

Pressure dependence of viscosity

Jörn W. P. Schmelzer

Institut für Physik der Universität Rostock, Universitätsplatz, 18051 Rostock, Germany and Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13565-905 São Carlos, Sao Paulo, Brazil

Edgar D. Zanotto

Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13565-905 São Carlos, Sao Paulo, Brazil

Vladimir M. Fokin

Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, UFSCar, 13565-905 São Carlos, Sao Paulo, Brazil and S. I. Vavilov State Optical Institute, Uliza Babushkina 36-1, 193171 St. Petersburg, Russia

(Received 3 August 2004; accepted 1 December 2004; published online 11 February 2005)

We reanalyze the pressure dependence of viscosity of liquids of constant composition under isothermal conditions. Based exclusively on very general considerations concerning the relationship between viscosity and “free volume,” we show that, at moderate values of pressure, viscosity increases, as a rule, with increasing pressure, provided the liquid is in stable or metastable (undercooled) equilibrium states. However, even if the behavior of the viscosity is governed by free volume effects, deviations from a positive pressure dependence are possible, when the liquid’s thermal expansion coefficient is negative. We derive an equation that allows one to quantitatively determine the pressure dependence of viscosity, which requires, in the simplest case, only the knowledge of the temperature dependence of viscosity at constant pressure, the thermal expansion coefficient, and the isothermal compressibility of the liquid. As an example, the negative pressure dependence of water in the range of temperatures 0–4 °C and of several silicate liquids, such as albite, jadeite, dacite, basalts, etc., could be explained in such a way. Other glass-forming liquids initially (for moderate pressures) show a positive pressure dependence of viscosity that changes to a negative one when subjected to high (\sim GPa) isostatic pressure. A detailed analysis of water and already mentioned silicate melts at GPa pressures shows that, in addition to free volume effects, other pressure induced structural transformations may have to be accounted for in a variety of cases. By this reason, the theoretical analysis is extended (i) in order to describe the pressure dependence of viscosity for systems that are in frozen-in thermodynamic nonequilibrium states (glasses, i.e., undercooled liquids below the glass transition temperature T_g) and (ii) to systems which undergo, in addition to variations of the free volume, pressure induced changes of other structural parameters. In such cases a decrease of viscosity with increasing pressure may occur, in principle, even if the thermal expansion coefficient is positive. In this way, the present analysis grants a general tool to estimate the pressure dependence of viscosity and supposedly settles the controversy in the current literature. © 2005 American Institute of Physics. [DOI: 10.1063/1.1851510]

I. INTRODUCTION

While the temperature dependence of viscosity at isobaric conditions is well established (the viscosity increases with decreasing temperature), current discussion on the dependence of viscosity on external pressure (at isothermal conditions) shows a spectrum of controversial statements. For example, in Refs. 1–5 it is concluded that the viscosity must increase, as a rule, with increasing pressure and this expectation has been confirmed in a variety of experimental studies.^{1–5} In contrast, the opposite was experimentally found for some glass-forming silicate liquids, such as basalt, dacite, jadeite, and albite^{6–13} and mentioned as a principal possibility (taking as an example the behavior of water) also in Ref. 2. In these cases, a decrease of the viscosity of about one order of magnitude has been reported for pressures increasing by two to five times. For a variety of silicate and alumi-

nosilicate melts, an even more complex nonmonotonic behavior of viscosity in dependence on pressure was found at high pressure in the range of GPa.¹⁴

The mentioned decrease of viscosity with increasing pressure, obtained in certain ranges of pressure and temperature, was denoted as *anomalous* and being in contradiction with the results of “free volume” theories of viscosity.^{10,14} This specification of the negative pressure dependence of viscosity as anomalous indicates that an increase of viscosity with increasing pressure is considered as the rule, but that deviations are also possible. In this way, the question arises on how such kind of behavior can be explained theoretically and whether they are, indeed, exceptions.

One attempt in this direction was put forward by Gupta.¹⁵ Later on, Bottinga and Richet¹⁰ also derived an equation for the pressure dependence of viscosity based on a

generalization of the Adam–Gibbs equation.¹⁶ Gupta concluded that, in most cases of interest, an increase of viscosity with increasing pressure must be expected, although exceptions are possible (according to his approach) when the relaxational expansion coefficient $\Delta\alpha$ —the difference between the thermal expansion coefficient of the equilibrium liquid and the glass at given values of pressure and temperature—is negative. However, to compute the pressure dependence of viscosity the resulting equation requires the knowledge of the differences between the entropies of equilibrium liquid and glass, and the relaxational expansion coefficient. The respective data are seldom available, and for temperatures above the glass transition temperature data are not available, in principle.¹⁰ By this reason, it is of interest to express the pressure dependence of the viscosity by more accessible thermodynamic coefficients, which refer exclusively to the liquid in the actual state considered, avoiding in this way, in addition, some inconsistency inherent in approaches like those followed in Refs. 10 and 15 (see also Sec. VI).

Alternative theoretical approaches connect the decrease of viscosity with structural changes of the respective systems under pressure (coordination changes, Si–O bond weakening, changes of degree of polymerization, changes of Q^n distribution, formation of fivefold and sixfold coordinated Si species, etc.), which are not described appropriately by free volume concepts.^{9–11,14,17–21} For these complex systems, a decrease of the viscosity with pressure is observed as a rule, at least, for sufficiently high (\sim GPa) pressures. In this way, one has to check, first, whether a decrease of viscosity with increasing pressure is, indeed, in contradiction with free volume theories (without favoring any particular viscosity theory) and, second, how to incorporate such additional structural effects generally into the theory independently of the particular mechanism of structural change considered. By above mentioned reasons, and in order to arrive at some solution to the referred controversy on the effects of pressure on viscosity, it is highly interesting to revisit this problem in order to develop a comprehensive picture of this phenomenon. The realization of this task is the aim of the present contribution.

The paper is organized as follows. In Sec. II, we derive an equation determining the pressure dependence of viscosity of multicomponent liquids of constant composition in stable or metastable equilibrium states for the case that free volume variations determine the behavior. This relation connects the kind of response of viscosity on pressure (increase or decrease of viscosity with increasing pressure) with the sign of the thermal expansion coefficient of the liquid. It describes, at least, in a qualitatively correct way the pressure dependence of the viscosity of most liquids at moderate pressures. One exception, the pressure dependence of viscosity of water at moderate pressures, is analyzed in detail in Sec. III. In order to cover also this and similar cases, the basic equation is generalized in order to account for additional structural changes of the system with respect to pressure variations and their effect on viscosity. As a first step, this equation is extended in Sec. IV in order to describe the pressure dependence of the viscosity for systems in “frozen-in” thermodynamic nonequilibrium states (undercooled liquids

below the glass transition temperature, i.e., glasses). In Sec. V, this approach is further generalized giving the possibility to account for the effect of pressure induced changes of the structure of the liquids on the change of viscosity with pressure. As it turns out such mechanisms determine basically the pressure dependence of the viscosity of a variety of glass-forming liquids, in particular, at high pressures (cf., also Ref. 22). A summary of the basic conclusions and discussion of the results (Sec. VI) completes the paper.

II. ANALYSIS: APPLICATION OF FREE VOLUME CONCEPTS

We first consider liquids of constant composition in (stable or metastable) thermodynamic equilibrium states (i.e., above the respective glass transition temperature). According to the Gibbs phase rule, the number of degrees of freedom of the system is equal to 2, and thus one can choose temperature and pressure as the independent variables determining the properties of the system. In such cases, the viscosity η can be considered as a function of pressure and temperature, i.e.,

$$\eta = \eta(p, T). \quad (1)$$

In their extended investigation of similarities and differences of liquid-vapor and liquid-solid phase transitions, Skripov and Faizullin^{4,5} analyzed the dependence of viscosity η on temperature T and pressure p for several classes of liquids. They restricted their analysis to the cases where the thermal expansion coefficient of the liquid is positive (this property is fulfilled at atmospheric pressure for most but not all liquids). The analysis of both literature data and their own results led those authors to conclude that the following relations must be fulfilled

$$\left(\frac{\partial\eta}{\partial T}\right)_p < 0, \quad (2)$$

$$\left(\frac{\partial\eta}{\partial p}\right)_T > 0. \quad (3)$$

These relations imply that the viscosity must decrease with increasing temperature (for isobaric processes), and must increase with increasing pressure (at isothermal conditions). Moreover, considering the viscosity as a function of pressure and temperature, i.e., $\eta = \eta(p, T)$, they wrote down the following identity:

$$\left(\frac{\partial\eta}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_\eta \left(\frac{\partial p}{\partial\eta}\right)_T = -1. \quad (4)$$

Equation (4) follows from purely mathematical considerations and does not involve originally any physics.

Taking into account the viscosity dependencies given by Eqs. (2) and (3), they concluded that the inequality

$$\left(\frac{\partial p}{\partial T}\right)_\eta > 0 \quad (5)$$

must be fulfilled. This equation—appearing here first as a purely mathematical relation—has, of course, a quite definite physical meaning. As mentioned earlier, the viscosity of liq-

uids of constant composition in (stable and metastable) thermodynamic equilibrium states can be considered as a function of two state variables, pressure and temperature, i.e., $\eta = \eta(p, T)$. However, if one considers viscosity as constant [i.e., $\eta = \eta(p, T) = \text{const}$], then this relation gives a dependence between pressure and temperature (at constant viscosity). So Eq. (5) means that—in order for the viscosity to remain constant—an increase of temperature leads to effects which can be compensated by an increase of pressure.

It should be stressed that Eqs. (2) and (3) are corroborated by a variety of experimental results and lead to the theoretical consequence given by Eq. (5). However, one can easily reverse above argumentation. Indeed, taking into account general concepts connecting viscosity with the free volume in the liquid^{4,5,23,24} we can analyze theoretically how the partial derivative $(\partial p / \partial T)_\eta$ should behave. Taking into account, in addition, Eq. (2), one can arrive then at the desired theoretical prediction concerning the pressure dependence of the viscosity.

Indeed, following the classical work of Ya. I. Frenkel,²³ the essence of free volume concepts can be expressed as follows: (i) free volume uniquely determines the value of the viscosity η ; (ii) free volume is uniquely determined by the total volume $V(p, T)$ of the liquid and not by pressure p and temperature T separately. Frenkel mentioned Batchinskij's equation as one example for such type of dependence. The respective ideas have been developed later on by different authors advancing particular models of free volume theories for the dependence of the viscosity on the thermodynamic state parameters. In contrast to such earlier attempts, here we employ only above given essence of free volume concepts without specifying any particular models for viscous flow.

In order to proceed we realize that the free volume of liquids, as a rule, decreases with pressure. This way, in order to reestablish the value of the free volume (and the resulting value of viscosity), one has to vary the temperature to such extent as to compensate the changes of free volume due to the effect of pressure. Consequently, from such general theoretical considerations, one arrives directly at the inequality Eq. (5), but now independently of the knowledge of experimental data. Taking exclusively the dependence given by Eq. (2) from experiment, we then arrive, utilizing Eq. (4), at Eq. (3). In this way, employing only general concepts connecting viscosity with free volume of the liquid (and assuming the absence of any other structural changes in addition to densification) we can conclude that, in isothermal conditions, the viscosity has to increase, as a rule, with increasing pressure. However, exceptions from this general rule are possible, as will become evident from the following quantitative analysis.

In addition to the qualitative conclusions given above, one can easily formulate a method to quantitatively estimate the pressure dependence of viscosity (in isothermal conditions) provided the temperature dependence of viscosity (at constant pressure) and some other purely thermodynamic characteristics of the liquid are known. Indeed, according to above analysis, we may connect variations in viscosity with variations of free volume and suppose that the free volume is uniquely connected with the total volume of the system.

Then, in order to secure constancy of viscosity, one has to demand that the total volume of the system is kept constant if both pressure and temperature are varied slightly by dT and dp , respectively. From

$$dV(p, T) = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp = 0, \quad (6)$$

we then get the following result

$$\left(\frac{\partial T}{\partial p} \right)_\eta \cong \left(\frac{\partial T}{\partial p} \right)_V = - \frac{\left(\frac{\partial V}{\partial p} \right)_T}{\left(\frac{\partial V}{\partial T} \right)_p}. \quad (7)$$

With Eq. (4), we finally obtain

$$\left(\frac{\partial \eta}{\partial p} \right)_T = \left(\frac{\partial \eta}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_T = - \frac{\kappa_T(p, T)}{\alpha_T(p, T)} \left(\frac{\partial \eta}{\partial T} \right)_p, \quad (8)$$

where κ_T is the isothermal compressibility and α_T the isobaric thermal expansion coefficient, i.e.,

$$\kappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad \alpha_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p. \quad (9)$$

Let us, now, analyze the possible consequences from Eq. (8). For systems in (stable or metastable) thermodynamic equilibrium, the condition of thermodynamic stability

$$\kappa_T = - \left(\frac{\partial p}{\partial V} \right)_T > 0 \quad (10)$$

(or $\kappa_T > 0$) must be fulfilled. Taking into account Eq. (2), it follows that the signs of the derivatives $(\partial T / \partial p)_\eta \cong (\partial T / \partial p)_V$ and $(\partial \eta / \partial p)_T$ are determined by the sign of the thermal expansion coefficient, which is (at atmospheric pressure), as a rule, a positive quantity. In these cases, Eq. (8) predicts an increase of viscosity with increasing pressure. Skripov and Faizullin^{4,5} restricted their analysis to such cases. Consequently, their conclusion is correct as far as this condition is fulfilled.

However, a few substances have negative thermal expansion coefficients in certain ranges of temperature at atmospheric pressure. For these exceptional cases, Eq. (8) predicts a decrease of viscosity with increasing pressure. The best known example is water in the range of temperatures from 0 to 4 °C. In this way, we expect a decrease of viscosity of water with increasing pressure in this temperature range. This conclusion is confirmed, however, as we will see from the analysis in the subsequent section, the situation with respect to the pressure dependence of water is much more complex.

As for water in the temperature range 0–4 °C, mentioned above silicate anomaly, i.e., the decrease of viscosity with increasing pressure experimentally found for a variety of glass-forming silicate liquids, such as basalt, dacite, jadeite, and albite,^{6–13} could be similarly explained provided the thermal expansion coefficients of these systems are negative in the respective ranges of pressure and temperature.

This seems to be the case for lithium disilicate at the considered values of pressure and temperature.²⁵ There are indications that also other glass-forming liquids—such as albite, jadeite, dacite, basalts, etc.—show a negative thermal expansion coefficient when subjected to high (\sim GPa) isostatic pressures. However, to the best of our knowledge, direct experimental measurements of the thermal expansion coefficients of the respective systems in the GPa-pressure range are very rare. Thus, more definite experimental analyses are required before some final conclusions can be drawn on this issue.

Summarizing, we first conclude that free volume concepts do not, in general, forbid a decrease of viscosity with increasing pressure. They lead to such result as well, if the thermal expansion coefficient of the liquid is negative in the respective ranges of pressure and temperature. However, at low and moderate pressures, the thermal expansion coefficient is, in general, a positive quantity and, in such cases, the viscosity should increase with increasing pressure provided the behavior is determined by free-volume effects.

As a second conclusion, we can state: If the viscosity of a liquid decreases with increasing pressure and the thermal expansion coefficient is positive, then the pressure dependence for these anomalously behaving systems cannot be explained, in principle, exclusively by free volume concepts. One example in this respect will be analyzed in detail in the subsequent Sec. III.

The question, “for which classes of liquids free volume concepts in the most general form, as employed here and resulting in Eq. (8), can give a satisfactory description of the pressure dependence of viscosity,” will be addressed in a separate investigation.²⁶ Here we concentrate, in the subsequent analysis, on the solution of the complementary task to establish the general form of the equations describing the pressure dependence of the viscosity if free volume concepts alone are not sufficient (cf., also Ref. 22). In such cases, alternative, more sophisticated approaches must be utilized. A general method to incorporate such additional effects into the theory will be outlined in Sec. V.

III. A FIRST EXCEPTION: WATER

In Figs. 1 and 2, density and thermal expansion coefficients of ordinary water are shown as functions of temperature for different values of pressure in the range 0–20 MPa. At 0 °C, water has negative thermal expansion coefficients in the range of pressures from 0 to 20 MPa. According to Eq. (8), one expects in this range a decrease of viscosity with increasing pressure. This is indeed the case as it follows, for example, from the results shown in Table I. However, it is evident from the same column of Table I that the viscosity of water at 0 °C decreases with increasing pressure also in the range where the isothermal expansion coefficient becomes positive. Consequently, in this range of pressures, Eq. (8) cannot describe the experimental data even qualitatively correctly.

In Figs. 3(a)–3(g), the viscosity of water (in μ Pa s) is shown as a function of pressure (in the range from 0 to 20 MPa) for different values of temperature (in the

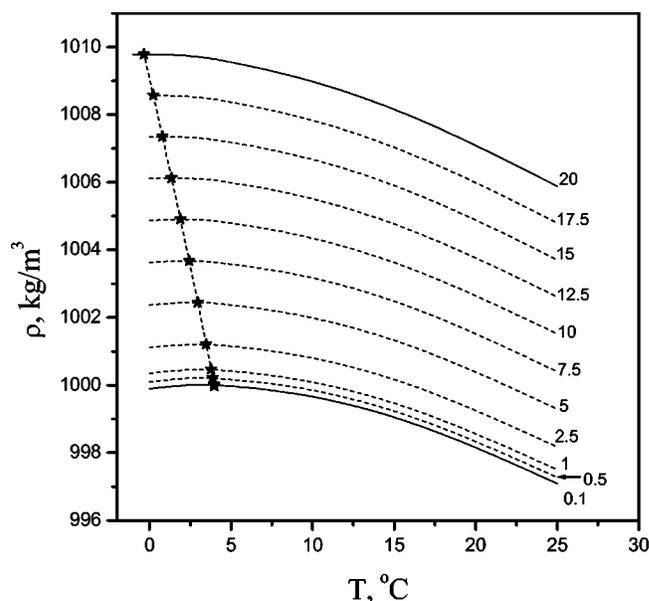


FIG. 1. Density of water vs temperature at different pressures (in MPa) as specified in the figure (Ref. 27). The line crossing the curves obtained for different pressures specifies the location of the density maximum. At the left-hand side of this line, the thermal expansion coefficient is negative. To the right-hand side of this line, the thermal expansion coefficient is positive.

range from 0 to 25 °C). In the whole range of temperature and pressure considered here, the slope $(d\eta/dp)_T$ of the curves $\eta = \eta(p, T = \text{const})$ does not depend on pressure and is exclusively a function of temperature. Latter dependence is illustrated in Fig. 3(h). As it turns out, the absolute value of the slope of the curves $\eta = \eta(p, T = \text{const})$ decreases with increasing temperature.

Figure 4 shows the viscosity of water as a function of pressure for wider ranges of the thermodynamic state parameters (pressure values in the range from 0 to 100 MPa and temperatures 0 and 25 °C). As evident from the figure, with an increase of temperature, the dependence of the viscosity on pressure changes qualitatively and a minimum occurs (illustrated in the figure for the temperature 25 °C). For values

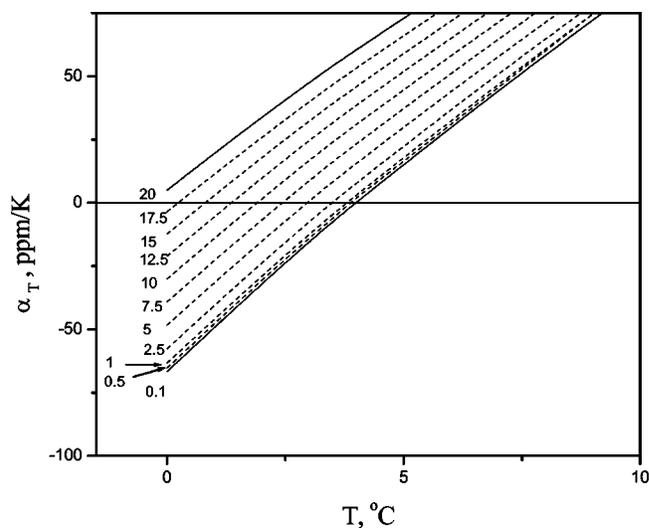


FIG. 2. Thermal expansion coefficient of water as a function of temperature at different pressures (in MPa) as specified in the figure (Ref. 27).

TABLE I. Values of the viscosity (in $\mu\text{Pa s}$) of ordinary water obtained with the aid of the recommended interpolation equation as a function of pressure (in MPa) and temperature (in $^{\circ}\text{C}$). Data are taken from Ref. 28. Note that, at high temperatures, some of the data refer to water vapor.

P (MPa)	Temperature ($^{\circ}\text{C}$)										
	0	25	50	75	100	150	200	250	300	350	375
0.1	1792	890.1	546.8	377.7	12.27	14.18	16.18	18.22	20.29	22.37	23.41
0.5	1791	890.0	546.9	377.8	281.8	182.5	16.05	18.14	20.24	22.34	23.39
1	1789	889.9	547.0	378.0	282.0	182.6	15.89	18.05	20.18	22.31	23.37
2.5	1786	889.5	547.3	378.4	282.4	183.0	134.6	17.76	20.02	22.23	23.31
5	1780	889.0	547.7	379.0	283.1	183.6	135.2	106.4	19.80	22.13	23.26
7.5	1774	888.5	548.2	379.7	283.7	184.2	135.8	107.1	19.66	22.09	23.26
10	1768	888.0	548.6	380.3	284.4	184.9	136.4	107.8	19.66	22.15	23.33
12.5	1762	887.6	549.1	381.0	285.1	185.5	137.0	108.4	87.42	22.37	23.51
15	1757	887.1	549.6	381.6	285.7	186.1	137.6	109.1	88.33	22.94	23.86
17.5	1752	886.8	550.1	382.3	286.4	186.7	138.2	109.8	89.21	66.99	24.51
20	1747	886.4	550.6	382.9	287.1	187.3	138.8	110.4	90.05	69.31	25.92
22.5	1742	886.1	551.1	383.6	287.7	187.9	139.4	111.0	90.86	71.17	47.79
25	1737	885.8	551.6	384.3	288.4	188.6	140.0	111.6	91.65	72.76	58.25
27.5	1732	885.5	552.1	384.9	289.1	189.2	140.6	112.2	92.41	74.18	61.97
30	1728	885.3	552.6	385.6	289.7	189.8	141.1	112.9	93.15	75.46	64.56
35	1719	884.9	553.7	386.9	291.1	191.0	142.3	114.0	94.58	77.74	68.36
40	1711	884.7	554.8	388.3	292.4	192.2	143.4	115.2	95.93	79.75	71.28
45	1704	884.5	556.0	389.7	293.7	193.4	144.5	116.3	97.23	81.56	73.71
50	1697	884.5	557.2	391.0	295.1	194.6	145.6	117.4	98.48	83.23	75.83
55	1690	884.6	558.4	392.4	296.4	195.7	146.7	118.5	99.69	84.78	77.73
60	1684	884.7	559.6	393.8	297.7	196.9	147.8	119.6	100.9	86.24	79.46
65	1679	885.0	560.9	395.2	299.1	198.1	148.8	120.6	102.0	87.62	81.06
70	1673	885.4	562.2	396.6	300.4	199.2	149.9	121.6	103.1	88.93	82.56
75	1669	885.9	563.5	398.0	301.7	200.4	150.9	122.7	104.1	90.17	83.97
80	1665	886.4	564.9	399.4	303.1	201.5	151.9	123.6	105.2	91.37	85.30
85	1661	887.1	566.3	400.8	304.4	202.6	153.0	124.6	106.2	92.52	86.57
90	1658	887.9	567.7	402.3	305.7	203.8	154.0	125.6	107.2	93.63	87.78
95	1655	888.7	569.1	403.7	307.0	204.9	155.0	126.5	108.2	94.70	88.94
100	1652	889.7	570.6	405.1	308.4	206.0	155.9	127.5	109.1	95.74	90.06

of pressure above those corresponding to this minimum, the viscosity behaves in the “normal” way, i.e., increases with increasing pressure. With a further increase of temperature, this minimum is shifted to lower values of pressure and disappears at all. Such situation is found, for example, at a temperature 40°C (and also for the temperatures $T \geq 50^{\circ}\text{C}$ shown in Table I). At these temperatures, the thermal expansion coefficient of water is positive and the viscosity of water increases with increasing pressure. In this temperature range, Eq. (8) gives a qualitatively correct description of the pressure dependence of the viscosity also for water. By this reason it is of interest to check to which extent Eq. (8) can give a quantitatively correct description.

A quantitative comparison of theoretical [based on Eq. (8)] and experimental results is shown in Figs. 5(a) and 5(b) for two temperatures, 40 and 150°C . In these figures, the results of computation of the product $[-(\kappa_T/\alpha_T)(\partial\eta/\partial T)_p]$ are shown by dashed lines [cf., Eq. (8)]. The data required for the computations are taken from Refs. 27 and 28. The full curves refer to the value of the quantity $(\partial\eta/\partial p)_T$ determined directly from experimental data on the dependence of viscosity on pressure and temperature of water as given in Ref. 28. As it turns out, for water the theoretical expression, based

exclusively on free volume concepts, leads to quantitative deviations with experimental data up to one order of magnitude. However, as evident from the figures as well, these deviations decrease with increasing pressure and temperature. Such behavior can be interpreted as a consequence of diminishing importance of structural rearrangements of water with increasing pressure and temperature in favor of free volume effects.

Summarizing the results of the analysis for the pressure dependence of the viscosity of water, we conclude that free volume effects alone are obviously not sufficient to give a correct interpretation of the dependencies observed. Consequently, one can expect the occurrence of similar effects also for other classes of liquids. By these reasons, in the subsequent sections we generalize Eq. (8) to account for the effects of variations of other structural parameters (in addition to free volume effects) on the pressure dependence of the viscosity.

IV. A FIRST GENERALIZATION: VISCOSITY OF GLASS-FORMING LIQUIDS IN FROZEN-IN NONEQUILIBRIUM STATES

So far, we have considered liquids in stable or metastable equilibrium states. However, in treating the behavior

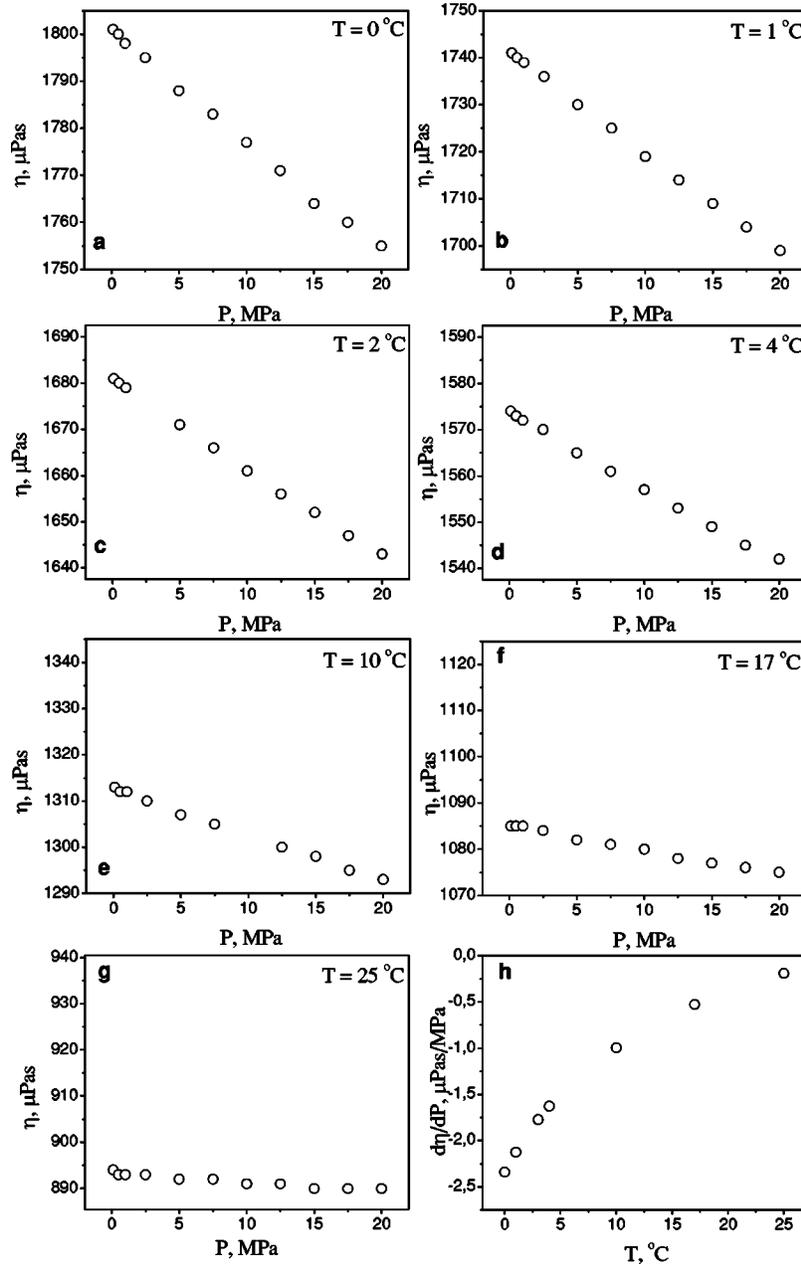


FIG. 3. Viscosity of water (in $\mu\text{Pa}\cdot\text{s}$) vs pressure (in the range from 0 to 20 MPa) for different values of temperature (in the range from 0 to 25°C) as indicated in the figures (a)–(g) and slope $(d\eta/dp)_T$ of the curves $\eta = \eta(p, T = \text{const})$ as a function of temperature (h).

of glass-forming melts near and, in particular, below the glass transition temperature, the concept of nonequilibrium (isostructural) viscosity gains importance.^{11,24,29–31} Such concepts apply if we deal with a glass (a frozen-in nonequilibrium state) which did not reach the respective metastable state yet. Also for such systems, it is obviously of interest to study the pressure dependence of viscosity.

In order to treat theoretically the dependence of the non-equilibrium viscosity on pressure, Eq. (1) must be modified. In the simplest approach, we can assume that the viscosity depends, in addition to pressure and temperature, on one additional order parameter ξ , which is a measure of the deviation of the state of the glass from the state of the respective metastable liquid (see, e.g., Ref. 24). In such cases, we have instead of Eq. (1),

$$\eta = \eta(p, T, \xi). \quad (11)$$

Here we will restrict the analysis to such states where the characteristic times of relaxation processes to the respective stable or metastable equilibrium state are large as compared with the characteristic times of variation of pressure or temperature. In such cases, we can generalize Eq. (4) considering changes of the state parameters T , p , and η of the system, the value of the order parameter ξ being fixed. We then get

$$\left(\frac{\partial\eta}{\partial T}\right)_{p,\xi} \left(\frac{\partial T}{\partial p}\right)_{\eta,\xi} \left(\frac{\partial p}{\partial\eta}\right)_{T,\xi} = -1. \quad (12)$$

Instead of Eqs. (6)–(8), we then obtain

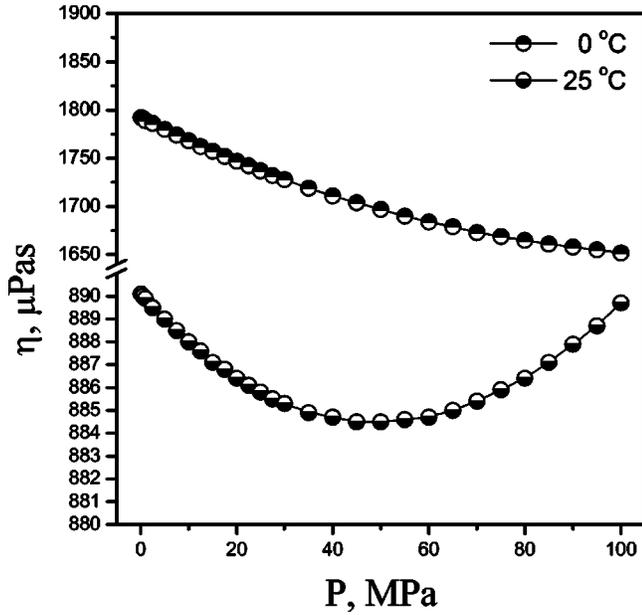


FIG. 4. Viscosity of water as a function of pressure (in the range from 0 to 100 MPa) at 0 and 25 °C.

$$dV(p, T, \xi) = \left(\frac{\partial V}{\partial T} \right)_{p, \xi} dT + \left(\frac{\partial V}{\partial p} \right)_{T, \xi} dp + \left(\frac{\partial V}{\partial \xi} \right)_{p, T} d\xi = 0, \quad (13)$$

$$\left(\frac{\partial T}{\partial p} \right)_{\eta, \xi} \cong \left(\frac{\partial T}{\partial p} \right)_{V, \xi} = - \frac{\left(\frac{\partial V}{\partial p} \right)_{T, \xi}}{\left(\frac{\partial V}{\partial T} \right)_{p, \xi}}, \quad (14)$$

$$\left(\frac{\partial \eta}{\partial p} \right)_{T, \xi} = \left(\frac{\partial \eta}{\partial T} \right)_{p, \xi} \left(\frac{\partial V}{\partial p} \right)_{T, \xi} = - \frac{\kappa_{T, \xi}(p, T, \xi)}{\alpha_{T, \xi}(p, T, \xi)} \left(\frac{\partial \eta}{\partial T} \right)_{p, \xi}. \quad (15)$$

The derivations can be performed similarly with identical results if ξ is replaced by a set of order parameters $\{\xi_i\}$ (cf., Sec. V).

Equation (15) is widely identical to Eq. (8) with the only difference that all quantities entering Eq. (15) now depend on one or a set of additional order parameters. Assuming that Eq. (2) remains valid in a modified form as

$$\left(\frac{\partial \eta}{\partial T} \right)_{p, \xi} < 0, \quad (16)$$

the sign of the pressure dependence of the viscosity is determined, again, by the signs of thermal expansion coefficient and compressibility. As it turns out, the thermal expansion coefficient is, as a rule, a positive quantity, again (cf., Fig. 6), at least, for atmospheric pressures.

One should note, however, that for the considered case of frozen-in nonequilibrium states the stability condition, Eq. (10), is not necessarily fulfilled (the system is not in a state of a stable thermodynamic equilibrium). This way, devia-

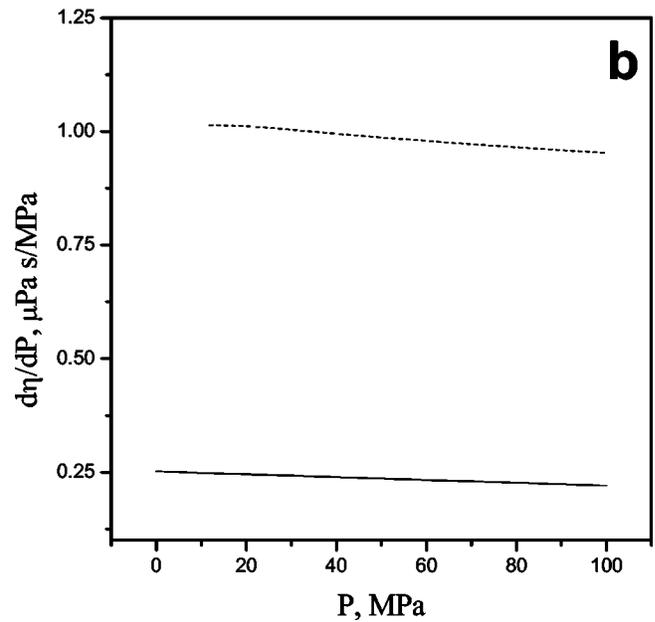
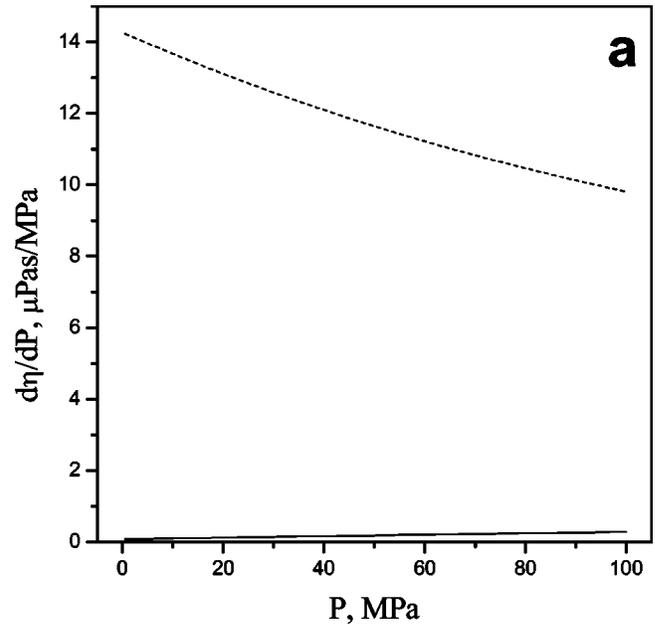


FIG. 5. Quantitative comparison of theoretical [based on Eq. (8)] and experimental results for the pressure dependence of the viscosity of water at 40 °C (a) and 150 °C (b). The results of computation of the product $[-(\kappa_T/\alpha_T)(\partial\eta/\partial T)_p]$ (cf., Eq. (8)) are shown by dashed lines. The full curve refers to the value of the quantity $(\partial\eta/\partial p)_T$ determined directly based on experimental data on the dependence of viscosity of water on pressure and temperature as given in Ref. 28. The values of α_T , κ_T , and the density of water, required for the computations were taken from Ref. 27.

tions from a positive pressure dependence of the viscosity may also occur when the system is characterized (at positive values of the isothermal expansion coefficient) by positive values of the partial derivative $(\partial V/\partial p)_{T, \xi}$. Whether such cases are indeed realized in nature is a topic for a separate analysis.

V. STRUCTURAL CHANGES OF LIQUIDS AND THEIR EFFECT ON THE PRESSURE DEPENDENCE OF THE VISCOSITY

As outlined in a variety of papers (e.g., Refs. 14 and 17–21), liquids, in general, and silicate melts, in particular,

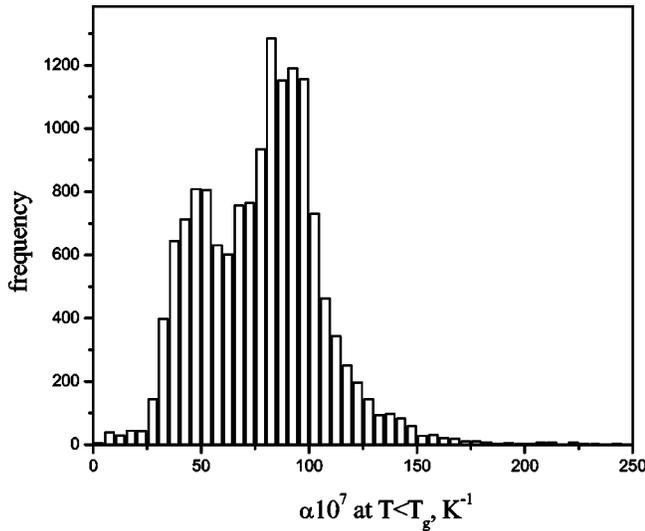


FIG. 6. Frequency distribution histogram of the thermal expansion coefficient α_T for 14 794 silicate glasses below T_g (data are taken from Ref. 32).

can exhibit a variety of additional mechanisms of structural adjustments (change in the degree of polymerization, coordination numbers, frequency of distribution of different structural units, formation of fivefold and sixfold coordinated Si, etc.), when subjected to high isostatic pressures, as compared exclusively with variations of free volume. Such changes occur most easily at sufficiently high temperatures when the liquid is in stable or metastable equilibrium states. For such cases, we have to introduce, at least, one additional state variable describing the change of the mentioned structural properties with pressure. In such cases, the viscosity can be expressed via Eq. (11), again, but now the parameter ξ has to be considered as a unique function of pressure and temperature.

Equations (12)–(15) retain their validity, but the change of viscosity with pressure has now to be written in the form

$$\left(\frac{d\eta}{dp}\right)_T = \left(\frac{\partial\eta}{\partial p}\right)_{T,\xi} + \left(\frac{\partial\eta}{\partial\xi}\right)_T \left(\frac{d\xi}{dp}\right)_T. \quad (17)$$

With Eq. (15) we arrive at

$$\left(\frac{d\eta}{dp}\right)_T = -\frac{\kappa_{T,\xi}(p,T,\xi)}{\alpha_{T,\xi}(p,T,\xi)} \left(\frac{\partial\eta}{\partial T}\right)_{p,\xi} + \left(\frac{\partial\eta}{\partial\xi}\right)_T \left(\frac{d\xi}{dp}\right)_T. \quad (18)$$

The first term on the right-hand side of Eq. (18) describes variations of the viscosity with increasing pressure provided additional structural rearrangements of the melt can be neglected. Latter effect is expressed primarily by the second term and determines, for example, the pressure dependence of viscosity for water at sufficiently low temperatures as discussed in detail in Sec. III.

Let us apply Eq. (18), as an additional example, to silicate melts and assume for this purpose that ξ in Eq. (18) describes the degree of polymerization. In general, one can expect that the viscosity increases then with increasing ξ . However, the degree of polymerization of silicate melts decreases with increasing pressure¹⁰ (at sufficiently high temperatures). By this reason, the second term in Eq. (18) gives a negative contribution which may (and this is very impor-

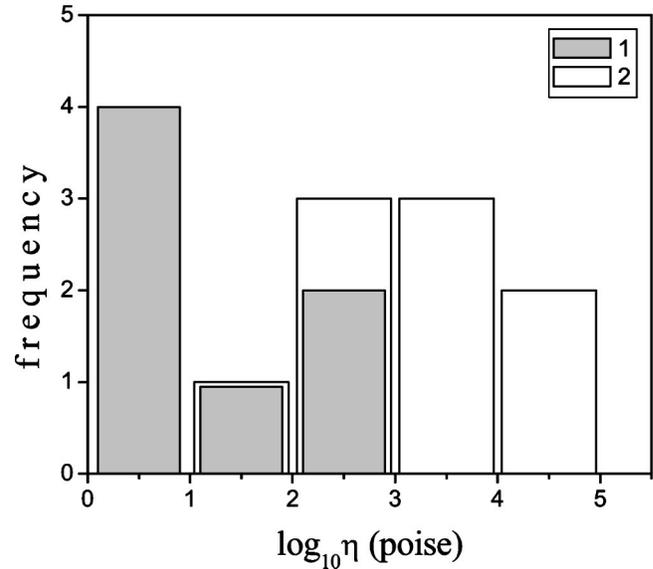


FIG. 7. Frequency distributions of silicate and germanium melts revealing (for pressures $p \leq 1$ GPa) positive (1) and negative (2) pressure dependencies of the viscosity. The independent variable is the viscosity of the respective systems at atmospheric pressure and temperatures above the respective melting temperatures. As it turns out systems with high viscosity show a trend to a negative pressure dependence, i.e., a decrease of viscosity with increasing pressure.

tant) overcompensate the first term. Similarly, in Ref. 33 an increase of viscosity of sulfur with pressure in the GPa range was reported and interpreted as the result of gradual structural changes (changing content of S_8 rings and variations of the degree of polymerization³⁴).

Note, however, that—since the second term in Eq. (18) is proportional to $(d\xi/dp)$ —it is effective only, if, in addition to free volume variations, structural changes occur (i.e., as far as ξ changes with variations of pressure). By this reason, the second term will become active in the course of increase of pressure only as far as pressure induced structural adjustments start to take place. In addition, we can expect from Eq. (18) that after some pressure interval—where the structural reorganization process proceeds—is overcome, the behavior is, again, determined by free “volume effects” with a normal increase of viscosity with a further pressure increase. Such switching from anormal to normal behavior (as well as the opposite switch from normal to anormal reaction with respect to pressure changes) is found, indeed, in a variety of silicate and aluminosilicate melts¹⁴ and, again, in the particular case of water analyzed in Sec. III.

Data on the pressure dependence of viscosity of silicate melts, given in Ref. 14, show another interesting feature demonstrated in Fig. 7. This figure shows the frequency distributions of melts having positive or negative pressure dependencies at atmospheric pressures and temperatures above the respective melting temperatures T_m . As the ordinate, the viscosity at atmospheric pressure is chosen. Despite the poor statistics, this distribution indicates the existence of a correlation between the value of the viscosity and the response to pressure variations: the higher the melt viscosity, the higher the probability of a negative pressure dependence. This trend may be caused by negative thermal expansion coefficients or

by the breakdown of free volume concepts. Indeed, high viscosities may be connected with low values of free volume. As a result, further increases of pressure cannot affect this parameter any more and other types of structural rearrangements gain importance. In this way, one can suggest the hypothesis that, for a variety of complex liquids (where other types of structural adjustments in addition to free volume may occur) with an increase of pressure—as a rule—a change from positive (governed by free volume) to a negative (governed by other types of structural adjustments) pressure dependence of the viscosity may be expected. Such kind of behavior is, indeed, observed for silicate melts¹⁴ where the respective structural rearrangements result in a decrease of viscosity. Following ideas similar to the principle of le Chatelier–Brown in thermodynamics, one may expect that this kind of behavior—decrease of viscosity resulting from structural reorganization—is dominating, but exceptions from this rule—i.e., structural reorganization leading to a further increase of viscosity—cannot be excluded.

One should note as well that the occurrence of additional structural rearrangements has an effect also on the first term on the right-hand side of Eq. (18). The quantities entering this term refer to the respective thermodynamic coefficients and kinetic parameters at constant values of the structure parameter ξ . However, in the course of the measurements such structural variations will also take place, as a rule, and will affect the values of these quantities. Taking into account these considerations, according to Eq. (9), we now have

$$\begin{aligned}\kappa_T &= -\frac{1}{V}\left(\frac{dV}{dp}\right)_T = -\frac{1}{V}\left\{\left(\frac{\partial V}{\partial p}\right)_{T,\xi} + \left(\frac{\partial V}{\partial \xi}\right)_T \frac{d\xi}{dp}\right\} \\ &= \kappa_{T,\xi} - \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_T \left(\frac{d\xi}{dp}\right)_T,\end{aligned}\quad (19)$$

$$\begin{aligned}\alpha_T &= \frac{1}{V}\left(\frac{dV}{dT}\right)_p = \frac{1}{V}\left\{\left(\frac{\partial V}{\partial T}\right)_{p,\xi} + \left(\frac{\partial V}{\partial \xi}\right)_p \frac{d\xi}{dT}\right\} \\ &= \alpha_{T,\xi} + \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_p \left(\frac{d\xi}{dT}\right)_p.\end{aligned}\quad (20)$$

While in the considered case the compressibility κ_T , measured experimentally and determining the response of the system to changes of pressure at constant temperature, is positive (thermodynamic stability condition), the coefficient $\kappa_{T,\xi}$ does not necessarily fulfill such condition.

The above given equations can be generalized to the case when several independent structural rearrangements of the liquid occur as a result of a pressure increase. In such case, we have to introduce a set of additional order parameters $\{\xi\} = \xi_1, \xi_2, \dots$ and Eq. (18) takes the form

$$\left(\frac{d\eta}{dp}\right)_T = -\frac{\kappa_{T,\{\xi\}}(p, T, \{\xi\})}{\alpha_{T,\{\xi\}}(p, T, \{\xi\})} \left(\frac{\partial \eta}{\partial T}\right)_{p,\{\xi\}} + \sum_i \left(\frac{\partial \eta}{\partial \xi_i}\right)_T \left(\frac{d\xi_i}{dp}\right)_T.\quad (21)$$

Employing Eq. (17) and a similar relation for the derivative $(d\eta/dT)_p$ and utilizing, in addition, Eq. (15), we can rewrite Eq. (18) as

$$\left(\frac{d\eta}{dp}\right)_T = -\frac{\kappa_{T,\xi}(T, p, \xi)}{\alpha_{T,\xi}(T, p, \xi)} \left\{ \frac{1 + \left[\left(\frac{\partial \eta}{\partial \xi}\right)_{p,T} / \left(\frac{\partial \eta}{\partial T}\right)_{p,\xi} \right] \left(\frac{d\xi}{dT}\right)_p}{1 + \left[\left(\frac{\partial \eta}{\partial \xi}\right)_{p,T} / \left(\frac{\partial \eta}{\partial p}\right)_{T,\xi} \right] \left(\frac{d\xi}{dp}\right)_T} \right\} \left(\frac{d\eta}{dT}\right)_p.\quad (22)$$

This equation can be generalized similarly to Eq. (21), when several order parameters have to be incorporated into the description. It shows that, in the general case, the pressure dependence of viscosity is not exclusively expressed by compressibility and thermal expansion coefficient (reflecting free volume concepts), but also by the reaction of the system to other types of structural adjustments to pressure variation. In case that such additional processes do not occur, we obtain from Eq. (22), as a special case, Eq. (8), again.

VI. DISCUSSION

The equation for the pressure dependence of viscosity, derived by Gupta,¹⁵ has the form

$$\begin{aligned}\left(\frac{\partial \ln \eta}{\partial p}\right)_T &= \frac{CV(T, p)\Delta\alpha(T, p)}{T(\Delta S(T, p))^2} \\ &= \ln\left(\frac{\eta}{\eta_0}\right) \left\{ \frac{V(T, p)\Delta\alpha(T, p)}{|\Delta S(T, p)|} \right\},\end{aligned}\quad (23)$$

where ΔS is the entropy difference between the equilibrium melt and the glass, $\Delta\alpha$ the relaxational expansion coefficient (the difference between the thermal expansion coefficients between the equilibrium melt and the glass), and C a coefficient in the expression for the dependence of viscosity on the state parameters in the Adams–Gibbs model.^{15,16}

According to this expression, the sign of the temperature dependence of the viscosity is determined by the sign of the relaxational expansion coefficient. Gupta noted that this relation could be confirmed directly only for water in the range of temperatures from 1 to 4 °C, for which $\Delta\alpha$ is known and fulfills the condition $\Delta\alpha < 0$ and the viscosity indeed de-

creases with increasing pressure. As discussed here earlier in detail, this result—a decrease of the viscosity of water with increasing pressure—also follows directly from Eq. (8). In this case, this result is a consequence of negative thermal expansion coefficients of water in the range of temperatures 0–4 °C, where this condition is fulfilled. So both approaches allow one to predict a decrease of viscosity with increasing pressure and in both approaches such kind of behavior is connected with specific properties of the thermal expansion coefficient. However, we already mentioned that water exhibits a decrease of viscosity for wider ranges of pressure and temperature, where the thermal expansion coefficient is positive. It would be interesting to check Gupta's equation also for these broader ranges of thermodynamic state parameters. However, such task will meet, at part, principal difficulties discussed below.

A comparison of both approaches shows that Eq. (8) seems to be more satisfactory from a theoretical point of view than Eq. (23). Equation (8) connects the properties of a given system exclusively with other thermodynamic and kinetic properties of the system in the same state. In contrast, Eq. (23) involves differences between the properties of the equilibrium liquid and the glassy states. Such result is in contradiction with basic assumptions of thermodynamics, where, commonly, relationships are developed between different properties at the same state of the system without any reference to alternative possible states. Moreover, as mentioned in Ref. 10 in application to silicate glasses, there is no way to measure the coefficient of thermal expansion of the respective glass at temperatures above the glass transition.

We have shown in this paper that free volume concepts allow both an increase and decrease of viscosity with increasing pressure. The type of dependence is hereby determined by the sign of the thermal expansion coefficient. Since, in most cases of interest (at atmospheric pressures), the thermal expansion coefficient is positive, commonly the normal behavior, i.e., an increase of viscosity with increasing pressure is observed. However, the situation can become quite different for complex liquids and, in particular, at pressures in the GPa range and sufficiently high temperatures. Here reliable experimental data on the value of the thermal expansion coefficients are, to our knowledge, so far not available. As also demonstrated here, similar dependencies govern the behavior of the pressure dependence of liquids not only for liquids in stable and metastable equilibrium, but, with the limitations above discussed, they are also valid for glasses (liquids in frozen-in nonequilibrium states).

As a generalization, equations have been developed allowing one to incorporate the effect of additional structural variations of the liquids under consideration, which are not reflected by free volume concepts, on the form of the pressure dependence of the viscosity. These relations may result in a negative pressure dependence of the viscosity even in cases if the thermal expansion coefficient $\alpha_{T,\xi}$ is positive. They contain additional terms, which are effective, however, only in ranges of pressures and temperatures, where such additional structural changes indeed occur. By this reason, the respective equations allow one to predict an increase, a decrease and a nonmonotonic behavior of viscosity with

pressure, and cover all types of dependencies found in experimental analyses. Vice versa, latter behavior can be considered therefore as a strong indication of the existence of structural transformations in the liquid in the considered range of thermodynamic state parameters.

Summarizing the results of the analysis, we have shown from general assumptions concerning the dependence of free volume of liquids and viscosity that—at isothermal conditions and moderate pressures—the viscosity of simple liquids typically increases with pressure. In contrast, complex liquids, such as molten silicates, either show a negative pressure dependence starting from small pressures or change from a positive to a negative dependence at some sufficiently high threshold pressure. An equation is derived that allows one to determine the dependence of viscosity on pressure, provided (in the simplest case) that the temperature dependence of viscosity, the isothermal compressibility, and the isobaric thermal expansion coefficient of the liquid are known. This equation can be generalized to situations, when, in addition to free volume effects, other mechanisms of structural reorganization of the liquid with respect to pressure variations exist. In such situation, increases, decreases, and nonmonotonic behavior of viscosity with respect to pressure variations exist.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to the Deutsche Forschungsgemeinschaft (DFG), and to the State of São Paulo Research Foundation, FAPESP (Grant Nos. 99/00871-2, 03/12617-0, and 03/03575-2), CNPq, and Pronex for financial support. The discussions with Tihana Fuss (UMR, Rolla, USA) and the valuable help of M. L. F. Nascimento (LaMaV, UFSCar, Brazil) in data mining are deeply appreciated. The authors would like to express their thanks also to R. Feistel (Institut für Ostseeforschung, Rostock-Warnemünde, Germany) for supplying them with comprehensive sets of kinetic and thermodynamic data for water.

¹M. J. Aziz, E. Nygren, J. F. Hays, and D. Turnbull, *J. Appl. Phys.* **57**, 2233 (1985).

²I. Gutzow, B. Durschang, and C. Rüssel, *J. Mater. Sci.* **32**, 5389 (1997).

³I. Avramov, *J. Non-Cryst. Solids* **262**, 258 (2000).

⁴V. P. Skripov and M. Z. Faizullin, *Crystal-Liquid-Gas Phase Transitions and Thermodynamic Similarity* (Fizmatlit, Moscow, 2003) (English translation is in preparation).

⁵V. P. Skripov and M. Z. Faizullin, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer (Wiley-VCH, Berlin, 2005).

⁶H. Watanabe, *J. Phys. Earth* **323**, 333 (1975).

⁷I. Kushiro, *J. Geophys. Res.* **81**, 6347 (1976).

⁸I. Kushiro, H. S. Yoder, and B. O. Mysen, *J. Geophys. Res.* **81**, 6351 (1976).

⁹C. M. Scarfe, B. O. Mysen, and D. Virgo, in *Magmatic Processes: Physicochemical Principles*, edited by B. O. Mysen (The Geochemical Society, University Park, PA, 1987), Special Publication No. 1, p. 59.

¹⁰Y. Bottinga and P. Richet, *Geochim. Cosmochim. Acta* **59**, 2725 (1995).

¹¹P. Richet and Y. Bottinga, *Rev. Mineral.* **32**, 67 (1995).

¹²S. Mori, E. Ontani, and A. Suzuki, *Earth Planet. Sci. Lett.* **175**, 87 (2000).

¹³D. Tinker, C. E. Lesher, G. M. Baxter, T. Uchida, and Y. Wang, *Am. Mineral.* (to be published).

¹⁴G. H. Wolf and P. F. McMillan, *Rev. Mineral.* **32**, 507 (1995).

¹⁵P. K. Gupta, *J. Am. Ceram. Soc.* **70**, C-152 (1987).

¹⁶G. Adams and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).

¹⁷J. F. Stebbins and P. F. McMillan, *Am. Mineral.* **74**, 965 (1989).

¹⁸H. S. Waff, *Geophys. Res. Lett.* **2**, 193 (1975).

- ¹⁹L. V. Woodcock, C. A. Angell, and P. Cheeseman, *J. Chem. Phys.* **65**, 1565 (1976).
- ²⁰S. K. Sharma, D. Virgo, and I. Kushiro, *J. Non-Cryst. Solids* **33**, 235 (1979).
- ²¹X. Xue, J. F. Stebbins, M. Kanzaki, P. F. McMillan, and B. Poe, *Am. Mineral.* **76**, 8 (1991).
- ²²M. L. Ferrer, C. Lawrence, D. Kivelson, C. Alba-Simionescu, and G. Tarjus, *J. Chem. Phys.* **109**, 8010 (1998).
- ²³Ya. I. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, Oxford, 1946).
- ²⁴I. Gutzow and J. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization* (Springer, Berlin, 1995).
- ²⁵T. Fuss (private communication).
- ²⁶J. W. P. Schmelzer, I. Avramov, E. D. Zanutto, and V. M. Fokin (unpublished).
- ²⁷R. Feistel and E. Hagen, *Prog. Oceanogr.* **36**, 249 (1995); in addition, the PC-program *Seawater.exe* was employed (available via <http://www.io-warnemuende.de>) supplied by courtesy of R. Feistel.
- ²⁸International Association for the Properties of Water and Steam. Revised Release of the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance, 2003.
- ²⁹O. V. Mazurin, Y. K. Startsev, and S. V. Stoljar, *J. Non-Cryst. Solids* **53**, 105 (1982).
- ³⁰E. D. Zanutto and P. K. Gupta, *Am. J. Phys.* **67**, 260 (1999).
- ³¹O. V. Mazurin, *Vitrification* (Nauka, Leningrad, 1986) (in Russian).
- ³²Electronic database SCIGLASS, version 5.0, published by SciGlass, 2002.
- ³³H. Terasaki, T. Kato, F. Funakoshi, A. Suzuki, and S. Urakawa, *J. Phys.: Condens. Matter* **16**, 1707 (2004).
- ³⁴A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **81**, 780 (1959).