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Pressure dependence of viscosity, or is the earth's mantle a glass?

I Avramov

Institute of Physical Chemistry, Bulgarian Academy of Sciences 1113 Sofia, Bulgaria

E-mail: avramov@bas.bg

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Abstract

Little is known about the real conditions in the earth's interior because direct sampling is not feasible. The propagation of seismic waves is the only instrument for investigating the mantle. Therefore, viscosity η is of prime importance. Experimental data indicate that mantle viscosity is about 10^{22} Pa s. At such a high viscosity even molten materials behave like solids. The aim of the present paper is to demonstrate that, due to the extreme pressure, viscosity increases sharply. In this way the glass transition temperature increases faster than the melting point, so an important part of the mantle could be in a glassy state, although being molten.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The mantle comprises about 83% of the volume of the earth and 67% of its mass. Still, our knowledge is indirect since no means have yet been devised for directly sampling the deep interior. There are estimations [1] for the dependence of pressure P (in Pa) on depth h (in km):

$$P = Hh^{1.17} \quad (1)$$

with a proportionality constant $H = 1.2 \times 10^7$. The other known property is viscosity, from the information originating from seismic studies. Mantle behaves in respect to wave propagation [2] as a solid material with viscosity varying between 10^{22} and 10^{23} Pa s. The inferred viscosity variations display a pronounced low-viscosity channel in the upper mantle [2] (between 100 and 300 km depth) and two viscosity maxima in the lower mantle, one at about the top of the lower mantle and the other at a depth of 2000 km. These lower-mantle viscosity maxima are not artefacts of the inversion procedure [2]. According to [1, 2], below a depth of about 1000 km, the mantle is an essentially homogeneous material, but above this level its physical properties are more varied, and there is evidence for second-order discontinuities [2].

It is assumed that the mantle consists of crystalline rocks, because of the widespread fallacy that molten systems are always fluid. These beliefs are wrong, 'molten' does not necessarily mean 'fluid'. Viscosity determines whether materials are fluid or rigid. Glasses are typical representatives

of liquids with solid-like behaviour. The glass transition appears at the temperature T_g at which viscosity is $\eta(T_g) = 10^{12.5}$ Pa s. Below the glass transition temperature viscosity increases sharply. Bodies start to behave like solids when viscosity exceeds 10^{14} Pa s. At such high viscosities the wave propagation in glasses is quite similar to that in crystals. To verify whether the mantle is molten but still solid like we need to test three temperatures:

- (1) The dependence $T(h)$ of temperature of the earth on depth h .
- (2) The dependence of the glass transition temperature $T_g(h)$ on the pressure $P(h)$ and through this on the depth h .
- (3) The dependence of the melting point $T_m(h)$ on the pressure $P(h)$ and through this on the depth h .

Following data published in [1], the dependence of temperature on the depth can be approximated, with sufficient accuracy, as follows:

$$T(h) \approx 283\sqrt[3]{h+1}. \quad (2)$$

2. Viscosity and pressure

Recently, it was demonstrated [3, 4] that the pressure dependences of both the melting point and of the glass transition temperature depend on the entropy $S(T, P)$ of the system. The latter depends on temperature T and pressure P

(see [3, 4]) as follows:

$$S(T, P) = S_{go} + \int_{T_{go}}^T C_p d \ln \tilde{T} - \int_{P_o}^P \frac{\partial V}{\partial T} dP. \quad (3)$$

Hereafter the subscript *o* indicates that the corresponding property refers to the ambient pressure. i.e. T_{go} is the glass transition temperature at ambient pressure and S_{go} is the corresponding molar entropy. To derive equation (3), Maxwell's law $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$ was applied. In the following we adopt the most frequently used approximation that heat capacity is independent of temperature, i.e. C_p is the average value for the interval between T_{go} and T . Still, an explicit form of the dependence of $(\frac{\partial V}{\partial T})_P$ on P is needed to solve equation (3). Although in the literature there are no data, it is reasonable to assume that, at extremely high pressures, the volume V reduces in a somewhat inversely proportional way, namely:

$$V = V_o \left(\frac{\Pi}{P + \Pi} \right), \quad \text{or respectively} \quad (4)$$

$$\frac{\partial V}{\partial T} = \left(\frac{\partial V_o}{\partial T} \right)_P \left(\frac{\Pi}{P + \Pi} \right)$$

where Π is an internal pressure. In this case the solution of equation (3) leads to:

$$S = S_{go} + C_p \ln \frac{T}{T_{go}} - \kappa_o V_o \Pi \ln \left(\frac{\Pi + P}{\Pi + P_o} \right) \quad (5)$$

where $\kappa_o = \frac{1}{V_o} (\frac{\partial V_o}{\partial T})$ is the corresponding thermal expansion coefficient. Note that κ_o is the average value of the thermal expansion coefficient at the upper temperature T limit of equation (3). There is also an alternative way. If, in equation (3), we first take the pressure integral and then the temperature one, then κ_o is the average value at T_{go} . Only this time, C_p should be the average value at pressure P . Note also that κ_o is not always positive. There are cases (water, Si, albite) with negative κ_o values.

In the following expressions we take into account that the pressure at the surface is sufficiently low, i.e. $P_o \ll \Pi$. It has already been demonstrated [3, 4] that the pressure (respectively depth) dependence $T_g(h)$ of the glass transition temperature is:

$$T_g(h) = T_{go} \left(1 + \frac{P(h)}{\Pi_f} \right)^\beta = T_{go} \left(1 + \frac{Hh^{1.17}}{\Pi_f} \right)^\beta \quad (6)$$

where the dimensionless power β is proportional to the product $\kappa_o V_o \Pi$.

3. Melting point and pressure

So far, many attempts have been made (see for instance [2, 5]) to determine the pressure P dependence of the melting point $T_m(P)$ of components of the mantle. The Clausius–Clapeyron equation states:

$$\frac{dT_m}{dP} = \frac{V_f - V_c}{S_f - S_c} \equiv \frac{\Delta V}{\Delta S}. \quad (7)$$

Table 1. The values of the parameters used in calculations.

Parameter	Value
ΔS_{mo}	$3R$ (R is the ideal gas constant) ($J \text{ mol}^{-1}$)
V_{fo}	5×10^{-5} ($\text{m}^3 \text{ mol}^{-1}$)
V_{co}	$0.9 V_{fo}$
Π_f	0.2 (GPa)
Π_c	$1.1 \Pi_f$
κ_{fo}	8×10^{-5} (K^{-1})
κ_{co}	$0.9 \kappa_{fo}$
T_{go}	720 (K)

Hereafter the subscript *c* stands for the crystalline state and the subscript *f* stands for the amorphous state (not necessarily fluid!). In deriving the explicit form of $\frac{\Delta V}{\Delta S}$ equations (4) and (5) are taken into account. Denoting with ΔS_{mo} the melting entropy at no pressure, for $\frac{\Delta V}{\Delta S}$ we obtain

$$\frac{\Delta V}{\Delta S} = \frac{V_{fo} \frac{\Pi_f}{\Pi_f + P} - V_{co} \frac{\Pi_c}{\Pi_c + P}}{\Delta S_{mo} - \kappa_{fo} V_{fo} \Pi_f \ln \frac{\Pi_f + P}{\Pi_f} + \kappa_{co} V_{co} \Pi_c \ln \frac{\Pi_c + P}{\Pi_c}}. \quad (8)$$

For fast estimations one could use the approximate formulae

$$\frac{\Delta V}{\Delta S} \approx \frac{\Delta V_o}{\Delta S_{mo}} \frac{\Pi}{\Pi + P}. \quad (9)$$

Taking into account equation (7) the pressure dependence of the melting point is

$$T_m(h) \approx T_{mo} + \frac{\Delta V_o}{\Delta S_{mo}} \int_0^{P(h)} \frac{\Pi}{\Pi + P} dP = \frac{\Pi \Delta V_o}{\Delta S_{mo}} \ln \frac{\Pi + P(h)}{\Pi}. \quad (10)$$

Experimentally Rzoska *et al* [6] found the pressure dependence of the melting point quite similar to the predictions of equation (10).

In the computations that follow, the values of parameters listed in table 1 were used. To find realistic values, it is of decisive importance to know the bulk composition of the mantle. In estimating elemental abundances of the mantle a difficulty arises because direct sampling is not feasible. However, many authors assume that some volcanic eruptions have brought rock fragments of the mantle to the surface. Geophysical data on the properties of the upper mantle suggest that the principal components are oxides of silicon, magnesium and iron. The differences are mainly in the minor components such as aluminium oxide, calcium oxide and the alkalis. It is supposed that the common type of mantle-derived inclusion is peridotite, a silicate rock consisting largely of olivine, $(\text{Mg, Fe})_2\text{SiO}_4$, with minor amounts of orthopyroxene, $(\text{Mg, Fe})\text{SiO}_3$, and diopside, $\text{CaMg}(\text{Si}_2\text{O}_6)$. The values of parameters listed in table 1 are chosen to be in the range expected for these compositions. Still, the real composition of the mantle is under question. The widespread assumption (see for instance Cyranosky [7]) is that it consists of silicates. If so, the number of oxygen atoms must surpass the overall numbers of atoms of all other elements. Is there a chain of stellar nuclear reactions leading to the synthesis of a vey large number of oxygen atoms? One of the reasons for assuming

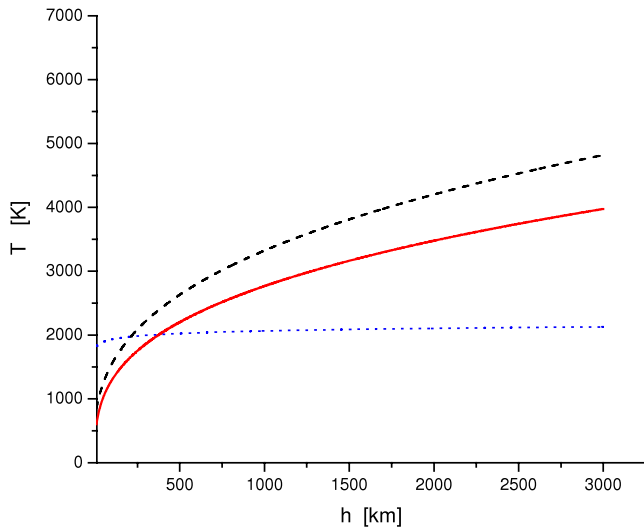


Figure 1. The dependences on depth h of the computed temperatures as follows: the mantle temperature $T(h)$ (solid line), the glass transition temperature $T_g(h)$ (dashed curve) and the melting point $T_m(h)$ (dotted line).

a silicate composition for the mantle is the observation of a large number of silicate meteors. However, these meteors are formed in space beyond the Martian orbit. The outer planets are gas giants because elements had partially separated in the original solar nebula. So, it is logical to assume that there is a deficit of oxygen in the mantle. Oxygen ions are relatively large and tend to form SiO_4 tetrahedra with large voids, i.e. low density. Therefore silicates rather flow on the top of the mantle like slag in metallurgical furnaces. The attempt to fit existing viscosity data could give a key to answer the problem of chemical composition of the mantle.

Figure 1 shows the depth h dependences of the three temperatures: the mantle temperature $T(h)$ (according to equation (1)), the glass transition temperature $T_g(h)$ (according to equation (6)) and the melting point $T_m(h)$ (according to equation (10)). The dashed curve is for the glass transition temperature, the solid line represents the mantle temperature (according to equation (2)) while the dotted line gives the melting point. It is seen that mantle temperature approaches the melting point at depth of $h \approx 400$ km. At this depth, however, the glass transition temperature is already much higher, so that material remains solid, although molten.

According to [3, 4] viscosity depends on temperature and on pressure as follows:

$$\lg \eta = \lg \eta_\infty + (12.5 - \lg \eta_\infty) \left(\frac{T_g(P)}{T} \right)^\alpha \quad (11)$$

where the dimensionless ‘fragility’ parameter depends on composition. It is about $\alpha \approx 1$ for pure SiO_2 and increases steadily with the quantity of modifying oxides. Figure 2 gives the predicted dependence of viscosity on depth h for $\alpha = 3$ (solid line) together with experimental data according to results reported in [2] (solid points).

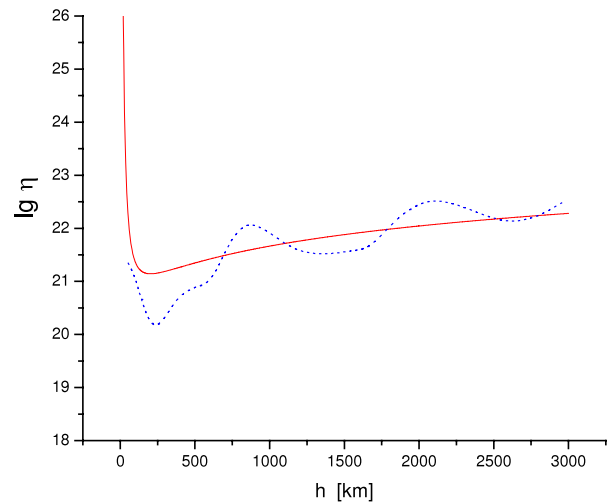


Figure 2. The predicted dependence of viscosity on depth h . The dotted line is experimental dependence according to [2].

4. Discussion

The glass transition temperature is not an equilibrium property; it depends on the cooling rate. Here we adopt as T_g the temperature at which the equilibrium viscosity is $10^{12.5}$ Pa s. Although this is an equilibrium property, it is approximately equal to the temperature at which a glass transition will be observed experimentally if material is cooled at about -10 K min^{-1} . Frequently, a question is asked: why would a glassy material fail to crystallize over geological timescales? The answer is simple: at the extremely high temperatures and pressures of the mantle, material is above the melting point although it behaves like a solid because the high pressure increases viscosity.

It seems that amber is the only substance having a glass transition temperature above the melting point at no pressure. Is it possible to increase the glass transition above the melting point for other compositions? The answer could be positive, if pressure is applied. As soon as this is the case in the bowels of our planet, the aim of the present paper is to demonstrate the possibility that an important part of the earth’s mantle is in glassy state. This means that with increasing the pressure, the glass transition temperature $T_g(P)$ increases faster than the melting point $T_m(P)$. In this way, inside the bowels of the earth, there are certain materials that are molten but at the same time behave like a solid, being below the corresponding glass transition temperature.

So far we do not know the real conditions in the earth’s interior. The only direct experimental data [2] concern viscosity. This is why it is important to study all possible models predicting viscosity values close to experimental findings. This could allow us in future to make a better description of the earth’s interior. The prediction of the glassy state of the mantle is not unambiguous. This is just one possibility that should be considered. According to the present study, the predicted result depends on the suppositions about the initial values. This is an advantage, because accurate knowledge of the initial values will enable us to predict

the chemical composition. At present we have only rough estimations. In this way we could have in the future an additional key for testing the composition of the mantle.

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