

## Viscosity of suspensions and glass: Turning power-law divergence into essential singularity

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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, an effective-medium viscosity  $\eta(\phi)$  for arbitrary  $\phi$  is derived, 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 a 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.

GLASS has become a paradigm of complexity, much as turbulence is. The very thought of it gives a sense of uneasiness, without our being able to put the finger on anything in particular. One might say that glass is what glass does. But, whatever it does, it does so slowly. This extreme slow dynamics defines an 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<sup>1</sup>. The present work derives the VF law<sup>2</sup>.

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 timescale at what is identified as the glass transition temperature  $T_g > T_0$ , thus making the glass transition a kinetic crossover. This inverse exponential VF law is well known to hold for the fragile structural-glass-forming liquids<sup>1</sup>. But, significantly, it is also obeyed by a broad class of soft-matter systems that exhibit the extreme slow dynamics<sup>1</sup>. This includes 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 variable and the control parameter, and the underlying physics is that of jamming or blocking, by rigid granular contacts<sup>3-6</sup>. And, similarly for the case of a dense suspension of microspheres<sup>1</sup>. 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<sup>7</sup>, 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 other derivations of the VF law which are based on the idea of marginal scaling<sup>6</sup> and some simple exclusion models<sup>8-11</sup>.

We start with the expression, due originally to Einstein<sup>12</sup>, 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  $\delta n$  being 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<sup>13</sup>. We can iterate eq. (1) to higher volume fraction  $\phi$ , in the spirit of an EMT, by the recursion relation

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

where the factor  $(1-\phi)$  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  $\delta\phi \rightarrow 0$ , we obtain the differential equation

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

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<sup>14</sup> (with  $\alpha=1$ ), or from the Mode Coupling Theory<sup>15</sup> giving the critical behaviour (with  $\alpha=2$ ). Both these exponent values lie in the range for the parameter  $\alpha$  as described below.

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Equation (4) giving this critical behaviour is, however, in error in that it mathematically fails to incorporate fully the physically important excluded-volume effect. The point is that the liquid fraction  $(1-\phi)$  in the denominator of 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<sup>16</sup>. This, therefore, effectively replaces  $(1-\phi)$  by  $(1-\phi)^2$ . Equation (4) then gets modified accordingly to

$$\frac{d\eta}{\eta} = \frac{\alpha}{(1-\phi)^2}, \quad (5)$$

giving

$$\eta(\phi) = (\eta(0)e^{-\alpha})e^{\alpha(1-\phi)}. \quad (6)$$

Equation (6) is already of the VF form as an inverse exponential function of  $\phi$  diverging essentially at  $\phi=1$ . This, however, needs a refinement 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 reach the three-dimensional rigidity. Therefore,  $(1-\phi)$  above must be displaced to  $(\phi_0-\phi)$ . Thus, we finally have

$$\eta(\phi) = (\eta_0 e^{-\alpha/\phi_0}) e^{\alpha/(\phi_0-\phi)}, \quad (7)$$

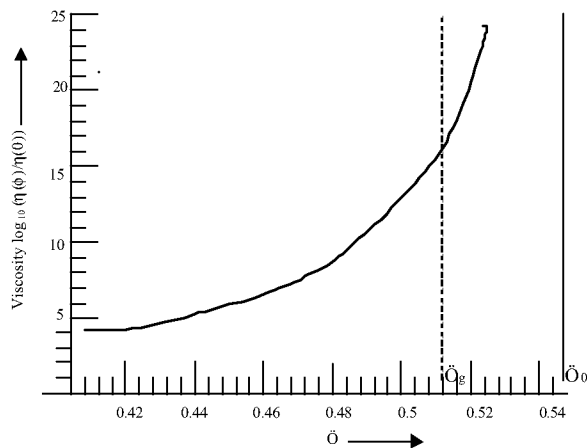
which tends to  $\eta(0)$  for  $\phi \rightarrow 0$  (pure liquid), and diverges as  $\phi \rightarrow \phi_0$  from below (the glassy state).

Equation (7) is our main result. For the simplest case of spherical, non-spinning particles, we have<sup>12,13</sup>  $\alpha=2.5$ , while for particles free to spin,  $\alpha=1$ . Also, we can estimate the rigidity percolation threshold<sup>17</sup> ( $\phi_0^{3D}$ ) in three dimen-

sions from its 2D value,  $\phi_0^{2D} \cong 0.80$  by use of the simple relation  $\phi_0^{3D} = 4/3\pi^{1/2} (\phi_0^{2D})^{3/2}$ . We get  $\phi_0^{3D} \cong 0.54$ . In Figure 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, for example a suspension of microspheres in a viscous liquid, its extension to the glass forming supercooled liquids is plausible as discussed earlier. Then  $\phi$  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 law,  $\eta(T) = \eta_0 \exp[DT_0/(T-T_0)]$  as  $T \rightarrow T_0$ , from the above.

I would like to conclude with the following remarks. The above fluid-mechanical model implies physically that the derivation may apply more readily to fragile rather than to strong (network forming) liquids. As noted above, the numerical value of  $\alpha$  occurring in eq. (7) depends on the particle shape (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 becoming a function of temperature, and, therefore, a thermodynamic parameter, eq. (7) shows how shear viscosity (a transport property) is actually controlled by 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 VF law, where the idling liquid-like fraction essentially retains its bare low value  $\zeta(0)$ . Extension to 2D systems is straightforward.



**Figure 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.

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16. It is amusing to note in passing that the all important replacement of  $(1-\phi)$  by  $(1-\phi)^2$  here is akin to the so-called inspection paradox of the probability theory, where the occurrence of an interval must be weighted by the probability of that interval being inspected at random, the latter probability being proportional to the size of the interval itself.
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## Microwave-assisted steps in the synthesis of poly(3-thiophenylacetic acid)

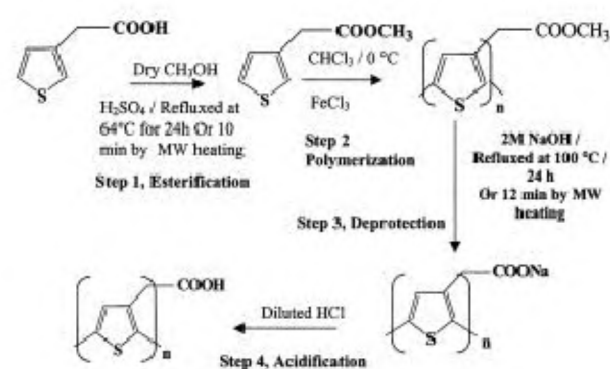
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An efficient and microwave-assisted irradiation method (MWR) has been developed for the total synthesis of poly(3-thiophenylacetic acid) (P3TAA), in which the total synthesis consists of esterification of 3-thiophenylacetic acid (3TAA) and hydrolysis of poly(3-thiophene methylacetate) in aqueous alkaline media. Relative yields in esterification and hydrolysis were compared under MWR and conventional refluxing (CR) methods at ambient atmospheric pressure. The esterification of 3TAA by MWR yielded 90% in 10 min of irradiation. The corresponding yield obtained was 49% when CR was employed. The relative yield of P3TAA was enhanced approximately twofold, while the whole reaction time was reduced threefold when MWR was employed.

In recent years, synthesis of processable conjugated polymers (CP) have been under intense investigation due to

their potential applications in many electrical devices such as photovoltaic cells, rechargeable batteries, electrochromic devices, chemical and optical sensors, anti-static coatings, etc.<sup>1–14</sup>. Particularly, in many photovoltaic devices, CPs have been utilized as hole-conducting medium<sup>6–12</sup> and few attempts have been made to use them as sensitizers for wide band gap semiconductors<sup>13,14</sup>. However, to use CPs as a sensitizer, rigid bonding such as the chemical bonding between carboxylic moieties in the Ru-complex dyes and semiconducting substrate is required<sup>14,15</sup>. The carboxylic groups enable the necessary electronic coupling between the sensitizer and the semiconductor surface. In this context, poly(3-thiophenylacetic acid) (P3TAA) is one of the best-known conducting polymers, which possesses suitable band matching with many inorganic semiconductors used in the dye-sensitized photovoltaic cells<sup>14</sup>. However, the chemical polymerization of this polymer mainly consists of three steps, including esterification of monomer, oxidative polymerization and hydrolysis of esterified polymer. In order to protect from the oxidative decomposition of the carboxylic acid moiety of 3-(thiophenylacetic acid) (3TAA), during the oxidative-coupling polymerization and to obtain the polymer successfully, esterification and hydrolysis processes have to be essentially carried out. Therefore, it should be emphasized that esterification and hydrolysis processes (as shown in Scheme 1) are crucial in this complete polymerization reaction. In the total synthesis of P3TAA, the conventional oil bath with long refluxing time is employed<sup>16</sup>. Therefore, in the synthesis of P3TAA in a large scale, it is required to establish a rapid and efficient synthesis method. In this context, microwave irradiation (MWR) has many specific characteristics for promoting chemical reactions. The radiation passes through the walls of the glass reaction vessel and heats only the reactants and/or solvent, avoiding local overheating at the reaction walls, which can eliminate the side reactions<sup>17–21</sup>. Therefore, in order to speed up the process and to obtain higher yields of P3TAA, we have employed MWR in the total synthesis of P3TAA. Here we report an efficient MWR-assisted



Scheme 1. Complete conventional polymerization reaction mechanism of poly(3-thiophenylacetic acid).

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