Pressure and temperature dependence of viscosity of glassforming and of geoscientifically relevant systems

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Abstract

The paper discusses a model of viscosity η of glassforming melts in an attempt to predict the dependence of η on temperature T and on pressure P. The equation, derived here, describes with excellent accuracy all existing experimental viscosity data including those of glassforming melts, igneous materials and polymers. It is demonstrated that the activation energy $E(T_g)$ can be expressed through the glass transition temperature T_g as $E(T_g) = \varepsilon R T_g$ where $\varepsilon R = 260 \pm 10\%$ in J/(mol K). The dependencies of the parameters of the viscosity equation are discussed for certain geoscientifically relevant systems.

According to the model the relaxation time of the mantle is about 32 000 years, a time suspiciously close to the period during which the direction of magnetic poles changes.

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1. Introduction

The investigations of phenomena involving transport processes in magma are particularly difficult because of the strong variation of viscosity with temperature, with pressure and with composition. Viscosity determines whether materials behave fluid-like or have properties of rigid bodies. Materials start to behave solid-like when viscosity exceeds 10^{14} Pa s. Waves propagation in glasses is quite similar to that in crystals. Glasses are typical representatives of liquids with solid-like behaviour. Therefore, it is not reliable to distinguish between the crystalline and vitreous state by means of seismic data.

Igneous melt viscosity is one of the most important properties responsible for the development of magmatic

systems. Viscosity, self-diffusion coefficient and diffusion coefficients of particles are of particular importance for the crystallization processes. In geoscience, there is a fundamental interest in predicting the viscosity of the mantle. The aim of the present article is to develop an adequate model for the temperature and pressure dependence of viscosity of melts and to apply it to describe the lava and mantle behaviour in agreement with experimental indications (Stacey, 1969; Forte and Mitrovica, 2001).

2. The model

There is a plethora of articles discussing the temperature dependence of viscosity. The basic assumption is that macroscopic motion is a result of the random jumps of the building units (hereafter called molecules) of the system. Therefore viscosity is proportional to the

reciprocal of the average jump frequency $\langle v \rangle$ of the molecules:

$$\eta = \frac{G}{\langle v \rangle} \qquad (1)$$

According to Maxwell the coefficient of proportionality G is equal to the elasticity modulus G_∞, i.e:

$$G = G_\infty \qquad (2)$$

On the other hand, according to Frenkel's equation, G is expressed through the molar volume V_f, the temperature T and the ideal gas constant R as follows:

$$G = \frac{RT}{V_f} \qquad (3)$$

Experimental data on glasses near the glass-transition temperature give for the elasticity modulus a value of $G_\infty \sim 10$ GPa (Mazurin et al., 1985). From Eq. (3), a value of $G \sim 1$ GPa is expected.

To move, the molecules have to overcome activation energy barriers (Glasstone et al., 1941) created by the resistance of the surrounding molecules. Therefore, the mean jump frequency, and related to it viscosity, are thermally activated:

$$\langle v \rangle = v_\infty \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

so that

$$\eta = \eta_\infty \exp\left(\frac{E}{RT}\right) \qquad (5)$$

Here η_∞ is a pre-exponential constant:

$$\eta_\infty = \frac{G}{v_\infty} \qquad (6)$$

If the effective activation energy E is temperature independent, the experimental data should give a straight line when plotted in Arrhenius coordinates, $\lg\eta$ vs. $1/T$. In many cases this does not happen, so one has to assume that the activation energy could depend on temperature T and on pressure P.

It is useful to define as a reference state the equilibrium state of the system at which viscosity has the value of $\eta_g = 10^{12.5}$ Pa s. This is a typical value at the glass transition temperature (see for instance Vogel, 1985; Gutzow and Schmelzer, 1995). The corresponding temperature we denote as T_g. It is well known that the experimentally determined glass transition temperature depends on the measured property as well as on the

heating (or cooling) rate. Note that T_g is always in the glass-transition interval and, therefore, it has a value close to that of the experimentally determined glass-transition temperature (within $\pm 2\%$ of accuracy). Eq. (5) permits to determine the activation energy at the glass transition temperature in the following way:

$$E(T_g) = 2.3R(12.5 - \lg\eta_\infty)T_g = R\varepsilon T_g \qquad (7)$$

where ε is a dimensionless constant $\varepsilon = 2.3\lg(\eta_g/\eta_\infty)$. The accuracy with which ε is determined depends on the accuracy at which $\lg\eta_\infty$ is known. Although the maximum vibration frequency of a single atom is about 10^{13}s^{-1}, the building unit responsible for viscosity consists of a number of atoms and, therefore, it has lower vibration frequency. Garkova et al. (2004) have demonstrated, based on relaxation experiments, that for $45Na_2O-40B_2O_3-10Al_2O_3-5In_2O_3$ glassforming melt $v_\infty \approx 10^{12\text{s}-1}$. Taking into account Eq. (6) it follows that $\log\eta_\infty \approx -2$. If we chose instead of T_g some other reference temperature T_r, the value of εT_r will be different. The particular value of the reference temperature $T_r = T_g$ is a problem of convenience. Our choice is suitable to determine the activation energy in the glass transition interval. Earlier (Avramov, 2005), on the basis of experimental data on more then 100 substances, we have demonstrated that $\log\eta_\infty \approx -1.5 \pm 1.5$ where the viscosity is in Pa s, so that $\varepsilon = 32 \pm 10\%$. A similar result follows from the experimental data on multicomponent and geochemically relevant systems, summarized in Table 1. According to it $\varepsilon = 33 \pm 4$. Bartenev (1966) has shown that, for relaxation of polymers, $\varepsilon \approx 31$. It follows that the value of $R\varepsilon \approx 260 \pm 10\%$ J/(mol K) is quite universal, independent on the nature of the investigated substance. So, the activation energy for viscous flow is given, at the glass transition interval, as follows:

$$E(T_g) = 260T_g \pm 10\% \text{ J/mol} \qquad (8)$$

Eq. (8) is based on the single assumption that viscosity is a thermally activated. Therefore, it is valid for all substances and all models discussed below.

First Turnbull and Cohen (1970) developed a "free volume" model according to which the motion occurs by movement of molecules into some voids large enough. Macedo and Litovitz (1963) discuss the probability of forming a hole. Scherer (1989) has shown that the values of parameters, needed to fit the viscosity data within the frameworks of this approach, are unrealistic. It is logical to consider the motion as a cooperative process involving a simultaneous rearrangement of a large number of molecules. The Adam and