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Intrinsic roughness of glass surfaces

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Abstract. It is shown that the spectrum of thermal surface height fluctuations on a supercooled liquid close to the glass transition contains a narrow quasielastic component, which describes slow fluctuations freezing in at the glass transition. The spectrum is obtained from a dynamic susceptibility which is calculated using the theory of viscoelasticity.

1. Introduction

When a supercooled melt is cooled through the glass transition range, part of the thermal fluctuations of the liquid in metastable equilibrium is frozen in. As a result, for example, in a glassy material static density fluctuations of long wavelength exist [1–7]. They represent an intrinsic property of a glass in bulk. In this paper we address the question of whether an analogous effect occurs at a glass surface. At the surface of a liquid fluctuations of vertical displacement are caused by thermally excited capillary waves (ripplons). As is shown in the present paper, at the surface of a very viscous supercooled liquid near the glass transition these fluctuations become very slow and are finally frozen in at the glass transition. We calculate the spectrum of these slow fluctuations of vertical surface displacement and derive their frozen-in intensity in the glassy state, which is a measure of the intrinsic roughness of a glass surface.

The freezing in of long-wavelength density fluctuations in bulk glass can be treated theoretically using the theory of viscoelasticity, or, with greater precision, of thermoviscoelasticity [8], in combination with the fluctuation dissipation theorem. We follow a similar route here to calculate the intrinsic surface roughness of glass prepared by cooling of a melt.

To our knowledge, the validity of the viscoelastic theory for density fluctuations in bulk has not been contested for inorganic glasses like fused quartz and borosilicate glasses [9]. However, in polymeric glasses and in organic glasses of molecules of low molecular weight strong polarized light scattering at small wavevectors has been observed [4–7], which cannot be explained by the viscoelastic theory. In these cases the result of the viscoelastic theory is only a lower limit to the observed scattering in bulk. At present the physical origin of the excess scattering is not well understood. It is left to future experimental investigations to show whether a similar situation exists with regard to frozen-in surface height fluctuations. It is possible that, for a certain class of glass forming materials, the result derived in this paper also represents only a lower limit.

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2. Linear response theory

The spectrum of thermal surface height fluctuations is calculated by applying linear response theory to the reaction of a liquid surface to an external force. The surface extends in the x and y directions, with the liquid at rest filling the half space $z < 0$. Let $P_z(\boldsymbol{r}, t)$, with $\boldsymbol{r} = x\boldsymbol{e}_x + y\boldsymbol{e}_y$, be a position- and time-dependent external force field (per unit area) acting on the liquid surface, and

$$P_z(\boldsymbol{r}, t) = \frac{1}{\sqrt{A}} \sum_{\boldsymbol{k}} \tilde{P}_z(\boldsymbol{k}, t) \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}) \qquad \text{with } \boldsymbol{k} = k_x\boldsymbol{e}_x + k_y\boldsymbol{e}_y \tag{1}$$

its spatial Fourier representation. A is the total surface area. In the usual way, periodic boundary conditions are assumed. The corresponding perturbation Hamiltonian reads

$$H_1(t) = -\iint_{(A)} \mathrm{d}^2r\, P_z(\boldsymbol{r}, t) u_z(\boldsymbol{r}) = -\sum_{\boldsymbol{k}} \tilde{P}_z(-\boldsymbol{k}, t)\tilde{u}_z(\boldsymbol{k}) \tag{2}$$

where $u_z(\boldsymbol{r})$ is the vertical surface displacement and $\tilde{u}_z(\boldsymbol{k})$ its spatial Fourier transform. For a harmonic time dependence of a weak external force

$$\tilde{P}_z(\boldsymbol{k}, t) = P_{z,0} \exp(-\mathrm{i}\omega t) \tag{3}$$

to linear approximation the resulting surface displacement is given by

$$\tilde{u}_z(\boldsymbol{k}, t) = P_{z,0} \mathrm{e}^{-\mathrm{i}\omega t} \chi_{zz}(k, \omega) \tag{4}$$

where $\chi_{zz}(k, \omega)$ is the dynamic susceptibility of the vertical surface displacement with respect to a surface force of wavevector $\boldsymbol{k}$ parallel to the surface plane, and angular frequency ω. According to the classical fluctuation dissipation theorem the imaginary part $\chi''_{zz}(k, \omega)$ of this dynamic susceptibility determines the spectrum $S_{zz}(k, \omega)$ of thermal surface displacements of wavevector $\boldsymbol{k}$:

$$S_{zz}(k, \omega) = \int_{-\infty}^{+\infty} \mathrm{d}t \exp(\mathrm{i}\omega t)\langle u_z(\boldsymbol{k}, t) u_z(-\boldsymbol{k}, 0)\rangle = 2k_\mathrm{B}T\chi''_{zz}(k, \omega)/\omega. \tag{5}$$

The following sum rule expresses the total intensity of the spectrum in terms of the static susceptibility $\chi_{zz}(k, \omega = 0)$:

$$S_{zz}(k) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi} S_{zz}(k, \omega) = k_\mathrm{B}T\chi_{zz}(k, 0). \tag{6}$$

From $S_{zz}(k)$ the mean square vertical surface displacement is obtained as

$$\overline{u_z^2} = \int \frac{\mathrm{d}^2k}{(2\pi)^2} S_{zz}(k). \tag{7}$$

The dynamic susceptibility $\chi_{zz}(k, \omega)$ can be calculated from the solution of the linearized hydrodynamic equations which govern the motion of the liquid surface. For an external surface force

$$P_z(x, t) = P_{z,0} \exp[\mathrm{i}(kx - \omega t)] \tag{8}$$

the solution for the vertical surface displacement has the same form with a complex, frequency-dependent amplitude:

$$u_z(x, t) = u_{z,0} \exp[\mathrm{i}(kx - \omega t)]. \tag{9}$$

The dynamic susceptibility is obtained as the amplitude ratio:

$$\chi_{zz}(k, \omega) = u_{z,0}/P_{z,0}. \tag{10}$$

3. Calculation of $S_{zz}(k, \omega)$

We first neglect gravity. The calculation is an extension of the treatment of Rayleigh waves on the surface of an isotropic elastic medium [10]. The supercooled liquid near the glass transition is described as a viscoelastic medium with frequency-dependent shear and bulk modulus $G(\omega)$ and $K(\omega)$. $G(\omega)$ is related to a frequency-dependent shear viscosity $\eta(\omega)$ by

$$G(\omega) = -\mathrm{i}\omega\eta(\omega). \tag{11}$$

Here we assume that the properties of the supercooled liquid remain unaltered right up to the surface on the length scales of our interest. In addition, the effect of surface tension is taken into account. The surface tension α is assumed to be independent of frequency. The displacement field $\boldsymbol{u}(x, z, t)$ in the viscoelastic liquid is the sum of a transverse part

$$\boldsymbol{u}_{\mathrm{t}}(x, z, t) = a(\kappa_{\mathrm{t}}\boldsymbol{e}_x - \mathrm{i}k\boldsymbol{e}_z)\exp[\mathrm{i}(kx - \omega t) + \kappa_{\mathrm{t}}z] \tag{12}$$

and a longitudinal part

$$\boldsymbol{u}_{\mathrm{l}}(x, z, t) = b(\mathrm{i}k\boldsymbol{e}_x + \kappa_{\mathrm{l}}\boldsymbol{e}_z)\exp[\mathrm{i}(kx - \omega t) + \kappa_{\mathrm{l}}z] \tag{13}$$

where the expressions for κ_{t} and κ_{l} read

$$\kappa_{\mathrm{t}} = \sqrt{k^2 - \omega^2\rho/G(\omega)} \qquad \kappa_{\mathrm{l}} = \sqrt{k^2 - \omega^2\rho/C_{\mathrm{l}}(\omega)}. \tag{14}$$

The real parts of κ_{t} and κ_{l} are the inverse penetration depths of the transverse and longitudinal components of the displacement field, respectively, and must be positive. $C_{\mathrm{l}}(\omega)$ is the longitudinal elastic modulus, which in terms of shear modulus $G(\omega)$ and bulk modulus $K(\omega)$ is given by

$$C_{\mathrm{l}}(\omega) = K(\omega) + \tfrac{4}{3}G(\omega). \tag{15}$$

ρ is the mean density. The coefficients a and b are determined by the boundary conditions at the liquid surface, which are

$$\sigma_{zz} = P_z + \alpha\frac{\partial^2 u_z}{\partial x^2} \tag{16}$$

and

$$\sigma_{xz} = 0. \tag{17}$$

The components of the stress tensor are

$$\sigma_{zz} = C_{\mathrm{l}}(\omega)\frac{\partial u_z}{\partial z} + \left[K(\omega) - \frac{2}{3}G(\omega)\right]\frac{\partial u_x}{\partial x} \tag{18}$$

$$\sigma_{xz} = G(\omega)\left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x}\right). \tag{19}$$

Solving equations (16) and (17) for a and b, one obtains the following result for the dynamic susceptibility:

$$\chi_{zz}(k, \omega) = \left(\alpha k^2 - G^2(\omega)\frac{\left(2k^2 - \omega^2\rho/G(\omega)\right)^2 - 4\kappa_{\mathrm{t}}\kappa_{\mathrm{l}}k^2}{\omega^2\rho\kappa_{\mathrm{l}}}\right)^{-1}. \tag{20}$$

The effect of gravity is easily included for the incompressible liquid ($K(\omega) \to \infty$). It leads simply to the replacement of αk^2 by $(\alpha k^2 + \rho g)$, where g is the acceleration due to gravity. Since $\kappa_1 \to k$ in the incompressible limit, the expression for the dynamic surface susceptibility χ_{zz} including the effect of gravity can be written explicitly as

$$\chi_{zz}(k,\omega) = \frac{k/\rho}{gk + (\alpha/\rho)k^3 - (\omega + 2\mathrm{i}\nu(\omega)k^2)^2 - 4\nu^2(\omega)k^4\left(1 - \mathrm{i}\omega/\nu(\omega)k^2\right)^{1/2}} \tag{21}$$

where $\nu(\omega) = \eta(\omega)/\rho$ is the frequency-dependent kinematic viscosity of the viscoelastic liquid. In terms of a 'damping function' $\Gamma(k,\omega)$, defined as

$$\Gamma(k,\omega) = 4\nu(\omega)k^2 + (\mathrm{i}/\omega)(2\nu(\omega)k^2)^2\left(1 - \left(1 - \frac{\mathrm{i}\omega}{\nu(\omega)k^2}\right)^{1/2}\right) \tag{22}$$

and the frequency $\omega_s(k)$ of the surface wave of an ideal incompressible fluid, given by

$$\omega_s(k) = \left(gk + \frac{\alpha}{\rho}k^3\right)^{1/2} \tag{23}$$

this result can be written as

$$\chi_{zz}(k,\omega) = \frac{k/\rho}{-\omega^2 + \omega_s^2(k) - \mathrm{i}\omega\Gamma(k,\omega)}. \tag{24}$$

The square root occurring in the damping function derives from the *ansatz* equations (12–14), and is typical of a surface response function. As shown below, the corresponding branch cut of $\chi_{zz}(k,\omega)$ in the complex ω plane is responsible for the appearance of a continuous band in the spectrum of surface height fluctuations in the elastic limit ($G(\omega) \sim G(\infty)$). The band describes the emission of transverse sound waves into the bulk elastic medium by excitation of its surface.

From the expression (21) the static susceptibility $\chi_{zz}(k,\omega=0)$ and the total intensity $S_{zz}(k)$ (equation (6)) are obtained as

$$\chi_{zz}(k,\omega=0) = \frac{1}{\rho g + \alpha k^2} \tag{25}$$

and

$$S_{zz}(k) = \frac{k_B T}{\rho g + \alpha k^2}. \tag{26}$$

For the mean square vertical surface displacement $\overline{u_z^2}$ one calculates the result

$$\overline{u_z^2} = \frac{k_B T}{4\pi\alpha}\ln\left(\frac{\alpha k_c^2}{\rho g}\right) \tag{27}$$

where an upper cut-off wavevector k_c is introduced. $\sqrt{\rho g/\alpha}$ plays the role of a lower cut-off wavevector. For $\alpha = 0.1$ kg s^{-2} and $T = 10^3$ K, the root mean square displacement $\left(\overline{u_z^2}\right)^{1/2}$ is of the order of 5 Å, depending only weakly on k_c. Denoting the denominator of expression (21) by $D(k,\omega)$, the spectrum $S_{zz}(k,\omega)$, equation (5), is written as

$$S_{zz}(k,\omega) = -2k_B T(k/\rho)\frac{\mathrm{Im}\,D(k,\omega)}{|D(k,\omega)|^2}\frac{1}{\omega}. \tag{28}$$

This result can be shown to be equivalent to an unwieldy expression obtained by Harden *et al* [11] in a different way. These authors did not calculate the spectrum via the dynamic susceptibility, but derived their result directly from the equations of motion of the theory of viscoelasticity, augmented by terms describing fluctuating stresses.

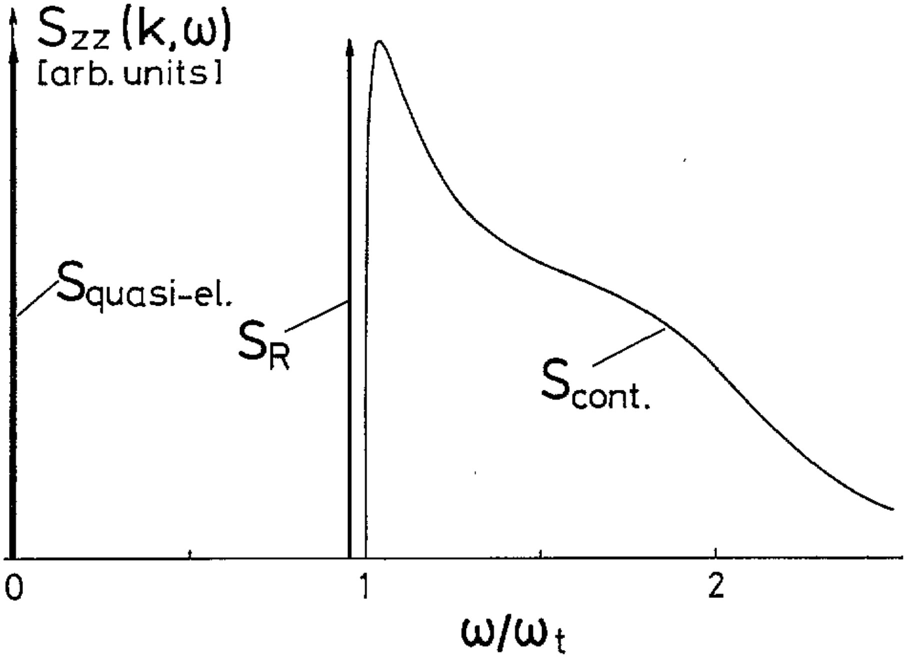

Figure 1. The spectrum $S_{zz}(k, \omega)$ of vertical surface height fluctuations in region III.

4. Discussion of the spectrum for a Maxwell–Debye model

To discuss the variation of the spectrum $S_{zz}(k, \omega)$ with increasing viscosity we apply a simple Maxwell–Debye model, which has a single relaxation time τ. We neglect the small effects of a finite compressibility. For the Maxwell–Debye model, the frequency dependence of the kinematic viscosity $\nu(\omega)$ is given by

$$\nu(\omega) = \frac{\nu_0}{1 - \mathrm{i}\omega\tau} \tag{29}$$

where ν_0 is the low-frequency value of hydrodynamics. With equations (29) and (11), the relations

$$\nu_0/\tau = G(\infty)/\rho = c_{\mathrm{t}}^2(\infty) \tag{30}$$

between ν_0, the high-frequency shear modulus $G(\infty)$ and the velocity $c_{\mathrm{t}}(\infty)$ of high-frequency shear waves in bulk follow. The expression (21) for the dynamic susceptibility $\chi_{zz}(k, \omega)$ then contains, in addition to the relaxation rate τ^{-1}, two characteristic frequencies, which can be chosen either as the frequency ω_{s} of the surface wave in an ideal fluid (equation (23)) and that of the hydrodynamic viscous shear mode

$$\omega_\nu(k) = \nu_0 k^2 \tag{31}$$

or as ω_{s} and the frequency ω_{t} of the elastic shear mode for long relaxation time $\omega_{\mathrm{t}}\tau \gg 1$, which is given by

$$\omega_{\mathrm{t}}(k) = c_{\mathrm{t}}(\infty)k = (\omega_\nu/\tau)^{1/2}. \tag{32}$$

We are mainly interested in the domain of wavevectors accessible to light scattering experiments ($k = \mathrm{O}(10^5\ \mathrm{cm}^{-1})$), in which the effect of gravity is completely negligible. In this domain, the ratio ω_s/ω_t is small compared to unity, since

$$\omega_s^2/\omega_t^2 = kl_0 \qquad l_0 = \alpha/G(\infty) = \mathrm{O}(10^{-7} - 10^{-8}\mathrm{cm}). \tag{33}$$

In the region of wavevectors where the continuum theory is valid, kl_0 is usually smaller than one. This may be different in the case of polymer solutions treated in [11]. In the following discussion we assume the condition

$$kl_0 \ll 1 \tag{34}$$

to apply. As a function of the relaxation rate relative to these frequencies we find three limiting cases of the spectrum $S_{zz}(k,\omega)$. In region I, where

$$2\omega_t^2/\omega_s \ll \tau^{-1} \tag{35}$$

holds, we have

$$\chi_{zz}(k,\omega) = \frac{k}{\rho}\left(-\omega^2 + \omega_s^2 - 4\mathrm{i}\omega\nu_0 k^2\right)^{-1} \tag{36}$$

and

$$S_{zz}(k,\omega) = 2k_\mathrm{B}T\,\frac{k}{\rho}\,\frac{4\nu_0 k^2}{(\omega^2-\omega_s^2)^2 + (4\omega\nu_0 k^2)^2}. \tag{37}$$

This result is due to thermally excited capillary waves in a liquid of low viscosity [12, 11]. The condition $\tau^{-1} = 2\omega_t^2/\omega_s$ marks the point of transition to overdamped capillary waves [13], at which $\omega_\nu = \omega_s/2$ holds. In region II well below this point, viz. for

$$\omega_t \ll \tau^{-1} \ll 2\omega_t^2/\omega_s \tag{38}$$

we find

$$\chi_{zz}(k,\omega) = \frac{1}{\alpha k^2}\left(1 - \mathrm{i}\omega/\gamma(k)\right)^{-1} \tag{39}$$

and

$$S_{zz}(k,\omega) = \frac{2k_\mathrm{B}T}{\alpha k^2}\,\frac{\gamma(k)}{\omega^2+\gamma^2(k)} \tag{40}$$

with the linewidth $2\gamma(k)$ given by

$$2\gamma(k) = \omega_s^2/\omega_\nu = kl_0/\tau \ll \omega_s. \tag{41}$$

The contribution of the overdamped capillary waves to the spectrum $S_{zz}(k,\omega)$ is quasielastic. The linear dependence of the linewidth $\gamma(k)$ on wavevector k is peculiar to overdamped capillary waves, and derives from the k dependence $\omega_s \propto k^{3/2}$. In region III with

$$\tau^{-1} \ll \omega_t \tag{42}$$

the spectrum is richer (figure 1), although the quasielastic part of the spectrum is modified only slightly compared with region II. Expanding in powers of $(\omega_t\tau)^{-1}$ for $\omega \lesssim \tau^{-1}$, we obtain the low-frequency part of the dynamic susceptibility as

$$\chi_{zz}(k,\omega) = \frac{1}{\rho c_t^2(\infty)k\,(kl_0 - 2\mathrm{i}\omega\tau/(1-\mathrm{i}\omega\tau))} \tag{43}$$

and the quasielastic part of the spectrum as

$$S_{zz}(k,\omega)|_{\mathrm{quasiel}} = \frac{2k_\mathrm{B}T}{\alpha k^2\,(1+kl_0/2)}\,\frac{\gamma(k)}{\omega^2+\gamma^2(k)} \tag{44}$$

where the linewidth

$$2\gamma(k) = \frac{1}{\tau}\frac{kl_0}{1+kl_0/2} \tag{45}$$

agrees to lowest order in kl_0 with the result (41) in region II. We note that the results (43)–(45) also hold when condition (34) is not fulfilled. The quasielastic component given by equation (44) was overlooked in [11]. Unlike in region II, the quasielastic line no longer exhausts the sum rule (26). The total intensity of the quasielastic line is slightly reduced to

$$S_{zz}(k)|_{\text{quasiel}} = \frac{k_B T}{\alpha k^2}\frac{1}{1+kl_0/2} \approx \frac{k_B T}{\alpha k^2}\left(1-\frac{kl_0}{2}\right) \tag{46}$$

where the last expression holds for small kl_0. The intensity difference goes into contributions from the elastic Rayleigh surface wave and the continuum of bulk elastic shear waves. The Rayleigh wave frequency is given by

$$\omega_R = \xi_0\omega_t \tag{47}$$

where $\xi_0 = 0.955$ is the zero of the function

$$h_0(\xi) = (2-\xi^2)^2 - 4(1-\xi^2)^{1/2}. \tag{48}$$

For $\omega \approx \pm\omega_R$, the dynamic surface susceptibility is given by

$$\chi_{zz}(k,\omega) = -\frac{2k}{\rho}\frac{\xi_0^3}{h_0'(\xi_0)}\frac{1}{\omega^2-\omega_R^2+\mathrm{i}\omega/\tau} \tag{49}$$

where the small effect of the surface tension α is neglected. The corresponding contribution to the spectrum $S_{zz}(k,\omega)$ is a pair of Lorentzians of half-width $(2\tau)^{-1}$, centred at $\pm\omega_R$, which are described by

$$S_{zz}(k,\omega)|_R = \frac{2k_B T}{\rho c_t^2(\infty)k}\frac{\xi_0}{h_0'(\xi_0)}\frac{(2\tau)^{-1}}{(\omega\mp\omega_R)^2+(2\tau)^{-2}}. \tag{50}$$

The numerical factor $\xi_0/h_0'(\xi_0)$ has the value 0.109. The intensity of the two lines due to Rayleigh waves is a fraction

$$0.218kl_0 \tag{51}$$

of the total intensity (26). The missing fraction

$$0.282kl_0 \tag{52}$$

of the total intensity (26) is found in the contribution of the continuum of the bulk elastic shear waves in the frequency regions $|\omega| > \omega_t$. Taking the limit $\tau \to \infty$, this contribution can be written as

$$S_{zz}(k,\omega)|_{\text{cont}} = \frac{8k_B T}{\rho c_t^3(\infty)k^2}\frac{\sqrt{1-s^{-2}}}{s^6-8s^4+24s^2-16} \tag{53}$$

with $s = \omega/\omega_t \geqslant 1$.

Below the glass transition of a supercooled highly viscous liquid, the average shear stress relaxation time exceeds the experimental time scale, e.g. of a calorimetric measurement. On this time scale, the quasielastic component of the fluctuation spectrum $S_{zz}(k,\omega)$, given by equation (44), becomes effectively elastic, corresponding to static, frozen-in fluctuations. Since the freezing in occurs at the glass transition temperature T_g, the intensity of the frozen-in surface height fluctuations of wavevector $\boldsymbol{k}$ is given by expression (46) for $T = T_g$, viz.

$$S_{zz}(k)|_{\text{frozen in}} = \frac{k_B T_g}{\alpha(T_g)k^2(1+kl_0(T_g)/2)}. \tag{54}$$

The validity of this result is not restricted to the Maxwell–Debye model, and also holds for a distribution of relaxation times. This follows from the general validity of the result (26) for the total spectral intensity, and (51), (52) for the intensity of the elastic Rayleigh wave and shear wave contributions, respectively.

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