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Configurational entropy and the non-Newtonian rheology of homogeneous silicate liquids

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Recently, the non-Newtonian viscosity of silicate liquids at high stress levels has attracted a fair amount of attention. Different explanations for this interesting phenomenon have been proposed. The purpose of the present paper is to demonstrate that an extension of the configurational entropy theory for the occurrence of the glass transition by Adam and Gibbs [J. Chem. Phys. **43**, 139 (1965)] suffices to explain the development of non-Newtonian viscosity in liquids under high stress before rupture occurs. Attention is drawn to the fact that under steady-state conditions the logarithmic values of reduced viscosities of silicate liquids under high stress show a linear dependence on the square of the applied stress. This relationship suggests that the elastic work done by the stress on the liquid is the cause of the generation of configurational entropy. Adding this contribution to the configurational entropy term in the Adam-Gibbs equation for the ensemble average of the configurational transition probability is all that is needed to explain the heretofore mentioned non-Newtonian viscosity in liquid silicates and a molecular-dynamics Lennard-Jones liquid.

I. INTRODUCTION

It is well known that the viscosity of silicate liquids is Newtonian. But there have been serious suggestions that at very small as well as fairly large stresses the proportionality between stress and strain rate is not maintained. Published evidence supporting the contention that at low stress levels silicate liquids display a non-Newtonian viscosity is indirect, see for instance, Refs. 1 and 2. But experimental work, done to verify this at low or very low stress, has not, to our knowledge, produced any proof.[2]

On the other hand the evidence[3-9] for non-Newtonian rheology of homogeneous silicate liquids at high stress is without ambiguity. Li and Uhlmann[3] showed that absolute rate theory could not explain the occurrence of this phenomenon in a homogeneous glass, with a Newtonian viscosity ranging from $10^{12.5}$ to $10^{16.1}$ Pa s at temperatures between 480° and 555 °C. Simmons, Mohr, and Montrose[4] examined how the rheology of the NBS-710 viscosity standard was affected by high strain rates between 560 °C and 600 °C. They recorded strain rate depending decreases of the viscosity of over a factor of 3 relative to the Newtonian viscosity of about 3.10^{10} Pa s, and demonstrated that these observed decreases could not be due to heating of their sample because of work done on it. They proposed a semiempirical equation:

$$\eta/\eta_0 = 1/\{1+(\tau d\varepsilon/dt)G_\infty/\sigma_{\text{limit}}\}\ , \tag{1}$$

where η/η_0 is the reduced viscosity, η_0 the Newtonian viscosity at low strain rate, and η the observed non-Newtonian viscosity; ε is the deformation, τ the shear relaxation time of the Newtonian liquid, and G_∞ the shear modulus at infinite frequency. σ_{limit} is proposed to be "the maximum shear stress developed in the system under steady-state conditions as the strain rate goes to infinity,"[5] it is a temperature- and material-dependent constant obtained by fitting Eq. (1) to observed values of the reduced viscosity under steady-state conditions. Available observations are in good agreement with Eq. (1). Guillemet and Gy[9] explained Eq. (1) by postulating that alkali-silicate liquids close to the glass transition behave like a Maxwell liquid, whose viscosity changes with temperature according to the Adam-Gibbs[10] theory as amended for pressure effects.[11,12] However, the applied pressure-effect correction has not been derived for the dynamic conditions under which the experiments on shear thinning were done and the possibility of a stress effect was not investigated. Besides, the Maxwell rheology model for liquids gives an incomplete description of silicate liquids.[13]

In this paper, the decrease of the viscosity in silicate liquids at high stress is analyzed in terms of the Adam-Gibbs configurational entropy theory for relaxation in glass-forming liquids.[10] The Adam-Gibbs explanation for the occurrence of the glass transition has not been an unqualified success. Since 1965 many other attempts have been published to explain this transition; a very condensed review of these essays can be found in Sethna, Shore, and Huang.[14] The work by Goldstein[15] illustrates very well how difficult it can be to extract from thermodynamic data a good estimate of the configurational entropy of organic liquids and thus to verify quantitatively the Adam-Gibbs theory. But Richet, Robie, and Hemingway[16] succeeded in obtaining from their own calorimetric measurements a good estimation of the configurational entropy of vitreous and liquid $CaMgSi_2O_6$, and similar estimates for $NAlSi_3O_8$ and $CaAl_2Si_2O_8$ from already published data. The strong evidence[16,17] in favor of the validity of the configurational entropy theory, in particular as applied to silicate liquids,[11,15,17-19] is not sufficiently well known or appreciated.

According to Adam and Gibbs the viscosity of a glass-forming liquid can be expressed as

$$\ln\eta = A_e + B_e/(TS_{\rm conf}) , \qquad (2)$$

where A_e and B_e are material-dependent adjustable parameters obtained by fitting (2) to measured viscosities. A_e and B_e are considered to be constant when compared with the temperature dependence of the product $TS_{\rm conf}$. Actually, Eq. (2) reproduces better the temperature dependence of viscosities ranging from 0.1 to 10^{12} Pa s of silicate liquids than any other, theoretically derived or empirically inspired, expression containing only two adjustable constants. But unfortunately, the determination of calorimetry of the configurational entropy ($S_{\rm conf}$) is neither simple nor precise, consequently few high-quality measurements are available at this moment. This question has been discussed by Neuville and Richet.[20]

In contrast with most other data published on non-Newtonian viscosity of silicate liquids, the numerous observations of Webb and Dingwell[7] at temperatures close to the glass transition are well described and tabulated. These authors measured the steady-state elongation rate of highly viscous liquid fibers of $Na_2Si_4O_9$ at constant stresses between 10^6 and $10^{8.5}$ Pa. These data have been used here to verify the usefulness of the configurational entropy theory and to show that the observed decrease of the viscosity of highly stressed liquids close to the glass transition can be explained adequately within the framework of this theory. Application of the proposed model to other data and geological processes are the subjects of another publication.

II. THE MODEL

Adam and Gibbs[10] showed that the ensemble average of the configurational transition probability for a liquid system is given by the expression

$$\langle W(T)\rangle = A \exp\{-C/(TS_{\rm conf})\} , \qquad (3)$$

where A and C are material-dependent parameters whose temperature dependence can be neglected in comparison with that of the denominator $TS_{\rm conf}$. This transition probability is proportional to the reciprocal value of the relaxation time for structural rearrangements, the latter being proportional to the viscosity. Equation (2) is the straightforward consequence of this reasoning. The temperature dependence of the configurational entropy can be evaluated by means of

$$S_{\rm conf}(T) = S_{\rm conf}(T_g) + \int (\Delta C_p/T)dT , \qquad (4)$$

where it is supposed that $S_{\rm conf}(T_g)$ is known at the glass transition temperature T_g. ΔC_p indicates the difference between the heat capacities of the liquid and vitreous phases, it approximates the configurational heat capacity at constant pressure.[21] The heat capacities of silicate liquids at constant pressure vary linearly with temperature or are constant, while those of silicate glasses at temperatures close to T_g are constant.[22]

In order to apply Eq. (2) to explain the observations[7] of viscous thinning, the configurational entropy should be evaluated for a fiber liquid $Na_2Si_4O_9$ which is deformed at a steady rate at constant temperature by applying stress. To analyze this steady-state deformation process, it will be broken down schematically into recurring time steps Δt during which three consecutive processes take place: (1) under influence of a constant force F, a viscous liquid fiber is elastically elongated by an amount dL, (2) the elastic work done by F on the fiber causes the generation of internal energy (dU) and concomitantly of configurational entropy; and (3) subsequently, the elastic strain accumulating since the beginning of the time step Δt relaxes viscously, while the deformation remains constant. During a time step entropy is produced and consumed; the rate of entropy production is equal to

$$TdS/dt = dU/dt - FdL/dt . \qquad (5)$$

The internal energy change in the stretched fiber integrated over the time interval Δt should be zero, because of the steady-state character of the deformation process. Hence

$$\Delta U = \int (dU/dt)dt = 0 .$$

Therefore integration of Eq. (5) over the time interval Δt gives

$$T\Delta S(T,\sigma) = -F\Delta L = \sigma^2 V_m/(2E) , \qquad (6)$$

where the elastic modulus is indicated by E, the applied stress by σ and the molar volume of liquid $Na_2Si_4O_9$ by V_m. Because the applied stress is relatively small ($\sigma < 10^{8.5}$ Pa) and no changes of temperature of the stretched fiber have been observed,[4,5,7,8] it is supposed that a possible change in the vibrational entropy will be very small compared to the configurational entropy change. Thus as a first approximation, the configurational entropy produced by stretching of the fiber at constant temperature and under steady-state conditions is given by

$$\Delta S_{\rm conf}(T,\sigma) = \sigma^2 V_m/(2ET) . \qquad (7)$$

The elastic work done by the stress on the fiber is supposed to be a source of configurational entropy, which in turn is consumed by viscous deformation of the fiber. Using Eqs. (2) and (4) one obtains for the reduced viscosity η/η_0

$$\ln(\eta/\eta_0) = B_e(1/\{T[S_{\rm conf}(T) + \Delta S_{\rm conf}(T,\sigma)]\} - 1/[TS_{\rm conf}(T)]) . \qquad (8)$$

Because $|\Delta S_{\rm conf}(T,\sigma)| \ll |S_{\rm conf}(T)|$, the logarithm of the reduced viscosity should be proportional to the square of the applied stress

$$\ln(\eta/\eta_0) = -B_e \Delta S_{\rm conf}/(TS^2_{\rm conf}) = -B_e V_m \sigma^2/\{2E(TS_{\rm conf})^2\} . \qquad (9)$$

To derive Eq. (8) it was assumed that B_e is not affected by the applied stress; the hypothesis will be discussed in Sec. III.

The experiments[7] on $Na_2Si_4O_9$ showed non-Newtonian viscosity at stresses of more than 6.3×10^7 Pa. These observations at 747, 752, 755, 766, 777, and 779 K have been used in Figs. 1(a)–1(f) to demonstrate the linear dependence of the logarithmic reduced viscosity on σ^2. The needed input data are given in Table I. The quality of the fits of the expression

$$\log_{10}(\eta/\eta_0)=a+b\sigma^2 \tag{10}$$

to the data and the values obtained for a and b of Eq. (10) are given in Table II. According to Eq. (9), a in Eq. (10) should be equal to zero; this is the case, see Figs.

TABLE I. Thermodynamic and rheological input data for liquid $Na_2Si_4O_9$. $B_e=1.1782\times10^6$ J/mol (Ref. 11), $V_m=1.288\times10^{-4}$ m^3/mol; estimated, $C_{p,\text{glass}}=345.65$ J/(K mol) at $T=753$ K (Ref. 21), and $C_{p,\text{liquid}}=426.0$ J/(K mol) at $T=753$ K (Ref. 21).

Temp (K)	$\log_{10}[\eta_0(\text{Pa s})]^a$	S_{conf} (J/K mol)[b]
747.15	12.19	48.60
752.15	11.70	49.07
755.15	11.61	49.34
766.15	11.20	50.35
777.15	10.88	51.34
779.15	10.75	51.52

[a] Adopted η_0 values are in agreement with measured Newtonian viscosities and their error limits (Refs. 7 and 24).

[b] Values calculated from data in Refs. 11 and 21.

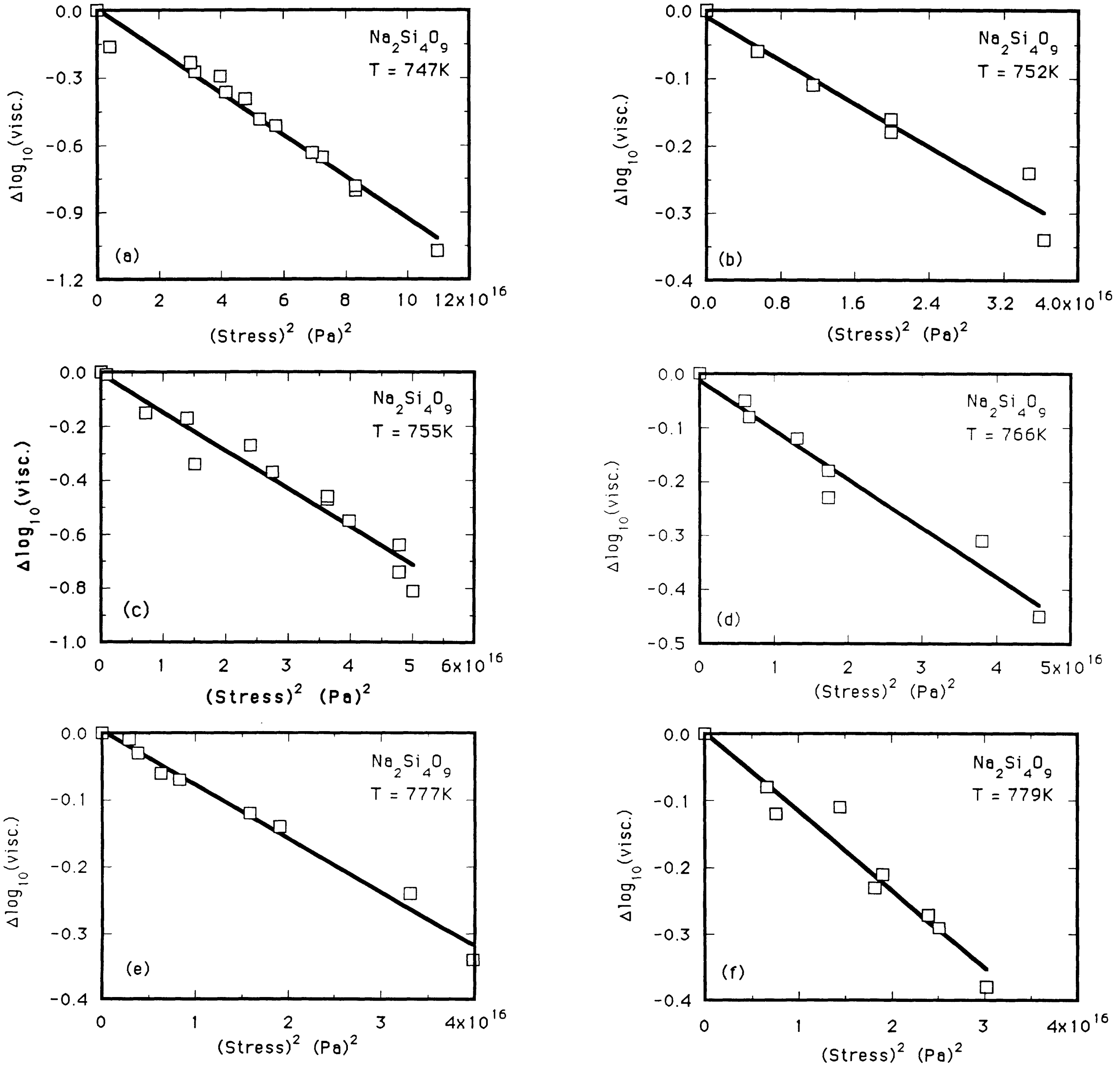

FIG. 1. (a)–(f) Plots of the observed reduced viscosities (Ref. 7) for liquid $Na_2Si_4O_9$ as a function of applied stress (Pa) at different temperatures.

TABLE II. Quality of fit of Eq. (10) to data (Ref. 7) and calculated values for E.

Temp (K)	a	$b(10^{-16}\ \mathrm{Pa}^{-2})$	R^2	E (GPa)
747.15	+0.007	−0.0934	0.971	2.78
752.15	−0.010	−0.0799	0.945	2.66
755.15	−0.006	−0.1415	0.946	1.53
766.15	−0.013	−0.0910	0.954	2.24
777.15	−0.000	−0.0804	0.986	2.59
779.15	+0.002	−0.1178	0.949	1.70

1(a)–1(f), when one takes into consideration the precision of the experiments.

III. DISCUSSION AND CONCLUSIONS

The proposed model requires the transformation of an elastic deformation into a viscous one. It has been pointed out[13] that such a conversion can be observed when an elastically deformed liquid is allowed to relax its internal structure, while the deformation is kept constant. The time constant for this process can be obtained by means of Eq. (3).

The obtained results listed in Table II show that Eq. (10) reproduces quite well the measured values. An anonymous referee suggested the possibility that the stress squared relationship is only apparent because of the rather small stress intervals over which the experiments could be performed.[7] To check this suggestion the data were also fitted to equations analogous to (10) except that the stress dependence was linear or cubic. In all cases the fit was significantly less good, at $T=747$ K [Fig. 1(a)] the squared correlation coefficient decreased from 0.97 (see Table II) to 0.77 for the linear case, while for the cubic one the constant term a became too large. More direct evidence in favor of the proposed proportionality between the logarithmic values of reduced viscosities and the squared value of the applied stress is shown in Fig. 2 for a rhyolitic melt close to its glass transition range. Webb and Dingwell[8] reported reduced viscosity observations for this substance over a stress range of 370 MPa. Equation (8) can be expressed easily in the form of Eq. (1), which is valid for all the recent observations of the non-Newtonian rheology of silicate liquids under high stress or experiencing large strain rates.

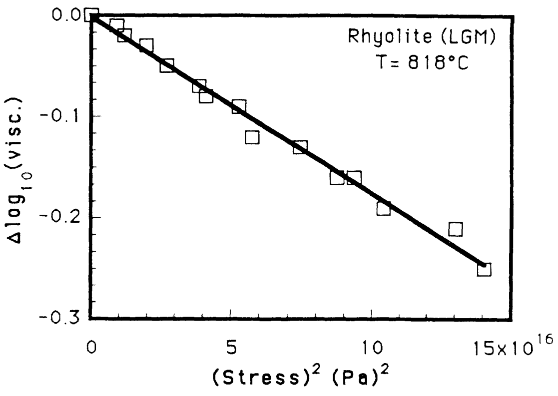

FIG. 2. Logarithmic values of the reduced viscosity of a rhyolitic melt as a function of the applied stress, based on the viscosity measurements of Webb and Dingwell (Ref. 8).

The values obtained for b, Eq. (10), can be used to calculate the elastic modulus for $Na_2Si_4O_9$ at temperatures of about 760 K, see Table II. These listed values of E do not evidence a temperature dependence. This is not surprising in view of the noise in the input data and the smallness of the temperature interval. The calculated average value of the elastic modulus cannot be verified because no experimental measurements of this modulus at temperatures close to the glass transition and for stresses up to 300 MPa seem to have been published for liquid $Na_2Si_4O_9$.

The calculated value of E depends on b [Eq. (10)], and on the variables occurring in Eq. (9), B_e, V_m, and S_{conf}, which are fairly well known. Possibly B_e is stress dependent; this case was not considered by Adam and Gibbs,[10] but if true this dependence should be taken into account, thus

$$\ln(\eta/\eta_0)=B_e\{(-\Delta S_{\mathrm{conf}}/S_{\mathrm{conf}})+(\Delta B_e/B_e)\}/(TS_{\mathrm{conf}}) \tag{11}$$

with

$$\Delta B_e=B_e(\sigma)-B_e(\sigma=0)\ .$$

As before $|\Delta S_{\mathrm{conf}}| \ll S_{\mathrm{conf}}|$, but also $|\Delta B_e| \ll |B_e|$ and according to Adam and Gibbs

$$B_e=\Delta\mu\sigma^*_{\mathrm{conf}}/k_B\ , \tag{12}$$

where $\Delta\mu$ is the potential energy hindering the cooperative rearrangement per flow unit in the liquid, $\sigma^*_{\mathrm{const}}$ is the configurational entropy of a minimal volume of liquid permitting a structural rearrangement, and k_B is Boltzmann's constant. Because $B_e(\sigma)<B_e(\sigma=0)$, the relaxed value of E calculated with Eq. (11) should be larger than calculated with Eq. (8), where the possible stress dependence of B_e has been ignored. It is likely that ΔB_e is also proportional to σ^2 and thus the fit of Eq. (10) to the experimental data[7] will not be affected.

Heyes *et al.*[23] have published a molecular-dynamics (MD) simulation of a 108 Lennard-Jones (LJ) particles system at constant temperature and volume under different values of applied shear stress. Results were given for the system being in a noncompressed state and when it is 10, 20, and 50% compressed. The four observations for the noncompressed system evidence a linear dependence of the logarithmic reduced viscosity on the squared value of the nondimensional applied stress once the steady state is reached. Figure 3(a) is a plot using these results and offers evidence that the proposed extension of the Adam-Gibbs model can be applied to LJ liquids. The relative variation of the applied stress amounted to a factor of 10, like the relative stress variations in the experiments of Webb and Dingwell.[7] The

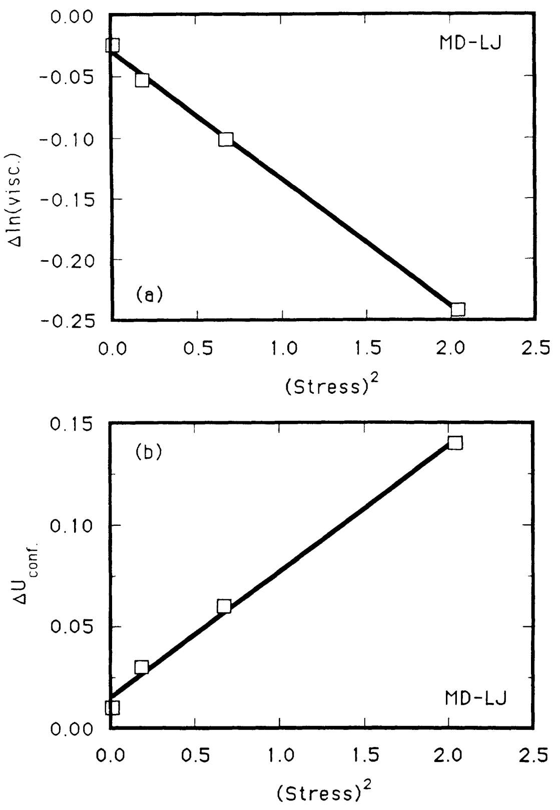

FIG. 3. (a) Logarithmic values of the reduced viscosity versus dimensionless stress (Ref. 23) for MD-LJ liquids. (b) Variation of the dimensionless configurational energy with applied dimensionless stress for a Lennard-Jones liquid at constant temperature, based on the MD results published by Heyes *et al.* (Ref. 23).

MD results[23] for compressed systems were too noisy to be useful for the preset purpose and it seemed doubtful whether or not a steady state was reached.

To derive Eq. (7), it was assumed that all the elastic work done on the isothermal system by the applied stress was transformed into configurational entropy, when the deforming fiber was in a stationary state. The MD results, for the noncompressed system, are in agreement with this hypothesis. This is shown by Fig. 3(b), which is a plot of the calculated increase, relative to the nonstressed system, of the dimensionless configurational entropy given by Heyes *et al.*[23] versus the square of the applied dimensionless stress at constant temperature and volume. The observed linear relationship between the squared stress on the system and the variation of the configurational energy, and thus of the configurational entropy, of the system are most readily accounted for if the herefore mentioned hypothesis is correct.

At the onset of non-Newtonian viscous flow in a soda-lime-silica liquid, Simmons and co-workers[4,5] and Guillemet and Gy[9] observed the occurrence of stress oscillations during constant deformation rate experiments. Similar oscillations were displayed during MD simulations of a Lennard-Jones liquid.[23] This phenomenon could be the result of the interplay between the rate processes involved in the structural relaxation after the occurrence of instantaneous elastic deformation, and another rate process associated with the slower occurring deformation due to delayed elasticity.

The remarkable fit for Eq. (10) to the observational data as well as to the MD calculations suggests strongly that the Adam and Gibbs configurational entropy theory describes correctly the stress dependence of the viscosity of silicate liquids, even if the rheology is non-Newtonian. The rheological behavior of the system is Newtonian as long as the increase is configurational entropy, as given by Eq. (7), is small relative to the configurational entropy of the nonstressed liquid. But when ΔS_{conf} becomes non-negligible with respect to S_{conf}, the viscosity of the liquid becomes stress dependent and smaller than that of the nonstressed system at the same pressure and temperature.

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