term of the interaction potential, since it represents the action of repulsive forces which contribute negligibly to the value of the integral for values of the integration parameter larger than d. It should be noted that parameter δ from the Lennard-Jones model is equivalent to the particle diameter d. Following on from that, we consider the average relative velocity of particles which is equal to: $v_{rel,a} = \sqrt{2}v_a$, where v_a represents the mean of the magnitude particles' velocity and is equal to:

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[6] Loeb, Leonard; The Kinetic Theory of Gases, Third edition. Mineola: Dover Publications, 1961, p. 221-224.

[7] Sutherland, William; The viscosity of gases and molecular forces, Philosophical magazine series 5, 36:223, p. 507-531.

$$v_a = \sqrt{\frac{8k_BT}{\pi m}}, \tag{6}$$

where k_B is the Boltzmann constant. We can subsequently introduce the expression for the effective diameter into the expression for the mean free path and obtain accordingly:

$$l_{mfp} = \frac{1}{\sqrt{2}\pi n d^2\left(1 + \frac{\pi m}{8k_BT}\right)}. \tag{7}$$

From the expression above, we can observe that the particle mean free path decreases at greater number densities, since this means that there are more neighbouring particles which it might collide with, and increases with greater temperature, since this means a particle has greater kinetic energy and is more likely to resist the attractive interparticle potential.

2.2. THEORETICAL TREATMENT OF MOMENTUM TRANSPORT

In order to obtain an expression for dynamic viscosity, we make certain assumptions. We form a model describing the behavior of gas at low enough pressure, so that we can treat the gas as being rarefied, and low enough temperature, so that collisions between constituent particles do not cause energy transfer into particles' rotational and vibrational degrees of freedom. We also assume that particles are isotropic, which means that its diameter and potential energy field remain constant in all directions. With that in mind, it should be stated that this model will give less accurate results at higher temperatures if we apply it to diatomic and polyatomic molecules. We also assume that intermolecular forces act on particles and affect their motion in space.

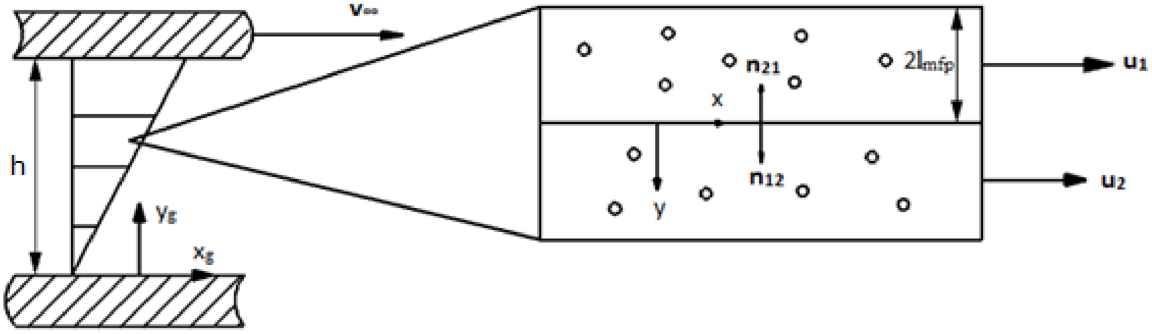

Fig. 3: Graphical representation of particle dynamics in a Couette flud flow.

Figure 3 shows the physical system on which we base our model. We can observe that it consists of a fixed lower and moving upper plate with fluid in between. It is noted that *x-y* is the local, while x_g-y_g is the absolute frame of reference. We assume that fluid is undergoing a two-dimensional Couette flow, which is caused by a force acting on the upper plate moving with velocity v_∞, therefore acting as the cause of shear stress. The image also describes motion of particles at the length scale of individual particles in a fluid flow. Comparing the motion of matter at different length scales, we can see that individual particles move about in a random way, while at larger scales fluid moves as a set of layers moving at a different velocities. We can write a generalized expression for particle velocity in the following way:

$$v_i = c_i - u_i, \tag{8}$$

where v_i is a velocity component as viewed from a stationary absolute frame of reference, c_i is a velocity component as seen by an observer moving together with the local reference frame and is probabilistic in its nature, while u_i is a component of the local reference frame velocity and accordingly a velocity component of the layer of fluid relative to the absolute reference system. It is assumed that individual fluid layers move only in the horizontal direction. Kinematics of fluid layers in this particular case can be described by this expression:

$$u_2 = u_1 - \frac{\partial u}{\partial y}\delta y, \tag{9}$$

with u_2 and u_1 being velocities of two different fluid layers, $\partial u/\partial y$ the velocity gradient with respect to vertical distance as shown in figure 3 and δy the thickness of each individual layer. We then propose that individual particles, which cross the interface between two distinct layers, eventually collide with a different particle in a way described in the previous section. Such collisions are of course elastic, as linear momentum and kinetic energy remain conserved in such a collision. These collisions represent an underlying mechanism causing the momentum flux between the two fluid layers, resulting in a force acting on the two fluid layers. This causes the shear stress experienced by the fluid. We then propose that each distinct layer of fluid has a thickness δy which is twice the size of particle mean free path l_{mfp} because we expect particles which transfer momentum between adjacent layers to originate from the centre of each such layer.

Following on from that, we can define as the ratio between the derivative of transferred momentum with respect to time and the surface area:

$$\tau_{yx} = \frac{F_{yx}}{A} = \frac{1}{A}\frac{d}{dt}\left(G_{12,yx} + G_{21,yx}\right). \tag{10}$$

In this expression, $G_{12,yx}$ and $G_{21,yx}$ represent macroscopic averages of particles' x axis components of linear momentum, transferred along the y axis from layer 1 to layer 2 and likewise from layer 2 to layer 1 due to binary collisions, with temporal derivative of the two representing a net macroscopic momentum flux. We can define a macroscopic value of a transferred property as a statistical average over all the possible values of that property that the constituent particles, which contribute to the transfer of that property, might carry. This is shown by the following expression:

$$\Psi = \int_{\partial c} \int_{t_1}^{t_2} dt \iint_A v_i \hat{n}_i \psi f(c_i)\, dA\, dt\, d^3 c_i. \tag{11}$$

In this equation, Ψ is the transferred property, $v_i\hat{n}_i$ represents the dot product of the particle velocity (as seen in an absolute frame of reference) and the unit normal, ψ is a property we can attribute to a particle (e.g. mass or momentum), $f(c_i)$ is the probability density function, dA is the surface differential and d^3c_i is the product of the velocity components' differentials over which we integrate. Since we are dealing with transport of momentum, variable ψ shall represent linear momentum carried by a particle. We can define it in the following way:

$$g_{12,i} = m_p v_{12,i} = m_p\left(c_{1,i} - u_{1,i}\right), \qquad g_{21,i} = m_p v_{21,i} = m_p\left(c_{1,i} - u_{1,i}\right). \tag{12}$$

Here, variable m_p denotes the mass of a single particle. The probability density function $f(c_i)$, which appears in equation 11, is a function of a continuous random variable which attributes a relative likelihood to each possible interval of values this random variable can have. In this case, it describes relative likelihood of particles having a velocity component in the range of some interval, or in other words, the fraction of the total number of particles whose velocity component is in this range. In our case, we can expect that particle velocity components in the y direction follow the single velocity component Maxwell – Boltzmann probability distribution, shown below:

$$f(v_i) = n\sqrt{\frac{m_p}{2\pi k_{\mathrm{B}}T}}\, e^{-\frac{m_p {v_i}^2}{2k_{\mathrm{B}}T}}\,. \tag{13}$$

In this expression, v_i represents a velocity component of a particle, m_p represents its mass, T represents the temperature and n the number density (number of particles per unit volume), while k_B stands for Boltzman's constant. A formal derivation of the Maxwell – Boltzmann distribution can be found in ref.[8].

An expression for macroscopic transfer of momentum is obtained by averaging horizontal components of particle momenta over the probability density function of the particle vertical velocity, since the horizontal momentum transferred over the boundary depends on particles' vertical velocity components. Combining eqs. 10, 11, 12 and 13 with respect to the local frame of reference, as seen in figure 3, and through proper definitions of quantities $v_{12,i}, v_{21,i}, \hat{n}_{12,i}$ and $\hat{n}_{21,i}$, we arrive at the following expression for shear stress:

$$\tau_{yx} = \rho\sqrt{\frac{m_{\mathrm{p}}}{2\pi k_{\mathrm{B}}T}}\left(\left(c_{1,x} - u_1\right)\int_0^{\infty} c_{1,y}\, e^{-\frac{m_p {c_{1,y}}^2}{2k_{\mathrm{B}}T}}\, dc_{y_1} - \left(c_{2,x} - u_2\right)\int_0^{-\infty} c_{2,y}\, e^{-\frac{m_p {c_{2,y}}^2}{2k_{\mathrm{B}}T}}\, dc_{y_2}\right), \tag{14}$$

with density ρ being the product of particle mass m_p and number density n. By solving the two integrals above, we obtain the following expression for shear stress:

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[8] Sethna, James; Statistical mechanics: Entropy, Order Parameters, and Complexity. Oxford: Clarendon press, 2011, p. 41-43.

$$\tau_{yx} = \rho\left(\left(c_{1,x} - u_1\right) - \left(c_{2,x} - u_2\right)\right)\sqrt{\frac{k_\mathrm{B}T}{2\pi m_\mathrm{p}}}. \tag{15}$$

Since probabilistic parts of horizontal velocity components $c_{1,x}$ and $c_{2,x}$ do not differ significantly between two adjacent layers, we can assume that the two are equal, which means that they in turn cancel out. We also take into account the fact that we conducted our derivation in a left-handed local reference frame, which means that the velocity gradient in equation 9 changes its sign when viewed from the global frame of reference, which is right-handed. The result of our derivation is the following expression for the coefficient of dynamic viscosity:

$$\mu = \frac{\sqrt{\frac{m_\mathrm{p}k_\mathrm{B}T}{\pi}}}{\pi d^2\left(1 + \frac{\pi\varepsilon}{8k_\mathrm{B}T}\right)}. \tag{16}$$

A more thorough and rigorous procedure of this derivation can be found in ref.[9].

3. RESULTS

We can compare predictions made by our theoretical model with experimental data for a diatomic gas, because we can expect diatomic molecules to behave somewhat similarly to isotropic particles. We compared our predictions with experimental data for molecular hydrogen H_2. Parameters in expression 16 therefore take on these values: $m_p = 3.35 \cdot 10^{-23}$ kg, $d = 292$ pm and $\varepsilon = 5.24628 \cdot 10^{-22}$ J. Data for Lennard-Jones model parameters is taken from ref.[10] 8. Boltzmann constant is equal to $k_B = 1.3806 \cdot 10^{-23}$ J/K.

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[9] Istenič, Enej; Deduction of the fluid dynamic viscosity coefficient based on statistical mechanics, B.Sc diss., University of Ljubljana, 2016. p. 28-33.

[10] Ahren, Jasper; Miller, James; Lennard-Jones parameters for combustion and chemical kinetics modeling from full-dimension intermolecular potentials, Combustion and flame 161, no. 1 (January 2014): p. 101-110.

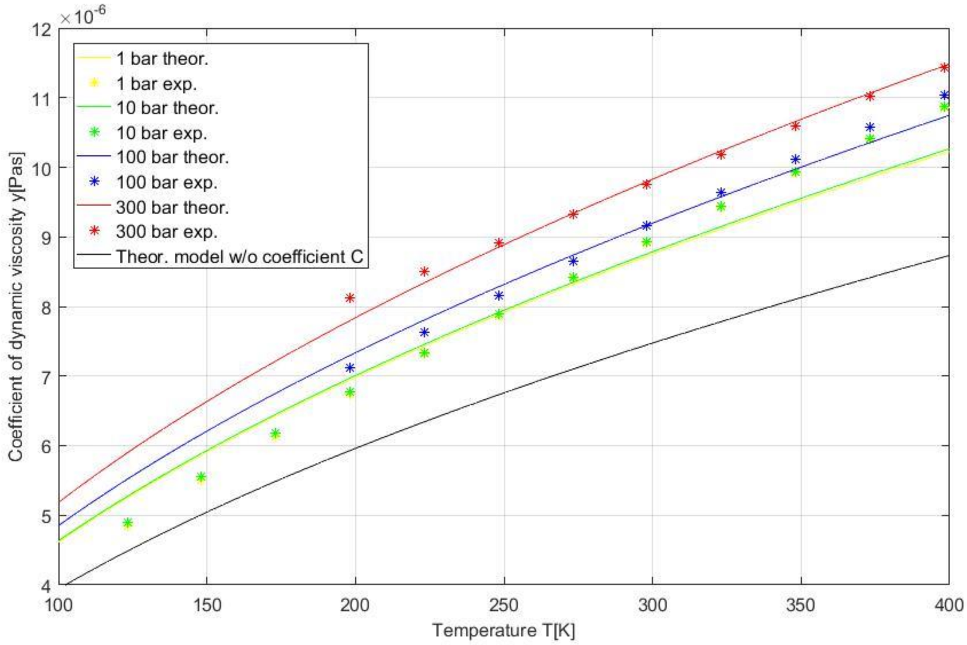

Fig. 4: Dynamic viscosity of molecular hydrogen H_2 as a function of temperature as predicted by eqs. 16 and 17 compared to experimental data.

Figure 4 shows how the coefficient of dynamic viscosity depends on temperature, as predicted by equation 16, and experimental results, adapted from ref.[11] 9. It is evident that the analytical model we developed does not quite match experimental data at hand, although it apparently manages to express the fact that the dynamic viscosity coefficient depends on an exponent of temperature, with the exponent being equal to 3/2. Experimental data shows that the dynamic viscosity coefficient is a function of pressure as well, since it appears to be greater at higher values of pressure. For that reason we multiply our model with a dimensionless coefficient *C*, which takes into account discrepancies between experimental data and our original model. We determined this coefficient *C* numerically with the method of least squares regression. The improved version of our model has the form:

$$\mu = \frac{C\sqrt{\frac{m_p k_B T}{\pi}}}{\pi d^2 \left(1 + \frac{\pi \varepsilon}{8 k_B T}\right)}. \tag{17}$$

Once again examining figure 4, we can see that coefficient *C* improves the accuracy of our prediction, although it does not entirely match the slope indicated by the experimental results. It can also be noted that dynamic viscosity increases with pressure. We postulate that this fact,

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[11] U.S. Department of Energy, Hydrogen analysis resource center; Hydrogen Viscosity at different temperatures and pressures. accessed August 1, 2016. http://hydrogen.pnl.gov/hydrogen-data/hydrogen-viscosity-different-temperatures\-and-pressures.

observed in figure 4, is caused by our assumptions about the fluid layer thickness and the way molecules interact. Firstly, we assumed that the thickness of a fluid layer is twice the size of the mean free path, which we had no justification for, although it is very certainly true that the layer thickness is of the order of the mean free path. Secondly, if pressure and consequently number density are high enough, the particle mean free path becomes comparable in length to the mean particle separation, which means that particles are in close proximity of one another at all times.

It is likely that under such conditions, a collision of two particles is influenced not only by their respective potential energy fields, but also by fields pertaining to nearby particles, which likely changes the dynamics of collisions. It also probably holds true that simultaneous collisions of multiple particles become more frequent under such conditions. Furthermore, if mean particle separation becomes low enough, we can expect attractive forces to prevent particles from even dispersing after an event of interaction, which happens at values of pressure and temperature close to conditions where a phase transition occurs.

4. CONCLUSION

Our derivation has shown that the coefficient of dynamic viscosity is a function of temperature as well the properties we can ascribe to constituent particles, such as their mass, diameter and the depth of the potential energy well. It also depends on pressure, although we were not able to quantify its influence on viscosity through theoretical methods. We created this model by assuming that an ensemble of particles behaves as a rarefied gas and that intermolecular forces act between pairs of particles. Consequently, the model gives most accurate predictions at values of parameters where these two assumptions hold true.

We could have improved our model of viscosity by describing the influence of interparticle forces on interactions more accurately, while we also could have accounted for the influence of neighbouring particles on a binary collision and simultaneous collisions of more than two particles.

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