Role of surface in apparent viscosity of glasses

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Two problems have intrigued experts for a long time: The one is within the context of the legend of flowing cathedral glass windows and the second is the inaccuracy appearing in very old thermometers of famous scientists. We relate this with the role of the surface on the apparent viscosity of glasses. The apparent viscosity could deviate from the bulk viscosity if the fraction w of the surface molecules, of small samples, is sufficiently large. The effect is more prominent at low temperatures, correspondingly at high viscosities. The interpretation is within the Avramov and Milchev viscosity model, combined with the predictions of the change of heat capacity for extremely small samples. We find that the apparent glass transition temperature could depend on the sample size, in agreement with experimental observations existing in the literature. In addition to glasses, the present results could be of importance for thin films and foams.

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I. INTRODUCTION

Recently it was assumed [1] that the mobility of the surface atoms could be much higher than that in the bulk. Therefore the surface atoms could play an important role even when they are a small fraction of all one. Numerical estimations have shown [1] that the surface mobility is sufficient to explain the statement, published in the Encyclopedia Britannica [2] (see also Ref. [3]), that the windows of medieval cathedrals are thicker in the lower parts. Tammann has remarked [4] that often glasses crystallize from the surfaces. Evidently, one of the reasons for preferential surface crystallization is the higher mobility. An alternative explanation by Blumberg [5] is the assumption that silica rich gels facilitate the nucleation process at the surface. The role of change in chemical composition and of stress on the surface was also accounted for in Refs. [6–8]. A thorough experimental investigation on the kinetics of surface induced crystallization was performed by Zanotto [9–11].

In an earlier article [1] we postulated that the mobility of surface atoms depends on the corresponding activation energy. In the present paper we develop an appropriate model for the surface viscosity so that the discussion started in Ref. [1] can be quantified and applied to different fields of interest.

II. THE MODEL

The starting point is the model of Avramov and Milchev [12–17]. It was shown that viscosity can be related to the entropy of the system according to the expression

$$\log_{10}\eta = \log_{10}\eta_o + \varepsilon \, \exp\left[-\frac{2(S - S_g)}{ZR}\right]. \tag{1}$$

Here the dimensionless parameter ε stands for $\varepsilon \equiv [\log_{10}(\frac{\eta_g}{\eta_o})]$; by definition, $\eta_g = 10^{12}$ Pa s is the viscosity at the glass transition temperature at which the molar entropy of the system is S_g; R is the ideal gas constant and Z is the coordination number of the main building units of the system. When the temperature is higher than the Debye temperature θ, the entropy is given, with sufficient accuracy, by the expression

$$S(T) = \text{const} + C\ln\frac{T}{\theta}, \tag{2}$$

where C is the upper limit of the specific heat. For monoatomic systems $C = 3R$, otherwise $C > 3R$, proportional to the number of independent atoms. According to Eqs. (1) and (2), the following approximation is justified:

$$\exp\left[-\frac{2(S - S_g)}{ZR}\right] \approx \left(\frac{T_g}{T}\right)^\alpha, \quad \alpha \equiv \frac{2C}{ZR}, \tag{3}$$

so that the temperature dependence of viscosity is

$$\log_{10}\eta = \log_{10}\eta_o + \varepsilon \left(\frac{T_g}{T}\right)^\alpha, \quad \text{or in non-log form,}$$

$$\eta = \eta_o 10^{\varepsilon(T_g/T)^\alpha}. \tag{4}$$

Usually viscosity expressions are given in logarithmic form. As the nonlogarithmic form is not frequently used, we give it here for information.

The free interface leads to a significant reduction of the total forces affecting atomic vibrations, both normal and parallel to the surface. There are experimental studies showing that the mean-square displacement of surface atoms is larger compared to that of the atoms in the bulk [18,19]. Therefore, the acoustic phonon spectrum of a small system is perturbed and the specific heat of phases with a comparable number of surface and bulk atoms is expected to differ from that of a large system [20–23]. This effect we already evaluated in Refs. [22–24]. In addition to θ, there is a "surface" Debye temperature θ_s determined as

$$\theta_s = s\theta. \tag{5}$$

Experimentally [18], it was found that for interfaces between the crystalline phase and vacuum, the dimensionless parameter s is between 0.5 and 0.85. For "free" amorphous interfaces the values of s are expected to be about the upper limit found for "free" crystalline interfaces, or even higher. Note that the mobility of atoms at interfaces between two condensed phases could be limited, so that the value of s could be equal to or even larger than one, leading to an increase of the surface viscosity. Following Eqs. (2) and (5), the difference between the molar entropies of the surface and the bulk is given by

$$\Delta S_s(T) \equiv S_s(T) - S(T) \approx C\ln\frac{\theta}{\theta_s} = -C\ln s. \tag{6}$$

The viscosity η_s of the surface layer will be derived starting from expressions similar to Eq. (1), and only the entropy $S(T)$ is to be replaced by that of the surface layer, $S_s(T) = S(T) + \Delta S_s(T)$.

The glass transition temperature T_{gs} of the surface layer is the temperature at which the surface viscosity $\eta_{gs}(T_{gs})$ is equal to the value of η_g. This corresponds to the condition $S_s(T_{gs}) = S(T_g)$, so that

$$T_{gs} = sT_g. \tag{7}$$

The surface viscosity is determined by the expression

$$\log_{10s} = \log_{10}\eta_o + \varepsilon \left(\frac{sT_g}{T}\right)^\alpha, \tag{8}$$

or, in a nonlogarithmic scale, the surface viscosity is

$$\eta_s = \eta_o 10^{\varepsilon(T_{gs}/T)^\alpha}. \tag{9}$$

It is seen that surface viscosity η_s can be expressed through the bulk viscosity η in one of the following useful forms:

$$\eta_s = \eta 10^{\varepsilon(T_g/T)^\alpha(s^\alpha-1)}, \quad \text{or in log form,}$$

$$\log_{10}\eta_s = \log_{10}\eta + \varepsilon \left(\frac{T_g}{T}\right)^\alpha (s^\alpha - 1). \tag{10}$$

Although the "surface" molecules move much faster, their contribution to the overall mobility is not always significant. The reason is that their fraction w could be relatively low. The "apparent" viscosity η_{app} of a sample with a surface fraction of molecules w and bulk fraction $1 - w$ is determined by the condition

$$\frac{1}{\eta_{\text{app}}} = \frac{w}{\eta_s} + \frac{1-w}{\eta}. \tag{11}$$

In Fig. 1 we show the bulk viscosity according to Eq. (4) as a solid line, the surface viscosity is according to Eq. (10) (dashed
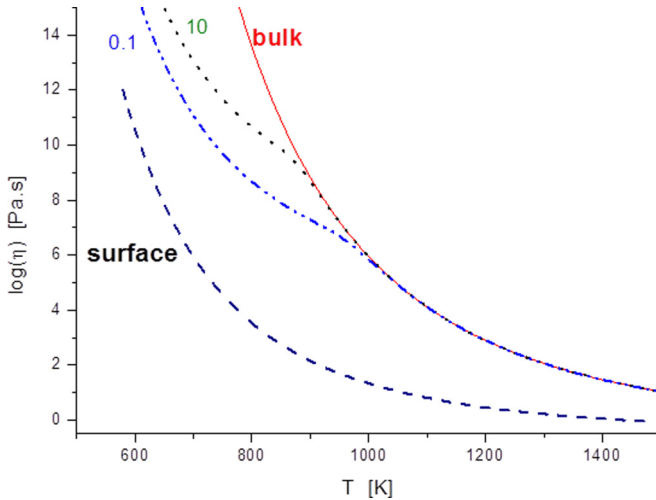

FIG. 1. (Color online) The temperature dependence of viscosity of a typical window glass ($T_g = 828$ K, $\alpha = 3.5$, $Z = 4$). The solid line is for bulk viscosity; the dashed line is for surface viscosity; the dotted line is for an "apparent viscosity" 10 mm thick flat plate; the dashed-dotted line is for a 0.1 mm thick flat plate. Note that the thinner is the plate, the more important is the contribution of the surface viscosity.

line), and the "apparent viscosity" is according to Eq. (11). The surface fraction $w = \frac{2d_o}{h-2d_o}$ is determined for a plate of thickness h with two flat surface layers, each of thickness d_o. The plate is about 10 mm thick (dotted line) or 0.1 mm thick (dashed-dotted line). The values of the adjusting parameters are typical for window glass ($T_g = 828$ K, $\alpha = 3.5$, $Z = 4$). The contribution of the surface viscosity appears only at low temperatures where the bulk viscosity is very high and $\eta_s \ll \eta$.

III. DISCUSSION

Similar results can be obtained within the framework of the Einstein model of heat capacity, keeping in mind the well-known approximation $\theta_E \approx \theta \sqrt[3]{\frac{\pi}{6}}$ relating the Einstein, θ_E, and the Debye, θ, temperatures.

Both the Einstein and the Debye heat capacity models are developed for crystalline phases only. In practice, the heat capacity of glasses is undistinguishable from that of the corresponding crystals (see, for instance, Refs. [25,26]). If the heat capacity of the glass remains higher than that of the crystals, the Kauzmann paradox will be unavoidable. Concerning the melts, the corresponding heat capacity function is more complicated and an additional configuration term is needed to describe it properly. Therefore, for liquids, the present approach is only the first approximate solution of the problem. At high temperatures the bulk viscosity is relatively low so that the additional lowering of the surface viscosity is of minor importance, unless the sample is very thin, as is the case for foams. On the other hand, at relatively low temperatures, in the vicinity of T_g, the entropy correction is important, because the viscosity of the surface layer is much lower as compared to the bulk viscosity. Therefore it plays an important role for the "apparent viscosity," as demonstrated in Fig. 1.

It is a widespread belief that the break in temperature dependence of viscosity (see, for instance, Refs. [27,28]) is due to the transition to the nonequilibrium state at low temperatures. A similar assumption has been made in Refs. [29,30] in interpreting the relaxation time. Up to now, I have also used this hypothesis [12–16]. Here an alternative explanation is demonstrated. Recently Welch *et al.* [29] managed to measure the relaxation kinetics of a 0.7 mm thick glassy plate at room temperature. This is an extraordinary accomplishment. This was not expected to be possible because the relaxation time was projected to be enormous. It is normal that comments [30] regarding this result appeared immediately. The present finding that the contribution from the surface layers could bring about a similar change in the viscosity offers the possibility of a different interpretation and should be tested in the future. If the break appears in the vicinity of η_g, the relaxation time is high, so it is easy to explain the change with a transition to the "frozen-in," nonequilibrium state. On the other hand, the experimental results on the viscosity of salol [31,32] cannot be explained as easily because the break appears at a relatively low viscosity (about 10^7 Pa s). Figure 2 presents these results. The solid line is according to Eq. (11) for $s = 0.89$, $T_g = 218$ K, $\alpha = 8$, and $\log_{10}\eta_o = -2.7$. The surface fraction was assumed to be $w \approx 2 \times 10^{-7}$ (this corresponds to a flat sample, 1 mm thick). It was already predicted [12] that relatively large values of the power α are expected for organic substances. For comparison, the inset of the figure
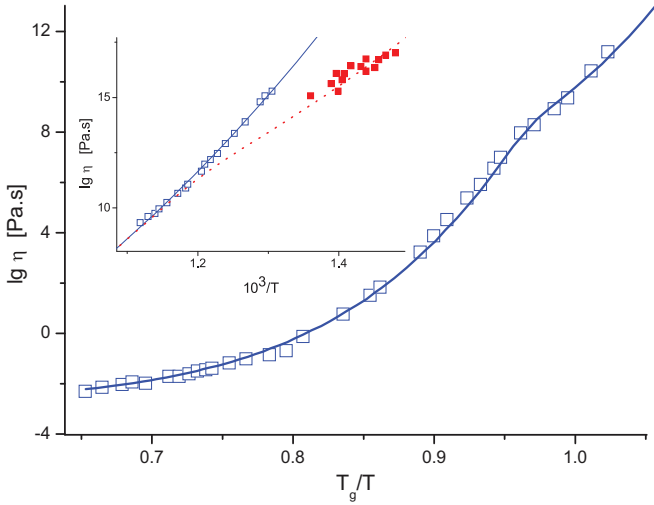
FIG. 2. (Color online) The temperature dependence of the viscosity of salol according to Refs. [31,32] (open points). The solid line is according to Eq. (16) for a flat sample, 1 mm thick, with $s = 0.89$, $T_g = 218$ K, $\alpha = 8$, $\log h_o = -2.7$. For comparison, the inset gives results on window glass from Yue [28].

gives results on window glass from Refs. [28–30,33,34]. In this case both the nonequilibrium effects as well as those caused by the surface layers lead to similar results. According to the present model, the threshold temperature T_t depends on surface fraction w_t [respectively the transition thickness $h_t(T)$]. This is the temperature at which the contribution of the molecules moving at the surface is equal to that in the bulk:

$$\frac{w_t}{\eta_s(T_t)} = \frac{1 - w_t}{\eta(T_t)}. \tag{12}$$

A combination of Eqs. (9) and (12) permits one to determine T_t as follows:

$$T_t = T_g \left[\frac{\varepsilon(1 - s^\alpha)}{-\log_{10}\left(\frac{w_t}{1 - w_t}\right)} \right]^{1/\alpha}. \tag{13}$$

If we consider again that w is determined for a flat sample of thickness h having two surface layers, the critical thickness at which the contribution of the surface mobility is equal to the bulk one is

$$h_t(T_t) = 2d_o \left[\frac{\eta(T_t)}{\eta_s(T_t)} - 1 \right]. \tag{14}$$

Table I shows what is the critical thickness $h(\eta)$ at which the surface and the bulk viscosity have an equal contribution, if the sample is a free flat film (or plate). If the samples are thinner than the corresponding $h(\eta)$, the role of surface viscosity prevails. For instance, if the bulk viscosity is of the order of 10^7 dPa s, the threshold thickness is about 0.1 mm. For higher bulk viscosities the relative contribution of the surface viscosity increases quickly.

According to the present finding, the break temperature depends on the value w of the surface fraction (respectively of the thickness h). The dependence of the glass transition temperature $T_{g,w}$ on the surface fraction w could be estimated from the condition that the apparent viscosity η_{app} is equal to

TABLE I. The critical thickness $h(\eta)$ at which the surface and the bulk viscosity have an equal contribution if the sample is a free flat film (plate). If the samples are thinner than the corresponding $h(\eta)$, the role of surface viscosity prevails.

$\eta(T)$ in dPa s	$h(T)$	Remark
10^4	$\sim 2\ \mu$m	Glass working point
10^5	~ 0.01 mm	Glass flow point
10^7–10^8	~ 0.1 mm	Andesite lava
		Glass softening point
$10^{11.3}$	~ 45 cm	Glass dilatometric softening point
10^{13}	~ 7 m	Glass transition temperature
$10^{14.5}$	~ 95 m	Glass strain point
$>10^{15}$	>500 m	Solidlike behavior

η_g (remember that by definition $\eta_g = 10^{12}$ Pa s):

$$\eta_{\text{app}}(T_{g,w}) = \eta_g. \tag{15}$$

There is an important difference between the glass transition temperature $T_{g,w}$ and the threshold temperature T_t. To determine $T_{g,w}$ we first note that, for $s < 1$, at low temperatures $\frac{w}{\eta_s} \gg \frac{1-w}{\eta}$, so that we can neglect the $1 - w$ term in Eq. (11). With this remark, by means of Eqs. (10) and (15), the glass transition temperature $T_{g,w}$ is determined as follows:

$$T_{g,w} = \frac{sT_g}{\left[1 + \frac{\log_{10} w}{\varepsilon} \right]^{1/\alpha}}. \tag{16}$$

It is common practice to determine $T_{g,w}$ experimentally as a point of break in the temperature dependence of a certain property (for instance, specific volume or heat capacity, etc.).

The authors of Refs. [35–37] find experimentally that the glass transition temperature of free polymer films is a function of film thickness (i.e., it depends on w), decreasing as the films are thinner. They assumed that, at the surface of the glassy film, a liquidlike layer exists. Masson and Green [38] have demonstrated that the shear viscosity of viscosity of entangled polystyrene films decreases with decreasing thickness for $25 < h < 50$ nm. Earlier expressions quite similar to Eq. (16) were proposed. In Ref. [35] the proposed expression (in terms of the present report) is

$$T_{g,w} = T_g \left[1 - \left(\frac{d_o}{h} \right)^\delta \right]. \tag{17}$$

In Ref. [39] the corresponding expression is

$$T_{g,w} = \frac{T_g}{\left[1 + \left(\frac{d_o}{h} \right)^\delta \right]}. \tag{18}$$

Essentially, Eqs. (16)–(18) are quite similar, taking into account that $w \ll 1$ is reverse proportional to h, making the term $\log_{10}(w)$ negative. I want to also remark that, for any $x \ll 1$, the expression $\frac{1}{1+x} \approx 1 - x$ is a fairly good approximation.

The experimental data from Ref. [35] on the dependence of the glass transition temperature on film thickness (in Å) of freely standing polystyrene films are given in Fig. 3. The solid line is according to Eq. (16) for the thickness of a surface layer $d_o = 73$ Å, $\varepsilon = 11$, $\alpha = 4$, and $sT_g = 365$ K, i.e.,
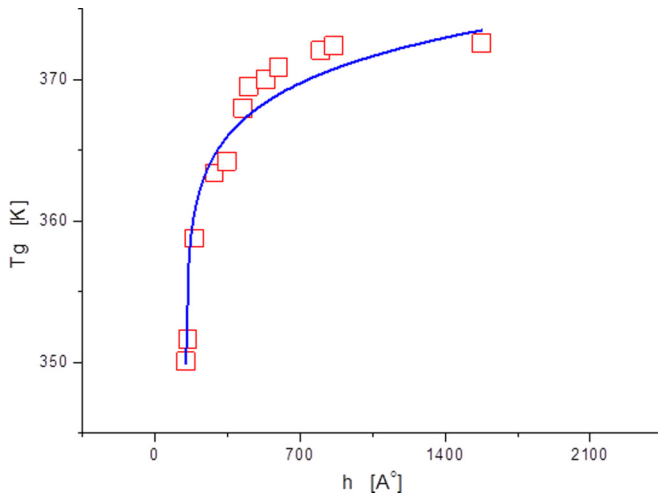
FIG. 3. (Color online) The dependence of the apparent glass transition temperature $T_{g,w}$ on the film thickness h (Å) of freely standing polystyrene films. The open points are experimental data from Ref. [35], and the solid line is according to Eq. (6) for a surface layer thickness $d_o = 73$ Å, $\varepsilon = 11$, $\alpha = 4$, and $sT_g = 365$ K.

$s \approx 0.97$. It is difficult to decide whether the values of ε, T_g, and α are equal to those of the bulk material. The reason is that the viscosity of polymers is very sensitive to their molecular weight, the presence of oligomers and water, as well as to the supermolecular structure. I can only note that the values are within the expected limits.

When the molecular interactions at the interface are stronger than those in the bulk, the apparent glass transition temperature increases [36,37]. In the framework of the present approach this corresponds to the case when $s > 1$. If at least one of the surfaces is not free (film deposited on a solid surface), the trend of the dependence of the glass transition

temperature on film thickness could change and $T_{g,w}$ could even increase when the film becomes thinner. The results of Ref. [40] have indicated that the viscosity of the film increases by about two orders of magnitude near solid substrates. The authors of Ref. [40] assumed that the "bottom" layer of polymer chains remained permanently adsorbed at the solid substrate. It is responsible for trapping subsequent layers, and propagating the effect of surface interactions to chains without direct contacts to the solid substrate. In terms of the present treatment this is an indication that, unlike the "free" surface, the parameter s could be larger than one for an interface with a solid substrate.

IV. SUMMARY

We have developed a model accounting for the role of surface on the apparent viscosity. There is a transition value of viscosity η_t (respectively a transition temperature T_t) at which the contribution of the surface becomes equal to that of the bulk. Evidently, the transition point depends on the fraction w of the surface molecules. As soon as the value of w is large for thin films and foams, in these cases the value of η_t is quite low. The situation is very different at low temperatures where the value of the bulk viscosity is high. In this case surface viscosity could have values millions of times lower than that of the bulk. Therefore, surface viscosity will be of importance, even for relatively large samples, despite the fact that the surface fraction of the molecules w is very small.

The aim of this paper is not to fit the experimental data. The aim is to show that the viscosity on the surface is different from that in the bulk. This difference leads to a break in the curve of the temperature dependence of the viscosity that is quite similar to that caused by nonequilibrium effects. It remains a tempting problem to find which of the two effects is responsible in each particular case.

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