

## Reply to “Comment on ‘Fitting of viscosity: Distinguishing the temperature dependences predicted by various models of supercooled liquids’ ”

D. Kivelson,<sup>1</sup> G. Tarjus,<sup>2</sup> X.-L. Xiao,<sup>3</sup> and S. A. Kivelson<sup>4</sup>

<sup>1</sup>*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095*

<sup>2</sup>*Laboratoire de Physique Theorique des Liquides, Universite Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*

<sup>3</sup>*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055*

<sup>4</sup>*Department of Physics, University of California, Los Angeles, California 90095*

(Received 3 June 1996)

We agree with Cummins in the preceding Comment [Phys. Rev. E **54**, 5870 (1996)] that the free-volume theory yields a fitting formula for log (viscosity or relaxation time) versus  $T$  data that is comparable in quality to that given by the theory of frustration-limited domains. We disagree with his arguments and conclusions, the latter suggesting that major flaws in the theory of frustration-limited domains have been uncovered. [S1063-651X(96)07611-8]

PACS number(s): 64.70.Pf

In his Comment [1], Cummins points out that in our article [2] on the fitting of the temperature dependence of the viscosity ( $\eta$ ) and relaxation times, we overlooked the expression given by the free-volume theory [3]. He then points out that this expression gives fits comparable in quality to that given by the expression obtained with the aid of the theory of frustration-limited domains, [2,4] both approaches requiring four adjustable parameters and giving excellent fits. We agree with Cummins on these points and with his inference that, based solely on these fits, the theory of frustration-limited domains cannot be judged superior. Furthermore, this inference is relevant to our paper [2], which was an attempt to evaluate, on the basis of such fits, the applicability of various models.

However, Cummins goes further in interpreting his fits, first maintaining that the free-volume fits are significantly superior to those made with the frustration-limited domain expression and then proposing that his analysis comes close to invalidating this latter theory. We interpret his analysis quite differently, finding that it neither challenges nor invalidates the theory.

First we comment on the theory of frustration-limited domains and our view of the relevance of the fits to establishing its applicability. It has been clearly stated in the presentation of the theory [4] that it is a macroscopic (collective) theory, valid only when the domain size is large compared to the molecular size. According to the theory, at  $T$ 's above  $T^*$  the liquid is purely “molecular” in the sense that the dominant processes can be explained in terms of individual molecules and their very local environments, and we know of no adequate theory for this regime [4]. As with all theories of collective phenomena, including ours, in order to make a comparison with experiment, one must *subtract the molecular background* from the data; this step may be important because the molecular background, even if small, may be significant. We have determined the molecular background in *the simplest fashion we know*, i.e., by extrapolating to low  $T$ 's a two-parameter fitting form, the Arrhenius function, obtained at  $T$ 's above  $T^*$ . Well above  $T^*$  the Arrhenius function generally works quite well, well enough for our pur-

poses, and arguably as well as any other *general* form. Well below  $T^*$ , where we expect collective effects to dominate, we find agreement with the theoretically suggested nontrivial  $(T^* - T)^{8/3}$  dependence. The resulting four-parameter fits with the frustration-limited domain expression are, we believe, matched only by those made with the free-volume expression. Cummins states that we compared a four-parameter fit with various three-parameter fits, neglecting the carefully stated fact that these three-parameter fits all apply only to very restricted temperature ranges and that more than four parameters are needed to extend these fits to the entire accessible temperature range.

In proposing a fitting procedure we specified [2,4] that whenever sufficient data are available in the high-temperature regime, the studies of the high- $T$  regime (well above  $T^*$ ) and those of the low- $T$  regime (i.e., all the other data) should be treated *as two separate experiments*. The former involves molecular liquids and the latter mainly collective phenomena (but also including the previously unused data from slightly above  $T^*$ ). Within the framework of the theory of frustration-limited domains this is justified, actually *required*, because the fits in the molecular regime should be independent of adjustments that improve fits in the low-temperature collective regime. We found that the two-parameter Arrhenius function gives adequate fits in the high- $T$  regime (see Fig. 2 of Ref. [2]) and that different choices of these two parameters in cases where the high- $T$  data could not be unambiguously assigned had little effect on the low- $T$  fits. Although the  $T$  dependence at high  $T$  may itself be interesting, it is not of major concern in the present context; in Ref. [2] we discussed the implications of slightly non-Arrhenius behavior in the analysis. We also noted that in some cases putative high- $T$  Arrhenius behavior may be missed because the data are not available at  $T$ 's sufficiently above  $T^*$  and that in those cases, unfortunately not uncommon, one is forced to use a single, overall, four-parameter fitting procedure.

There are, in our opinion, no bias-free fitting procedures, and because it gives purpose and imposes constraints, bias need not be rejected out of hand. So, for example, few today

would use a  $\chi^2$  minimization procedure directly on the  $\eta$  versus  $T$  data, but would focus on  $\log[\eta]$  versus  $T$  data; the  $\chi^2$ -minimization procedure would lead to quite different results in the two cases. Differences, but lesser ones, would be noticed between a  $T\log[\eta]$  versus  $T$  and a  $\log[\eta]$  versus  $T$  analysis, the former being the appropriate one if, as in the theory of frustration-limited domains, one wishes to focus on the activation energy, the latter being the one used by Cummins.

A high- $T$  Vogel-Fulcher (VF) fit may in some cases represent the high- $T$  data better than an Arrhenius fit [5], almost certainly so if one wishes also to include data that fall below  $T^*$ . But such a high- $T$  fit does not serve the purpose of describing the molecular background because it is strongly influenced by the upturn in the activation energy below  $T^*$  and because as an extrapolation formula it has a built-in divergence despite the fact that its  $T$  dependence above  $T^*$  is modest. Our picture can readily accommodate a modest  $T$  dependence in the high- $T$  activation energy, but the extrapolation formula that extends the data down to  $T_g$  must do no more than continue the slight  $T$  dependence observed in the molecular liquid at high  $T$ 's above  $T^*$ . In this context we take issue with Cummins's comment that the findings of

Uhlmann and co-workers, whose data we used [6,7] are "contrary to the crossover to high-temperature Arrhenius behavior assumed by Kivelson *et al.*" at  $T^*$  because their high- $T$  orthophenyl (OTP) data were analyzed in terms of a VF fit [7]. Uhlmann and co-workers took the high- $T$  range for OTP to be between 275 and 416 K, a region that we would readily agree does not look Arrhenius-like. However, we added data extending up to 540 K [8,9] and we believe that the data from 350 to 540 K are reasonably Arrhenius-like [2]. For Salol the data look less Arrhenius-like [5], but as explained above, if the extrapolation of the molecular behavior to  $T$ 's below  $T^*$  is carried out cautiously, the effect upon the collective parameters  $B$  and  $T^*$  is not great.

In summary, we believe that what one can conclude on the basis of the Cummins analysis is that, *strictly as fitting formulas*, the free-volume model and frustration-limited-domain model with Arrhenius high- $T$  behavior are quite comparable to each other in quality of fit. In Cummins's analysis the latter comes out better for OTP (although he has not used the highest- $T$  data available), the former for Salol. The frustration-limited-domain theory does better at low  $T$ 's in both cases, which is the main concern of the theory.

- 
- [1] H. Z. Cummins, preceding Comment, Phys. Rev. E **54**, 5870 (1996).
- [2] D. Kivelson, G. Tarjus, X.-L. Xiao, and S. A. Kivelson, Phys. Rev. E **53**, 751 (1996).
- [3] G. S. Grest and M. H. Cohen, Adv. Chem. Phys. **48**, 455 (1981); M. H. Cohen and G. S. Grest, J. Non-Cryst. Solids **61-61**, 749 (1984).
- [4] S. A. Kovelson, D. Kivelson, X.-L. Xiao, Z. Nussimov, and G. Tarjus, Physica A **219**, 27 (1995).
- [5] F. J. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **102**, 6251 (1995); **104**, 2043 (1996).
- [6] M. Cukierman, J. W. Lane, and D. R. Uhlmann, J. Chem. Phys. **59**, 3639 (1973).
- [7] W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. **76**, 2317 (1972).
- [8] E. McLaughlin and A. R. Ubbelohde, Trans. Faraday Soc. **54**, 1804 (1958); see also R. J. Greet and D. Turnbull, J. Chem. Phys. **46**, 1243 (1967).
- [9] Other high-temperature OTP data are given by G. Friz, G. Kuhlbornsch, R. Nehren, and F. Feiter, Atomkernenergie **13**, 25 (1968). We thank Dr. F. J. Stickel for bringing this to our attention.