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Unveiling the Relationships among the Viscosity Equations of Glass Liquids and Colloidal Suspensions for Obtaining Universal Equations with the Generic Free Volume Concept

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Abstract

The underlying relationships among viscosity equations of glass liquids and colloidal suspensions are explored with the aid of free volume concept. Viscosity equations of glass liquids available in literature are focused and found to have a same physical basis but different mathematical expressions for the free volume. The glass transitions induced by temperatures in glass liquids and the percolation transition induced by particle volume fractions in colloidal suspensions essentially are a second order phase transition: both those two transitions could induce the free volume changes, which in turn determines how the viscosities are going to change with temperatures and/or particle volume fractions. Unified correlations of the free volume to both temperatures and particle volume fractions are thus proposed. The resulted viscosity equations are reducible to many popular viscosity equations currently widely used in literature; those equations should be able to cover many different types of materials over a wide temperature range. For demonstration purpose, one of the simplified versions of those newly developed equations is compared with popular viscosity equations and the experimental data: it can well fit the experimental data over a wide temperature range. The current work reveals common physical grounds among various viscosity equations, deepening our understanding on viscosity and unifying the free volume theory across many different systems.

I. Introduction

For materials of glass transition temperatures like glass liquids (glass forming materials at liquid state) and polymeric materials, viscosity is always a key parameter for revealing structure changes, especially when materials go through glass transition temperatures. Although many physical models and empirical regression equations have been already established to account for the relationships between viscosity and temperature, new models are continuously proposed due to the limitations of current equations and the rich viscosity behaviors of glass forming materials. Take glass materials as an example: glass materials have been investigated for a very long time and many physical models as well as associated viscosity equations have been generated. However, new viscosity equations are still popping up for the purpose of fitting experimental data better in both low and high temperature regions [1,2,3,4]. Same things happen for polymeric materials [5] and colloidal suspensions [6]. One of common features among those systems is that viscosity may dramatically change whenever there is a phase transition induced by either the temperatures or by the concentrations of the components in the systems.

Generally speaking, two kinds of phase transitions are commonly observed: the first order and second order phase transitions [7]. The first order phase transition is typically related to temperature: at transition point temperature remains unchanged and the system either absorbs or gives off heat. The commonly encountered liquid evaporations and solid melting phenomena belong to this category. The second order phase transition is related to the changes of a characteristic correlation length or order parameter near criticality points. An example of such a second-order phase transition is the percolation transition induced by the particle volume fraction in colloidal suspensions [8]. The glass transitions observed in supercooled liquids and polymers are usually recognized as the second-order phase transition, caused by the percolated structures formed by the dynamic clusters [9]. Both the first order and second order phase transitions may induce dramatic viscosity changes. However, the second order phase transition is more complicated, as the free volume unoccupied by molecules or particles may have a complex relationship with temperature or particle volume fraction; In the first order phase transitions the free volume usually has a clear and simple relationship with temperature.

Free volume theories are frequently employed to treat phase transition phenomena for determining the mobility of molecules or segment chains [10,11,12,13,14,15,16,17]. The assumptions are that the phase transitions are always associated with the sizes of the free volumes available for molecules or segment chains to move freely in confined spaces. It is the free volume variations that mainly contribute to dramatic physical property changes, like the viscosity jump-ups observed in glass materials. Using the statistic method under an assumption that re-distribution of free spaces or holes doesn't require energy change, Cohen and Turnbull obtained the mobility of molecules in pure liquids [10,16]:

$$\ln m = \ln m_0 - \gamma v_c / v_f \qquad (1)$$

where m is the mobility of molecules, m_0 is a constant, γ is a numerical factor between 0.5 and 1, v_c is a critical hole volume, and v_f is the free volume per molecule. Fujita [11] introduced a specific volume parameter, *f*, and defined:

$$f = V_f / V \qquad (2)$$

where V_f is the total free volume in a liquid and V is the total volume of the liquid, $v_c/v_f = V/V_f$. Therefore, Eq. (1) may be re-written as:

$$\ln m = \ln m_0 - \gamma / f \qquad (3)$$

Or

$$m = m_0 \exp(-\gamma / f) \qquad (4)$$

Eq. (4) essentially has a same form as Boltzmann distribution equation. Many viscosity equations are found to have a similar form as expressed in Eq. (4). For examples, Doolittle's empirical viscosity equation [14] has an exact same form as Eq. (4) and Arrhenius's empirical viscosity equation is also very similar, if the parameter f is replaced with k_BT for the reason that f actually is proportional to k_BT and the parameter γ changes accordingly for keeping the term γ/f dimensionless. Intuitively, free volume is related not only to the size and the volume fraction of molecules but also to the temperature. High temperatures may create more free volume in the systems. Assuming that the specific volume fraction is directly proportional to the temperature:

$$f = A(T - T_0) \qquad (5)$$

where T_0 is the ideal glass transition temperature at which the atoms are completely frozen and the free volume is not going to decrease further, one may easily reach the well known Vogel-Fulcher-Tammann (VFT) [18,19,20] or identical Willams-Landel-Ferry (WLF) [15] equations in polymer science community for viscosity [21] and for ionic conductivity [22]. Replacing the parameter f in Eq. (4) with Eq. (5) and assuming the viscosity is directly proportional to the mobility of molecules, one may obtain:

$$\eta_T = A_1 \exp\left(\frac{A_2}{T - T_0}\right) \qquad (6)$$

where η_T is the viscosity, both A_1 and A_2 are constants. Also, assuming that the conductivity is directly proportional to the mobility of ions and applying the Nernst-Einstein equation leads to [22]:

$$\sigma = A_3 T^{1/2} \exp\left[-\frac{B}{R(T - T_0)}\right] \qquad (7)$$

where σ is the ionic conductivity, both A_3 and B are constants, and R is the gas constant. Note that in an electric field the mobility is mainly contributed from ions rather than neutral molecules and Eq. (1) should be used to account for the mobility of ions. Both Eq. (6) and (7) are called VFT equations. As one may see, a simple correlation between the free volume and the temperature successfully provides a powerful theoretical basis for empirical VFT equations of both viscosity and conductivity.

For colloidal suspensions, the free volume is thought to correlate with the particle volume fraction rather than temperature. As one may know, a viscosity equation of dilute colloidal suspensions developed in 1906 by Einstein may be shown below[23]:

$$\eta_s = \eta_m(1 + 2.5\phi) \qquad (8)$$

where η_s is the viscosity of a colloidal suspension, and η_m is the viscosity of liquid medium, and ϕ is the particle volume fraction usually below 1%. Ball[24] and Sudduth[25] extended Einstein's equation to concentrated colloidal suspensions with an interesting assumption that the effect of the particles in concentrated suspensions is the sum of the effect of the particles added sequentially to the system. The free volume unoccupied by the particles relative to the maximum packing fraction is considered as the specific free volume, i.e., the free volume per unit volume, and it may be expressed below:

$$f = \frac{\phi_m - \phi}{\phi_m} = 1 - \phi/\phi_m \qquad (9)$$

where ϕ_m is the maximum packing fraction. Again, the viscosity is assumed to increase with more particles added into the system, corresponding to the lower specific free volume expressed in Eq. (9). Since differentiating Eq. (8) leads to $d\eta_s = 2.5\eta_m d\phi$, the viscosity change expressed as $d\eta_s$ could be written as below by assuming that the viscosity change is inversely proportional to the specific free volume:

$$d\eta_s = 2.5\eta_s(1 - \phi/\phi_m)^{-1} d\phi \qquad (10)$$

Note that η_m is changed to η_s in Eq. (10), which directly comes from the assumption that viscosity change from the addition of a particle into the system will still follow Einstein's equation, if the system before this extra particle is added in is considered the "liquid medium" for this particle. Eq. (10) may be written in a more general form:

$$d\eta_s = 2.5\eta_s(1 - \phi/\phi_m)^{-n} d\phi \qquad (11)$$

where *n* is a positive number, When *n=0*, Eq. (11) becomes the Arrhenius viscosity equation[26]; when *n=1*, it becomes the Kreiger-Dougherty equation[27]; when *n=2*, the Mooney equation[28]. Hao[29,30] further extended this main idea that the viscosity of a suspension should be inversely proportional to the free volume in the suspension, and successfully unified viscosity equations for colloidal suspensions, polymer solutions, and polymer melts. The term $(1-\phi/\phi_m)$ is thought to represent the specific free volume and may be replaced with the free volume per unit volume estimated on the basis of inter-particle spacing equation[31,32,33]:

$$f = 15.29\phi(\sqrt[3]{\phi_m/\phi} - 1)^3 \qquad (12)$$

Several successful viscosity equations are obtained with particle shape information included[31,32,33], implying that this free volume approach works pretty well for both athermal granular powders and thermal systems like colloidal suspensions and polymeric systems.

As demonstrated above, two things are evident: The viscosity should inversely proportional to the free volume; and the free volume should change with both the temperature and particle volume fraction. The total free volume V_F may be written as:

$$V_F = x_1 V_T + x_2 V_V \tag{13}$$

where V_T is the free volume related to temperature and V_V is the free volume related to the volume fractions of molecules, clusters, or colloidal particles under consideration, x_1 andx_2 are fractional numbers and $x_1 + x_2 = 1$. Since the temperature variation may also induce the spatial constraints for molecules or clusters, fractional coefficients are necessary for correcting the overlapping effect arisen from both the temperatures and the volume fractions in the same time. For conciseness and simplification reason, the molecules, clusters, or colloidal particles whose shapes and sizes have a geometrical impact on the filling spaces, the volume fractions of those entities will be indistinguishably called the particle volume fractions in this article. Clearly, the viscosity and conductivity should be related to V_F, rather than only V_T or V_V individually as shown in literature. Many unresolved limitations and confusions associated with both viscosity and conductivity equations in literature may stem from that the free volume usually is linked to either temperatures or particle volume fractions, not both in the same time. For example, the molecular sizes are not considered in viscosity equations of many glass materials, though different compositions of the glass liquids do show quite different viscosity behaviors [2,34], even the compositions are just slightly modified [35]; Many viscosity equations in literature may only work for specific materials over either low or high temperature regions.

In this article, the free volume induced from both the particle volume fraction and temperature and the associated viscosity equations available in literature are analyzed. The underlying relationships among different viscosity equations are explored through deriving those equations with the focus on different free volume expressions. The commonality between the particle volume fraction and temperature in term of their contributions to the free volume is evaluated and a universal free volume expression is therefore proposed. New generic viscosity equations are thus derived by utilizing universal free volume expressions that work for both temperature and particle volume fractions in the same time. The purpose is to identify underlying mechanisms associated with glass transition phenomena observed in glasses, polymer materials, and colloidal suspensions, and to unify the free volume theory across those systems.

II. Derivations of Viscosity Equations

Let's first evaluate commonly used empirical viscosity equations in glass forming materials. For a material with the thickness *d* under a simple shear, according to the definition of viscosity, the viscosity of this material should be the ratio of the shear stress to the shear rate:

$$\eta = \frac{\tau}{v/d} = \frac{\tau_1}{m} \tag{14}$$

where τ is the shear stress and τ_1 is the shear stress related parameter, *m* is the mobility, *d* is the shear thickness, *v* is the velocity. Using Eq. (4) to replace the parameter *m* in Eq. (14) leads to :

$$\eta = \frac{\tau_1}{m_0 \exp(-\gamma/f)} = \frac{\tau_1}{m_0} \exp\left(\frac{\gamma}{f}\right) \tag{15}$$

If Eq. (5) is used to express the specific free volume parameter *f* in Eq. (15), one may easily obtain Eq. (6), which is the well known VFT equation. However, if the specific free volume follows the power law instead of simple linear relationship with the temperature:

$$f = CT^{\alpha} \qquad (16)$$

where C and α are constants, then Eq. (15) may be re-written as:

$$\eta = C_1 \exp\left(\frac{C_2}{T}\right)^{\alpha} \qquad (17)$$

where C_1 and C_2 are constants. Eq. (17) is another successful three-parameter viscosity model, the Avramov-Milchev (AM) equation [36], comparable to the successful VFT equation. In addition, the specific free volume may follow the exponential law with temperature:

$$f = C_3 T \exp\left(-\frac{C_4}{T}\right) \qquad (18)$$

then Eq. (15) will become:

$$\eta = C_1 \exp\left[\frac{C_5}{T}\exp\left(\frac{C_4}{T}\right)\right] \qquad (19)$$

Again, C_1, C_4 and C_5 are constants. Eq. (19) has the same form as the equation obtained by Mauro et.al, who claimed that this equation is superior to the VFT and AM equations in term of fitting low temperature viscosity [3]. Interestingly, when temperature is high and $C_4/T < 1$, $\exp(-C_4/T) \approx 1 - C_4/T$, Eq. (18) then may be expressed as:

$$f = C_3(T - C_4) \qquad (20)$$

Eq. (20) exactly is Eq. (5), which may lead to the VFT equation as shown earlier. Clearly, by assuming that the free volume may follow an exponential relationship with temperature as shown in Eq. (18), both Mauro's equation and the VFT equation can be easily obtained; the VFT equation can be regarded as an approximated form at high temperature regions. Naturally, since the Mauro's equation is directly coming from Eq. (18) without any approximations, it is anticipated to cover both low and high temperature regions and fits experimental data better than the VFT equation, which is evidenced in literature [3].

Instead of following the exponential law, the free volume may vary with temperature in a form of the common "S" shape logistic function that has a wide application in many fields like Fermi-Dirac distribution in physics [37] and population growth in ecology [38]. In such a case, the initial growth of free volume may follow the exponential law, and then starts to saturate and finally stops to grow with temperature. One may imagine that this scenario should match with what happens for polymers and glass materials with glass transition temperatures, when they go through from solid to liquid/melt states: at the beginning, the solid phase starts to lose intact crystalline structures and the free volume starts to grow; once the temperature approaches to the glass transition points, the free volume should be substantially boosted; when the temperatures are above the glass transition points, the increment of the free volume should become slower and slower, as the material theoretically is already in liquid phase; further raising temperatures up will not substantially increase the free volume and the free volume stops to grow. Therefore, the "S" shape logistic function may best reflect how the free volume is going to change with temperatures. According to the basic form of "S" shape logistic function, the specific free volume may thus be expressed as:

$$f = C_6 T \frac{1}{1+\exp\left(-\frac{C_4}{T}\right)} \qquad (21)$$

Replacing the parameter *f* in Eq. (15) leads to a new viscosity equation:

$$\eta = C_1 \exp\left[\frac{C_7}{T}\left[1+\exp\left(-\frac{C_4}{T}\right)\right]\right] \qquad (22)$$

where C_1, C_4 and C_7 are constants. Note that Eq. (22) may be re-written as $\eta = C_1 \exp\left[\frac{C_7 + C_7\exp\left(-\frac{C_4}{T}\right)}{T}\right] = C_1 \exp\left[\frac{E_\infty + E(T)}{T}\right]$, where E_∞ is a constant and $E(T) = C_7 \exp\left(-\frac{C_4}{T}\right)$, an exponential relationship with temperature *T*. Clearly, Eq. (22) has an exact form of the equation obtained by Schmidtke et al. [39,40,41]. In one of their article dealing with the reorientational correlation time of a series of molecular liquids [41], Schmidtke et al. found that both VFT, Eq. (6), and Mauro's equation, Eq. (19), are unable to correctly fit the experimental data at high temperature regions; while Eq. (22) can reproduce the salient features of experimental results. This clearly shows that Eq. (22) is superior to both VFT and Mauro's equation. For avoiding the redundancy and repetition, please refer to the literature [41] for more detailed information. When temperature is low, the constant C_4 is a positive number, and $\exp\left(\frac{C_4}{T}\right) \gg 1$, thus $\exp\left(-\frac{C_4}{T}\right) \ll 1$, Eq. (22) is reducible to Arrhenius viscosity equation; while when $\exp\left(-\frac{C_4}{T}\right) \gg 1$, then Eq. (22) is reducible to Eq. (19), Mauro's equation, implying that Eq. (22) may cover even a much wider range of temperatures than the Mauro's equation.

Furthermore, one may choose to use a generalized logistic function [42] and thus the specific free volume may be written as:

$$f = C_8 T \frac{1}{\left[1+\exp\left(-\frac{C_4}{T}\right)\right]^n} \qquad (23)$$

where C_8 and *n* are constants. Substituting Eq. (23) into Eq. (15) leads to another viscosity equation:

$$\eta = C_1 \exp\left[\frac{C_9}{T}\left[1+\exp\left(-\frac{C_4}{T}\right)\right]^n\right] \qquad (24)$$

where C_1 , C_4 ,C_9 , and *n* are constants. When n=1, Eq. (24) becomes Eq. (22). Using the approximation, $C_4/T < 1$, $\exp(-C_4/T) \approx 1 - C_4/T$, Eq. (24) may be written as:

$$\eta = C_1 \exp\left[\frac{(2T - C_4)^n C_9}{T^{n+1}}\right] \qquad (25)$$

Eq. (25) has the same form of the AM equation, Eq. (17). The only difference is that constant C_2 in Eq. (17) actually is dependent on temperature as shown in Eq. (25), which may provide a clue on why the application of the AM equation over entire temperature range sometimes is limited. The constant C_2 in Eq. (17) has either a linear or power law relationship with temperature and must be corrected in order to fit the experimental data using the AM equation.

In addition, Eq. (25) may be re-written as:

$$\eta = C_1 \exp\left[\frac{C_9}{T}\left[\frac{(2T-C_4)}{T}\right]^n\right] = C_1 \exp\left[\frac{2^n C_9}{T}\left[\frac{(T-C_4/2)}{T}\right]^n\right] \qquad (26)$$

Eq. (26) has a very similar form of the equation obtained using the avoid transition concept [43,44], which is found to have superior fitting properties to other models like Mauro's [45]. The only difference is that the denominator inside the term of n-power is the actual temperature rather than the so called avoided thermodynamic phase transition temperature, a constant. This difference shouldn't pose any negative impact on the regression, as the avoided phase transition temperature should be always larger than actual temperatures.

Interestingly, when $n=2$, Eq. (26) may become $\eta = C_1 \exp\left[\frac{4C_9}{T}\left[\frac{(T-C_4/2)}{T}\right]^2\right]$, which has a very similar form of the equation obtained by Chandler et al. [46,47] . Note that in Chandler's equation the term $\frac{4C_9}{T}$ was considered as a constant, which may provide a clue on why Chandler's equation can only work at a very narrow temperature range as recognized by both Chandler et al. [47] and Mauro et al. [3]. The quadratic form adopted by Chandler et al. seems to work pretty well for molecular liquids [47], and Chandler's equation will thus be compared with the newly obtained equations in this article, where the universal viscosity equations are sought and focused.

When the term of $\frac{C_9}{T}\left[1+\exp\left(-\frac{C_4}{T}\right)\right]^n < 1$, Eq. (24) may be approximated in another form as:

$$\eta = C_1 + \frac{C_1 C_9}{T}\left[1+\exp\left(-\frac{C_4}{T}\right)\right]^n \qquad (27)$$

If $C_1 \ll \eta$, Eq. (27) may be further re-written as:

$$\eta \cong \frac{C_1 C_9}{T}\left[1+\exp\left(-\frac{C_4}{T}\right)\right]^n \qquad (28)$$

When $n=3$, Eq. (28) can be expanded as:

$$\eta \cong \frac{C_1 C_9}{T}\left[1+3\exp\left(-\frac{C_4}{T}\right)+3\exp\left(-\frac{2C_4}{T}\right)+\exp\left(-\frac{3C_4}{T}\right)\right] \qquad (29)$$

Eq. (29) is similar to the two-exponential equation originally proposed by Douglas [48] to treat silica glasses and further extended by Doremus with the defect-mediated viscous flow model [2,49,50]. The Doremus' two exponential equation is found to fit the viscosity data of network liquids at both low and high temperatures very well [35]. Since Eq. (24) can be reduced to many currently available equations in literature, it may provide the best fit to experimental data of many different materials. However, Eq. (24) needs four parameters to fit the experimental data, while Eq. (17), Eq. (19) and Eq. (22) only need three parameters.

As demonstrated so far for glass materials, the empirical VFT equation, the AM equation, the Mauro's equation, Schmidtke's equation, Chandler's equation, the equation from the avoid transition model, the equation from Doremus' defect-mediated viscous flow model, and new equations presented in this article, may share a common and generic viscosity equation as a function of the free volume f_T as below:

$$\eta_T = A_1 \exp\left(\frac{A_4}{f_T}\right) \tag{30}$$

Again, both A_1 and A_4 are constants. Note that Eq. (30) is same as Eq. (15), but the free volume induced by temperature is emphasized. Eq. (30) represents the viscosity relationship with the free volume induced from temperature, and may serves as a generic form of viscosity equation for all different types of glass materials over a wide temperature range. The differences among those viscosity-temperature equations in literature stem from how the free volume parameter f_T is chosen. All those equations essentially are based on a same physical principle: the viscosity has an exponential relationship with the free volume, a very similar form as the Boltzmann distribution function with temperature.

For colloidal suspensions, the free volume is mainly controlled by the particle volume fraction rather than temperature. If the free volume has the relationship with the particle volume fraction as shown in Eq. (9), thus $df_V = -d\phi/\phi_m$, where f_V is the free volume contribution from particle volume fraction. Eq. (11) may be written as $\eta_s = A_5 \exp(\int f_V^{-n}\, d\phi)$. Therefore, a generic viscosity equation based on Eq. (11) may be written as:

$$\begin{aligned}\eta_s &= A_5 \exp\left(\int f_V^{-n}\, d\phi\right)\\ &= A_5 \exp(\int -\phi_m f_V^{-n}\, df_V)\\ &= A_5 \exp\left(-\frac{\phi_m}{1-n}\frac{1}{f_V^{n-1}}\right)\\ &= A_5 \exp\left(\frac{A_6}{f_V^{n-1}}\right) \qquad (31)\end{aligned}$$

where A_5 and A_6 are constants. If the free volume has the relationship with particle volume fraction as expressed in Eq. (12), then $d\phi = -0.403 f_V^{-2/3} df_V$. A generic viscosity equation based on Eq. (11) may be written as:

$$\begin{aligned}\eta_s &= A_5 \exp\left(\int f_V^{-n}\, d\phi\right)\\ &= A_5 \exp\left(\int -0.403 f_V^{-(n+\frac{2}{3})}\, df_V\right)\\ &= A_5 \exp\left(-\frac{0.403}{1/3-n}\frac{1}{f_V^{n-1/3}}\right)\end{aligned}$$

$$= A_5 \exp\left(\frac{A_7}{f_V^{n-1/3}}\right) \quad (32)$$

Clearly, both Eq. (31) and (32) have a similar mathematic form, dependent on which free volume expressions are chosen, Comparing Eq. (31) and (32) with Eq. (30), one may come to a conclusion that even those three equations mathematically are very similar and could be generically unified with Eq. (15) and expressed as:

$$\eta = A_7 \exp\left(\frac{A_8}{f^{n-a}}\right) \quad (33)$$

where a, n, A_7 and A_8 are constants, η is viscosity and f is the specific free volume. According to Eq. (13), f should be written as:

$$f = x_1 f_T + x_2 f_V \quad (34)$$

Thus Eq. (33) may be written as:

$$\eta = A_7 \exp\left[\frac{A_8}{(x_1 f_T + x_2 f_V)^{n-a}}\right] \quad (35)$$

Eq. (35) could be exactly re-written as:

$$\ln\eta = \ln A_7 + A_8 (x_1 f_T + x_2 f_V)^{a-n} \quad (36)$$

Note that $x_1 + x_2 = 1$, thus Eq. (36) requires at least seven parameters to fit the experimental data. By selecting proper f_T, f_V, a, and n, Eq. (36) may be easily reducible to Eq. (6), Eq. (17), Eq. (19), Eq. (22), and Eq. (24). In addition, if the term $\frac{A_8}{(x_1 f_T + x_2 f_V)^{n-a}} < 1$, then Eq. (35) may be approximated as:

$$\eta = A_7 + \left[\frac{A_7 A_8}{(x_1 f_T + x_2 f_V)^{n-a}}\right] \quad (37)$$

Eq. (37) may be reducible to Eq. (26) and Eq. (29), the equation derived from the avoid transition concept and the equation from the defect-mediated viscous flow model. Of course, Eq. (35) can be easily reduced to the viscosity equations of colloidal suspensions, too. Therefore, it may provide the best expression for modeling the viscosity of the materials with a second order phase transition like glass transition. However, it requires too many fitting parameters and is thus less useful in practice. The simplified versions may be good enough and will be evaluated in next section.

III Experimental comparison and further extensions

For demonstrating how the newly derived viscosity equations work, the experimental data from literature are used to compare. As mentioned earlier, Eq. (35) should be able to fit viscosity data of many materials, though more than seven constant parameters are required. Therefore the simplified or reducible versions of Eq. (35) will be used instead, for the reason that only a few fitting parameters are required. Eq. (22), which only requires three fitting parameters, is thus selected for comparison with experimental viscosity data. The viscosity data of a common silica glass over temperature range from 1273 to 2773 K is first selected [35,51,52] for analysis. Figure 1 shows the experimental data points directly from the literature [35,51,52] and the regressions with both Eq. (22) obtained in this article and Eq. (19) derived by Mauro et.al [3]. As shown in the previous section, Eq. (22) can be reduced to Eq. (19) at certain conditions and Schmidtke's experimental work [39,40,41] already demonstrates that Eq. (22) is superior to Eq. (19). However, both Eq. (22) and (19) are still used to fit the experimental data for pure comparison purpose only. The comparison presented in Figure 1 is solely for readers to gain an idea on how powerful those two equations are. In addition, Eq. (19) was claimed to adequately fit 568 different Corning silica glasses with the best accuracy in comparison with the VFT and AM equations, a very powerful equation. Theoretically, Eq. (22) should perform much better than Eq. (19). As shown in Figure 1, Eq. (22) fits the experimental

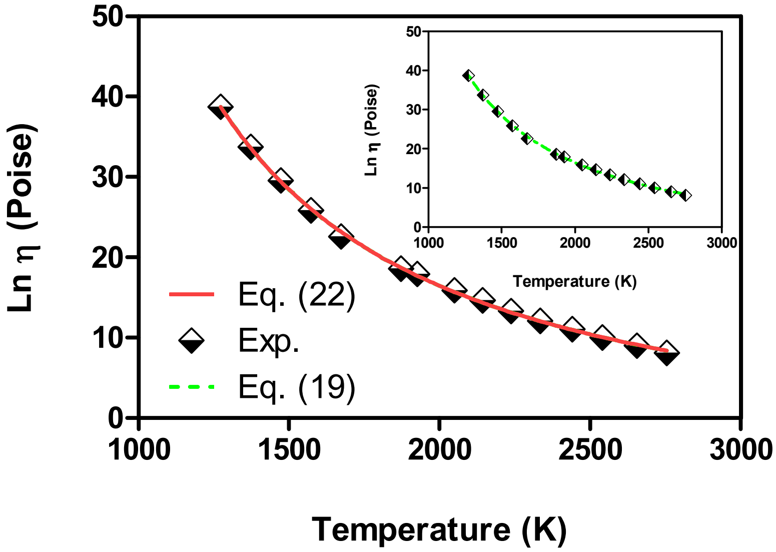

Figure 1 The experimental data of viscosity vs. temperature from the references [51,52] and predicted with Eq. (19) and Eq. (22). The fitting parameters used in Eq. (22) are $C_1 = 5.37 \times 10^{-4}, C_4 = -1.08 \times 10^3, C_7 = 1.77 \times 10^4$*, and the fitting parameters used in Eq. (19) are* $C_1 = 1.13 \times 10^{-3}, C_4 = 771.2, C_5 = 31607$*. The inset is the same experimental data fitted with Eq. (19). The R-squared values for fitting with Eq. (22) and Eq. (19) are 0.9998 and 0.9994, respectively.*

data as well as Eq. (19) in entire temperature range and the fitting quality in term of R-squared value, which is very close to one, is excellent. Note that the values of fitting parameter C_1 used in both Eq. (19) and (22) for achieving the best fittings are different, implying that the starting viscosity points are different and those two equations have different physical meanings. As indicated earlier, Eq. (22) may be reducible to Eq. (19) when $\exp\left(-\frac{C_4}{T}\right) \gg 1$, implying that Eq. (19) is a special case of Eq. (22) and Eq. (22) may cover a wide range of temperature than the Mauro's equation. Since both equations only need three fitting parameters, Eq. (22) is therefore preferred. It is worth mentioning that the same set of the experimental data shown in Figure 1 can be perfectly fitted with the Doremus's defect-mediated viscous flow model, the corresponded equation of which, however, may need six fitting parameters [35].

For further demonstrating the applicability of Eq. (22) in low temperature regions below 1273 K, the viscosity data of lead-silica glass, the standard reference material No.711, from the laboratory D listed in the literature [53], is plotted in Figure 2 and fitted with both Eq. (22) and Eq. (19) again. Both Eq. (22) and (19) give an excellent fit to the experimental data over the temperature range from 673 to 1648 K, and the goodness of fitting in term of R-squared values are very close to one. Note that the fitting constant C_4 in Eq. (22) for fitting those two sets of data showing in both Figure 1 and 2 is negative and $\exp\left(-\frac{C_4}{T}\right)$ is a relatively large number. Therefore, Eq. (22) essentially is reduced to Eq. (19), and thus it is not surprising to see both equations give a good fit to experimental data. Considering temperature ranges shown in both Figures 1 and 2, one may say that Eq. (22) seems to work very well for temperatures from 673 to 2773 K, a pretty wide range.

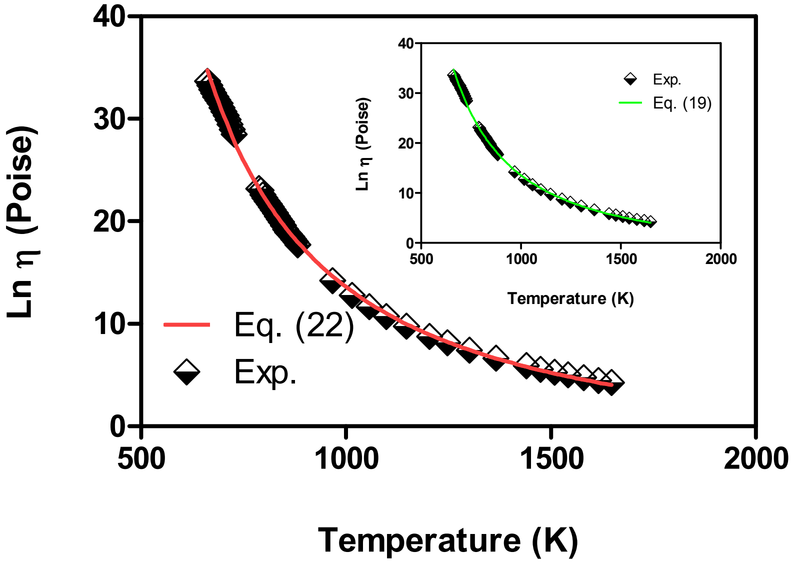

Figure 2 The experimental viscosity data of lead-silica glass from the reference [53] and predicted with Eq. (19) and Eq. (22). The parameters used in Eq. (22) are $C_1 = 1.04 \times 10^{-2}, C_4 = -9.3 \times 10^2, C_7 = 5.13 \times 10^3$ *, and the parameters used in Eq. (19) are* $C_1 = 2.58 \times 10^{-2}, C_4 = 764.5, C_5 = 8024$. *The inset is the same experimental data fitted with Eq. (19). The R-squared values for fitting with Eq. (22) and Eq. (19) are 0.9987 and 0.9986, respectively.*

We also would like to compare the commonly used equations mentioned in this article in a hypothetical manner for illustrating how different those equations are. The VFT equation expressed in Eq. (6), the Mauro's equation expressed in Eq. (19), the Chandler's equation expressed as $\eta = C_1 \exp\left[\frac{4C_9}{T_0}\left[\frac{\left(T-\frac{C_4}{2}\right)}{T}\right]^2\right]$, and Eq. (22) are plotted as Ln η against the temperature over a wide range in Figure 3. In low temperature regions, Eq. (22) and Eq. (19) overlap, and the difference between them becomes bigger once the temperature is over 500 K; the VFT equation basically follows a similar trend as both Eq. (19) and (22) at low temperature regions. The big difference shows up at high temperature regions, while both VFT and Eq. (19) predict a negative logarithmic viscosity, an unreasonably low viscosity. In contrast, Eq. (22) predicts a positive

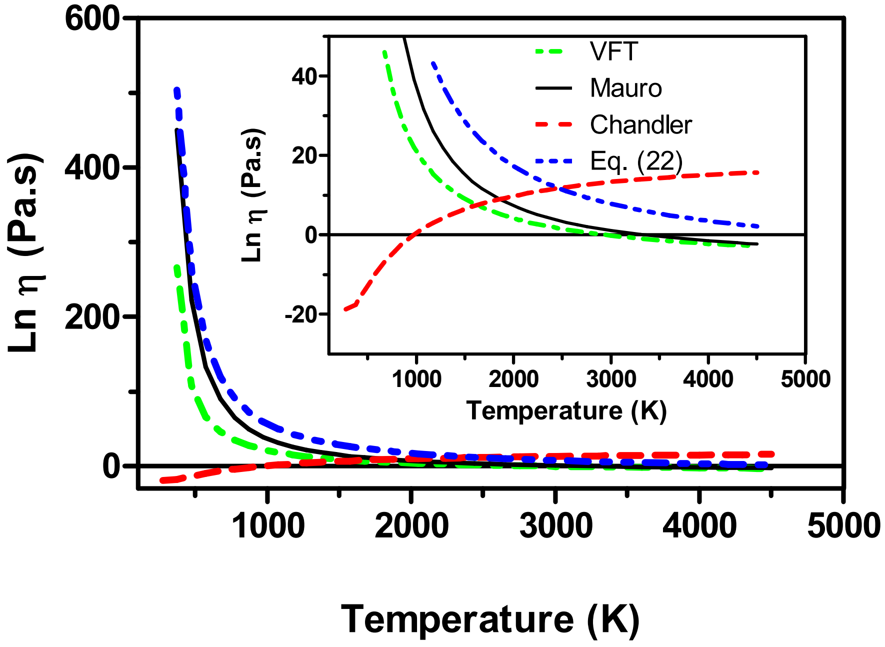

Figure 3 The VFT equation, Mauro's equation, Chandler's equation, and Eq. (22) are plotted as $Ln\,\eta$ *against temperature over a wide range. The VFT equation expressed in Eq. (6), the Mauro's equation expressed in Eq. (19), the Chandler's equation expressed as* $\eta = C_1 \exp\left[\frac{4C_9}{T_0}\left[\frac{\left(T-\frac{C_4}{2}\right)}{T}\right]^2\right]$*, and Eq. (22) are used and the constants in those equations are kept as same as possible. The parameters used in those equations are listed below: 1) VFT equation,* $A_1 = 5 \times 10^{-4}$, $A_2 = 2 \times 10^{4}$, $T_0 = 300$*; 2) Mauro's equation,* $C_1 = 5 \times 10^{-4}, C_5 = 2 \times 10^{4}$, $C_4 = 800$*;3) Chandler' equation,* $C_1 = 5 \times 10^{-9}, 4C_9/T_0 = 40$, $C_4 = 600$*, and those values are chosen on the basis of Chandler's article* [47]*; 4) Eq. (22),* $C_1 = 5 \times 10^{-4}, C_7 = 2 \times 10^{4}$, $C_4 = -800$. *The inset is the small scale of the main graph for clearly showing the differences among those equations at relatively small viscosity range.*

logarithmic viscosity over entire temperature range. On the other hand, The Chandler's equation seems to behave erratically, predicting that the logarithmic viscosity increases with temperature. The constants used in the calculations are chosen on the basis of Chandler's article [47], where more than 60 fragile glass formers are analyzed using Chandler's equation. Note that Chandler's equation only works at a narrow temperature range, as acknowledged by Chandler, and what is shown in Figure 3 doesn't disapprove the success of the Chandler's equation, as the temperature range shown in Figure 3 is very wide.

As shown earlier, Eq. (24) is powerful enough and is reducible to many viscosity equations like Eq. (22), Arrhenius equation, Mauro's equation, AM equation, the equation from the avoid transition model, and the equation from the defect-mediated viscous flow model, etc. It would be interesting to see what kind of relationship between viscosity and temperature that can be predicted with Eq. (24) with an additional fitting parameter, *n*. Figure 4 shows the viscosity predicted with Eq. (24) against temperature over a wide range, hypothetically spanning from 523 to 4773 K. The predicted viscosity is strongly dependent on the parameter *n*: low *n* values lead to low viscosities and high *n* values shift viscosity to substantially high regions. Theoretically, Eq. (24) may cover the whole viscosity-temperature spectra, if a series of *n* values from the low to the high is properly selected. It is thus anticipated that Eq. (24) may work for many glass materials over a wide temperature range with the parameter, *n*. Please keep in mind that Eq. (24) needs four fitting parameters and may be less sophisticated as Eq. (22) that only needs three fitting parameters.

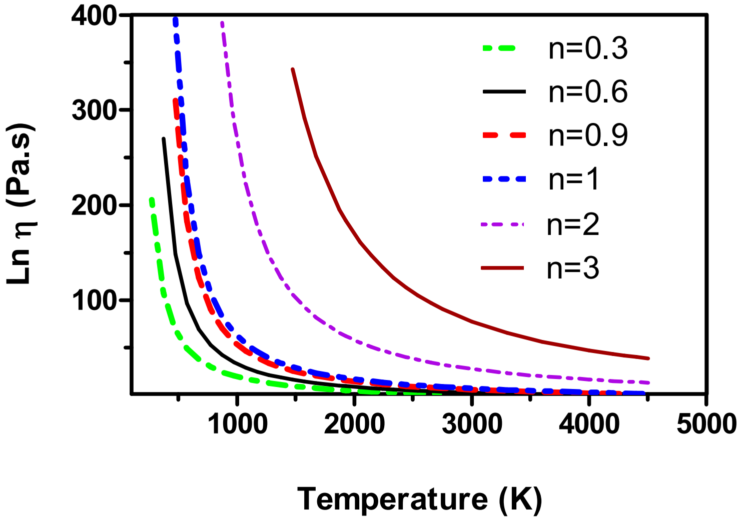

Figure 4, The viscosity predicted with Eq. (24) against temperature with the parameters, $C_1 = 5.37 \times 10^{-4}, C_4 = -1.08 \times 10^{3}, C_9 = 1.77 \times 10^{4}$.

IV Discussion

First, I would like to stress that the focus of this article, as indicated in the title, is on the glass forming liquids and colloidal suspensions, rather than simple liquids. There are many articles published on the viscosity of simple liquids using the free volume concept. Please refer to the literature 13 and 30 in this article for detailed information. I do believe that what are discovered in this article can be applied to simple liquids. However, I have to say that the viscosity behaviors of glass forming materials and colloidal suspensions are more complicated than that of the simple liquids. Correctly identifying those complex viscosity behaviors may be greatly helpful in analogously determining the viscosity of granular materials, which is the ultimate goal in my another future article.

The major goal of this article is to reveal the relationships among different viscosity equations, as indicated in the title. Each of those viscosity equations is backed by one or more complicated theories. It is this article that shows those viscosity equations are actually connected with simply mathematical relationships. The deep underlying physical mechanism is the second order phase transition phenomena, which play a key role in the physics of amorphous liquids and solids. The idea that a second order phase transition is behind the glass transition phenomenon is well recognized in physics and material sciences communities. Please refer to the standard text books such as “Mesoscopic Physics of Complex Materials”, written by Tsu-Sen Chow, Springer, 2000 [54] . This idea was originated by Gibbs and DiMarzio in 1958 [55].

This article is focused on theoretical side, and the obtained viscosity equations are obviously superior to other equations in theory. The experimental comparison is only for illustrative comparison purpose. For demonstrating the applicability of my universal equations, a large set of experimental data covering more than hundreds of thousands of materials is needed, especially the data cannot be well fitted by the equations currently available in literature. However, I don’t have access to those data and will rely on other experimentalists’ hard work.

As one may already realize, the relationships among the viscosity equations available in literature mathematically are pretty simple: the viscosity is inversely proportional to the mobility, and the mobility correlates with the free volume in an exponential form; the different viscosity equations can be obtained by assuming that the free volume has a different correlation with the temperature in glass liquids or with the particle volume fraction in colloidal suspensions. The underlying physical mechanism is that both temperature and particle volume fraction may induce the second order phase transition, which in turn has a big impact on the free volume that plays a critical role in determining viscosity. The universal viscosity equations that adequately cover how the free volume changes with both temperature and particle volume fraction, should work for many materials over a wide temperature range. The exponential correlation of the free volume to the temperature, more generally the generalized “S” shape logistic function relationship, seems to properly reflect the underlying physical principles; the resulted generic viscosity equations are reducible to many viscosity equations in the literature. The success of those equations may imply that the underlying physical mechanisms are properly identified and reflected.

Although one of the newly obtained viscosity equations seems to fit experimental data very well, I would like to emphasize that those fitting parameters lack of clear physical meanings. However, they may be attained once a microscopic free volume theory is built up on a more fundamental level. In this microscopic free volume theory, the common mathematical expressions for free volume, the linear, the power law, and the exponential law, should be able to render clear physical pictures. Right now, those relationships are mathematical possibilities, but they seem to work pretty well in many systems.

V Conclusions

The relationships among the viscosity equations available in literature are revealed in this article. Three common mathematical relationships: the linear, the power law, and the exponential law, if assumed to be the correlation of the free volume to the temperature, are found to easily lead to the VFT, the AM, and Mauro's equations. If the correlations of the free volume to the temperature are assumed to follow the logistic or generalized logistic functions, more generic viscosity equations are obtained and they are reducible to the VFT equation, the AM equation, Mauro's equation, Schmidtke' equation, Chandler' equation, the equation from the avoid transition model, and the equation from the Doremus' defect-mediated viscous flow model. The free volume induced by the temperature in glass materials essentially has the same mathematical form as the one induced by the particle volume fraction in colloidal suspensions. The underlying connection lies in the fact that both transitions physically are the second order phase transition. Using these commonalities, universal viscosity equations that may cover glass liquids, polymeric materials, and colloidal suspensions are thus obtained but need at least seven fitting parameters.

One of newly obtained viscosity equations, requiring only three fitting parameters, is compared with other popular viscosity equations and found to be capable of perfectly fitting experimental viscosity data of both silica glass and lead-silica glass over a temperature range from 673 to 2773 K. The success may imply that the approach employed in this article properly unveils the physical mechanism that governs the viscosity in those systems.

The generic viscosity equation that requires four fitting parameter is theoretically evaluated over a much wide temperature range from 523 to 4773 K. The predicted viscosity is strongly dependent on the power parameter in the equation and basically can cover the whole viscosity-temperature spectra. Note that those generic equations require many fitting parameters and are reducible to less generic forms or to the equations currently available in literature. The current work may provide a universal approach of correlating the viscosity to the free volume applicable to broad material systems with a unified approach.

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