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Comment on ''Fitting of viscosity: Distinguishing the temperature dependences predicted by various models of supercooled liquids''

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In a recent paper, Kivelson *et al.* [Phys. Rev. E **53**, 751 (1996)] presented fits to viscosity and relaxation time data for a variety of glass-forming liquids and concluded that the success of their model in fitting the data provides support for the existence of a high-temperature avoided critical point T^*. We compare fits obtained with the theory of Kivelson *et al.* with those of the free-volume theory and conclude that the analysis of Kivelson *et al.* does not provide convincing evidence for the applicability of their theory to supercooled liquids. [S1063-651X(96)07511-3]

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Recently, Kivelson *et al.* [1] have proposed a four-parameter function to describe the temperature-dependent viscosity $\eta(T)$ or structural relaxation time $\tau_\alpha(T)$ of glass-forming liquids, based on a conjectured, narrowly avoided high-temperature critical point [2]. They propose that, for $y(t)$ representing either $\eta(T)$ or $\tau_\alpha(T)$,

$$\log[y(T)]=\log[y_\infty]+E(T)/T, \tag{1a}$$

with

$$E(T)=E_\infty(T>T^*), \tag{1b}$$

$$E(T)=E_\infty+BT^*[(T^*-T)/T^*]^{8/3}(T<T^*), \tag{1c}$$

where T^* is said to be generally above the melting temperature T_m.

In Ref. [1], $\eta(T)$ and $\tau_\alpha(T)$ data for a variety of glass-forming materials were compared with Eq. (1), with two phenomenological fitting functions [Vogel-Fulcher (VF) and Ferry-Bassler] and with the idealized version of mode coupling theory (MCT) [3,4]. Both viscosity and relaxation-time data were included in the fits, but were not considered separately. The generally higher precision of $\tau_\alpha(T)$ data should provide a more meaningful test of competing theoretical functions than $\eta(T)$, but the viscosity data were emphasized in the comparisons. The authors concluded that the four-parameter function of Eq. (1) gave better fits to the experimental data than the other three-parameter functions considered, providing apparent support for the frustration-avoided critical point proposed in Ref. [2] as the physical origin of the dynamics of liquids approaching the liquid-glass transition.

The free-volume theory [5] also predicts a four-parameter function for $\eta(T)$ that, despite widespread concern over its underlying assumptions, is known to provide good fits to viscosity data; but free-volume fits were not included in the comparisons of Ref. [1]. Such a comparison is important since, unlike Eq. (1), the free-volume theory does not include a high-temperature avoided critical point.

We have analyzed viscosity data for orthoterphenyl (OTP) [6,7] and the recent high-precision dielectric relaxation-time data of Stickel *et al.* for Salol [8]. We performed nonlinear-least-squares fits with both the Kivelson *et al.* and free-volume predictions to this data in order to obtain a realistic evaluation of the validity of Eq. (1) for glass-forming liquids. In the fits, we used $\log_{10}$, with η in poise and τ in seconds.

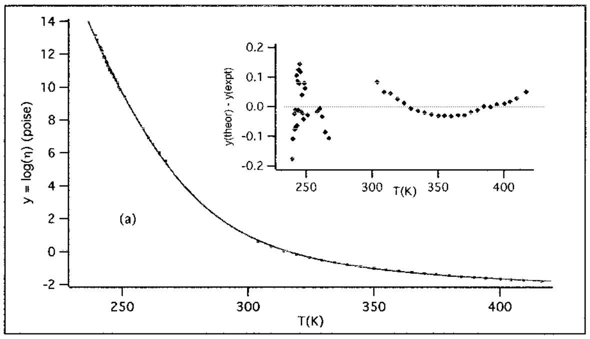
The free-volume theory, in the extended version developed by Cohen and Grest [5], predicts that the temperature-dependent viscosity $\eta(T)$ is given by a four-parameter function

$$\log_{10}(\eta)=A+B/\{T-T_0+[(T-T_0)^2+CT]^{1/2}\}. \tag{2}$$

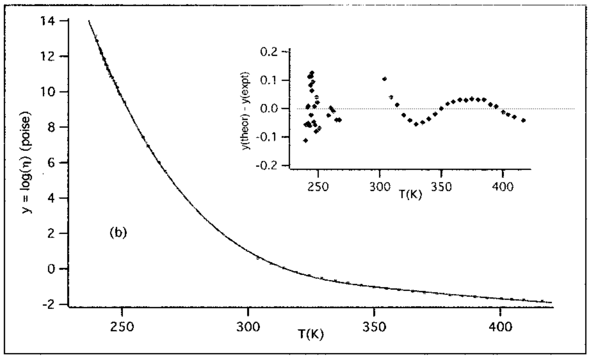
Note that at high temperatures where $(T-T_0)^2 \gg CT$, Eq. (2) is equivalent to the Vogel-Fulcher form $\log(\eta)=\log(\eta_\infty)-A/(T-T_0)$. Fits of Eq. (2) to the OTP viscosity data and Salol $\tau(T)$ data are shown in Figs. 1(a) and 2(a), respectively. The insets show the difference plots [$\log(\eta_{\text{theor}})-\log(\eta_{\text{exp}})$]. We also show the reduced χ^2, defined as $\chi^2=(N-n)^{-1}\Sigma[y_i-y(T_i)]^2$, where N is the number of data points, n the number of fitting parameters, $y_i=\log(\eta_{\text{expt}})$, and $y(T_i)=\log(\eta_{\text{theor}})$ [9].

For the Kivelson *et al.* theory, fits of Eq. (1) to the OTP viscosity data and Salol $\tau(T)$ data are shown in Figs. 1(b) and 2(b), respectively. Again, the difference plots are included as insets. The fitting parameters and χ^2 values resulting from these fits are shown in Table I, along with the values reported in [1], converted from ln to $\log_{10}$. While the OTP data are equally well fit by both models (with a slightly smaller χ^2 for the Kivelson *et al.* model), the fits to the high-precision Salol dielectric data clearly indicate that the free-volume model is superior. While both fits look reasonable, the difference plots indicate major systematic errors in the Kivelson *et al.* model, which has a χ^2 over three times larger than that of the free-volume model. Looking closely at the fits, one can see that the high-temperature Arrhenius behavior predicted by Eq. (1) is a major source of the error.

In carrying out the fitting procedures with Eqs. (1) and (2), we have kept all four parameters free, which is conventional for comparing different theories. In Ref. [1], a different procedure was followed in which fits were first carried out to Eqs. (1a) and (1b) to fix y_∞ and E_∞, and then these two parameters were constrained in fitting the low-temperature data to Eqs. (1a) and (1c). Such parameter con-



Free Volume Fit

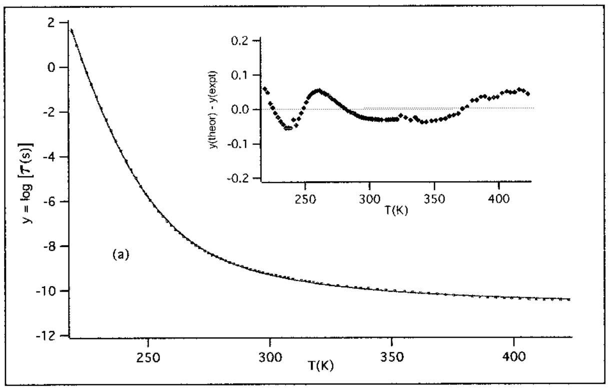


Kivelson Fit

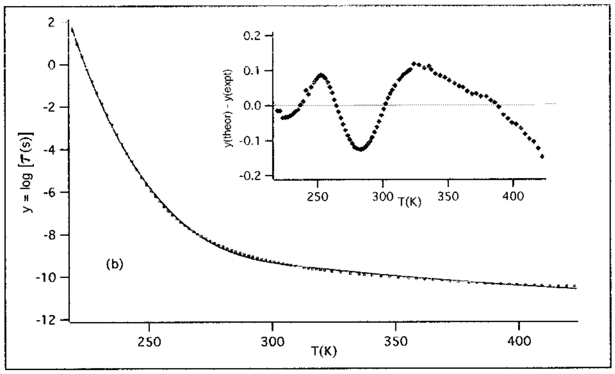
FIG. 1. OTP viscosity data [6,7] fit with (a) the free-volume model of Eq. (2) and (b) the Kivelson model of Eq. (1). The insets show the resulting differences $\log_{10}(\eta_{\rm theor}) - \log_{10}(\eta_{\rm expt})$. The resulting fitting parameters and χ^2 values are shown in Table I.

straints can, of course, only increase χ^2 relative to the value found with an unconstrained fit. More seriously, however, their approach rests on the assumption that $\eta(T)$ or $\tau_\alpha(T)$ must exhibit Arrhenius behavior at high temperatures. This idea, while widely believed, is not supported by experimental evidence.

The difference between the Arrhenius form $\exp(-A/T)$ and the VF form $\exp[-A/(T-T_0)]$ becomes increasingly more difficult to measure as T increases, but unless T_0 can be shown to decrease towards zero with increasing T, an approach to Arrhenius behavior cannot be claimed. Dixon [10] introduced an objective test in which VF fits are carried out over a temperature window whose center is displaced incrementally. He found that, for Salol, T_0 increases with increasing T, contrary to the trend required for approaching Arrhenius behavior. Following an exchange on this point [11], a previous fitting procedure for dielectric data [12], which (like that of Kivelson *et al.*) assumed high-temperature Arrhenius behavior, was abandoned. In Ref. [8], Stickel *et al.* analyzed their high-precision dielectric data on Salol and concluded that the high-temperature Arrhenius behavior previously claimed now appears unrealistic. As an aside, we note that the OTP viscosity data of Uhlmann and co-workers [6,7] analyzed by Kivelson *et al.* falls into two separate temperature ranges, and separate VF fits to the two ranges gave $T_0 \sim 184$ K for the low-temperature data and $T_0 \sim 246$ K for the high-temperature data [13], contrary to



Free Volume Fit



Kivelson Fit

FIG. 2. Salol relaxation time data [8] fit with (a) the free-volume model of Eq. (2) and (b) the Kivelson model of Eq. (1). The insets show the resulting differences $\log_{10}(\tau_{\rm theor}) - \log_{10}(\tau_{\rm expt})$. The resulting fitting parameters and χ^2 values are shown in Table I.

TABLE I. Fits of viscosity and relaxation time data to the Kivelson and free-volume theories.

Theory	OTP viscosity $\eta(T)$ (P) [a] ($T_m=331$ K)					Salol dielectric $\tau(T)$ (sec) [b] ($T_m=318$ K)				
Free volume	A	B	C	T_0	χ^2	A	B	C	T_0	χ^2
[Eq. (2)]	−2.655	252.8	6.39	278.7	4.25×10^{-3}	-10.96	190.13	5.15	249	1.20×10^{-3}
Kivelson	$\log(\eta_\infty)$	E_∞	B	T^*	χ^2	$\log(\tau_\infty)$	E_∞	B	T^*	χ^2
[Eq. (1)]	−6.313	1855	169.9	350.5	3.13×10^{-3}	-13.58	1268	175.5	310.3	3.85×10^{-3}
Ref. [1] [c]		1368	178.9	350			1398	171.1	304	

[a] References [6,7].

[b] Reference [8].

[c] The values of E_∞ and B in [1] have been divided by 2.303 to convert from ln to $\log_{10}$.

the crossover to high-temperature Arrhenius behavior assumed by Kivelson *et al.*

The frustration-avoided high-temperature critical point model proposed by Kivelson *et al.* [1,2] may prove to be relevant to the dynamics of supercooled liquids. Predictions based on their model for the dynamics of supercooled liquids, which have provided major tests of other theories in recent years, would make it possible to seriously test the applicability of their model. However, in view of the fact that no such predictions are yet available and that the free-volume theory (like their theory) provides a four-parameter fitting function for $\eta(T)$ or $\tau_\alpha(T)$ that produces fits of at least as good quality while making no claims for the existence of any high-temperature avoided critical point, we believe that there is not yet any convincing evidence for the applicability of their model to the dynamics of supercooled liquids and the liquid-glass transition.

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