Vogel-Fulcher law of glass viscosity: A new approach

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Starting with an expression, due originally to Einstein, for the shear viscosity $\eta(\delta \phi)$ of a liquid having a small fraction $\delta \phi$ by volume of solid particulate matter suspended in it at random, we derive an effective-medium viscosity $\eta(\phi)$ for arbitrary $\phi$ which is precisely of the Vogel-Fulcher form. An essential point of the derivation is the incorporation of the excluded-volume effect at each turn of the iteration $\phi_{n+1} = \phi_n + \delta \phi$. The model is frankly mechanical, but applicable directly to soft matter like a dense suspension of microspheres in a liquid as function of the number density. Extension to a glass forming supercooled liquid is plausible inasmuch as the latter may be modelled statistically as a mixture of rigid, solid-like regions ($\phi$) and floppy, liquid-like regions ($1-\phi$), for $\phi$ increasing monotonically with supercooling.

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Extreme slow dynamics defines approach to the glassy state. At the macroscopic scale, it manifests as a rise of shear viscosity, typically by 15 orders of magnitude, as that state is reached through supercooling of the glass forming liquid. The Vogel-Fulcher (VF) law describes that growth of viscosity [1]. This work derives the VF law [2].

A striking feature of the VF law is the essential singularity, rather than a power-law divergence, of the shear viscosity at a temperature $T_0$. The relaxation times, however, exceed the experimental time scale at what is identified as the glass transition temperature $T_g > T_0$, making thus the glass transition a kinetic crossover. This inverse exponential VF law is well known to hold for the fragile structural-glass forming liquids [1]. But, very significantly it is also obeyed by a broad class of soft-matter systems that exhibit the extreme slow dynamics [1]. This includes the purely mechanical systems, e.g., of weakly perturbed granular aggregates, where the degree of compaction and the perturbation strength, rather than mass density and temperature, are the relevant variables and the control parameter, and the underlying physics is that of jamming, or blocking, by rigid granular contacts [3-6]. And, similarly for the case of a dense suspension of microspheres [1]. Motivated by its ubiquity and universality, we have attempted a derivation of the VF law for a fluid-mechanical model of a liquid containing a volume fraction $\phi$ of solid
particulate matter suspended in it at random. It is an effective medium theory (EMT) along the line of Bruggemann’s asymmetric EMT [7], but it goes beyond the mean field by incorporating the solid-solid exclusion explicitly in real space, which indeed is the essential point of our derivation. This, frankly mechanical model can, however, be re-interpreted as a model for the glass forming supercooled liquid inasmuch as the latter may be re-approximated as a statistical mixture of short-ranged rigidity (solid-like fraction $\phi$) and the floppy liquid-like fraction $(1-\phi)$. In our view the present work complements the other derivations of the VF law which are based on the idea of marginal scaling [6] and some simple exclusion models [8-11].

We start with the expression, due originally to Einstein [12], for the shear viscosity $\eta(\delta\phi)$ of a liquid containing a small volume fraction $\delta\phi$ of solid particulate matter suspended in it at random:

$$\eta(\delta\phi) = \eta(0) (1 + \alpha\delta\phi) \quad (1)$$

where $\alpha$, of order unity, is a fluid-dynamic dimensionless parameter specifying the particle shape and the flow boundary condition, and $\delta\phi = (4\pi/3)a^3\delta n$ assuming spherical particles of radius ‘$a$’ with $\delta n$ the number density. The physical basis of Eq. (1) is that in the steady state the rigid parts of the liquid move practically as complete wholes, and hence the effect of their existence is to diminish the thickness of the layer, through which momentum has to be transported by the mobile molecules, and thus to increase the viscosity [13]. We can iterate Eq. (1) to a higher volume fraction $\phi$, in the spirit of an EMT, by the recursion relation

$$\eta(\phi + \delta\phi) = \eta(\phi) (1 + \alpha \delta\phi \frac{1}{1-\phi}), \quad (2)$$

where the factor $1/(1-\phi)$ in the denominator on the right-hand side ensures that the elemental increment $\delta\phi$ is reckoned relative to the liquid-like volume fraction $(1-\phi)$ remaining at the current stage of iteration. Now, proceeding to the limit $\delta\phi \to 0$, we obtain the differential equation

$$\frac{d\eta}{\eta} = \left( \frac{\alpha}{1-\phi} \right) d\phi \quad (3)$$

with the solution

$$\eta(\phi) = \eta(0)(1 - \phi)^{-\alpha} \quad (4)$$
that gives a power-law divergence for the effective shear viscosity $\eta(\phi)$. Here $\eta(0)$ is the ‘bare’ viscosity of the pure liquid with $\phi = 0$. Such a power-law temperature dependence is well known to follow from the viscosity feedback mechanism giving the Batchinski-Hildebrand law [14] (with $\alpha = 1$), or from the Mode Coupling Theory (MCT) [15] giving the critical behaviour (with $\alpha \approx 2$). Both these exponent values lie in the range for the parameter $\alpha$ as described below.

Equation (4) giving this critical behaviour is, however, in error in that it mathematically ignores the physically important excluded-volume effect. The point is that the liquid fraction $(1-\phi)$ in the denominator in Eq. (3) must be replaced by the liquid fraction $(1-\phi)$ as weighted by the probability that the incremental solid fraction $\delta\phi$, added at random, lands in it [16]. This, therefore, effectively replaces $(1-\phi)$ by $(1-\phi)^2$. Equation (4) then gets modified accordingly to

$$\frac{d\eta}{\eta} = \frac{\alpha}{(1-\phi)^2} \ d\phi$$

(5)

giving

$$\eta(\phi) = \left( \eta(0) \ e^{-\alpha} \right) \ e^{\alpha / (1-\phi)}.$$  

(6)

The expression in Eq. (6) is already of the VF form as an inverse exponential function of $\phi$ diverging essentially at $\phi = 1$. This, however, needs a refinement as dictated by the physics of the problem, namely, that the solid volume fraction $\phi$ need approach only the rigidity percolation threshold $\phi_0 (1)$ in order to attain the three-dimensional rigidity. Therefore, $(1-\phi)$ above must be displaced to $(\phi_0 - \phi)$. Thus, we finally have

$$\eta(\phi) = \left( \eta_0 e^{-\alpha / \phi_0} \right) \ e^{\alpha / (\phi_0 - \phi)}.$$  

(7)

which tends to $\eta(0)$ for $\phi \to 0$ (pure liquid), and diverges as $\phi \to \phi_0$ from below (the glassy state).

Equation (7) is our main result. For the simplest case of spherical, non-spinning particles, we have [12,13] $\alpha = 2.5$, while for particles free to spin, $\alpha = 1$. Also, we can estimate the rigidity percolation threshold [17] ($\phi_0^{3D}$) in three dimensions from its 2D value $\phi_0^{2D} \simeq 0.80$ by use of the simple relation $\phi_0^{3D} = 4 / 3 \pi^{1/2} (\phi_0^{2D})^3 / 2$. We get $\phi_0^{3D} \simeq 0.54$. In Fig. (1), we have plotted $\eta(\phi)$ against $\phi$ for the values of the parameters, $\alpha = 2.5$ and $\phi_0^{3D} = 0.54$. This is essentially a universal curve.
While Eq. (7) is expected to be directly applicable to, e.g., a suspension of microspheres in a viscous liquid, its extension to the glass forming supercooled liquids is plausible as indicated earlier. Then φ must be regarded as a function of temperature, increasing monotonically as the temperature decreases. This will turn Eq. (6) explicitly into the VF form, or its variant, the Vogel-Tammann-Fulcher (VTF) law, \( \eta(T) = \eta_0 \exp\left(DT_0/(T - T_0)\right) \) as \( T \to T_0 \) from above.

We would now like to conclude with the following remarks. The above fluid-mechanical model physically implies that our derivation may apply more readily to the fragile rather than to the strong (network forming) liquids. As noted above, the numerical value of \( \alpha \) occurring in Eq. (7) depends on the particle shape [12] (taken to be spherical here), and on whether the particles are free to spin (\( \alpha = 1 \)) or not (\( \alpha = 2.5 \)) in the presence of a shear rate. This can make the parameter \( \alpha \) temperature dependent, with the higher value \( \alpha = 2.5 \) appropriate to the lower temperatures. With the solid-like volume fraction \( \phi \) now become a function of temperature, and, therefore, a thermodynamic parameter, the equation (7) shows how the shear viscosity (a transport property) is actually controlled by the thermodynamics: The thermodynamically controlled liquid-like fraction (\( \phi_0 - \phi \)) acts as an idler taking up the shear rate. This is the simplest realization of a viscosity amplification that underlies the macroscopic slow dynamics described by the Vogel-Fulcher law, where the idling liquid-like fraction essentially retains its ‘bare’ low value \( \eta(0) \).

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FIG. 1. Plot of normalized shear viscosity $\eta(\phi)/\eta(0)$ against the solid-like volume fraction $\phi$ from Eq. (7) derived in the text, for $\alpha = 2.5$. Here $\phi_0$ is the rigidity percolation threshold, and $\phi_g$ marks the point $(\phi_g)/\eta(0) = 10^{15}$. The regime $0 < \phi < \phi_g$ is nominally the supercooled liquid; $\phi_g < \phi < \phi(0)$ the glassy liquid; and $\phi > \phi_0$ the rigid glassy solid.