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Surface roughness of supercooled polymer melts

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We report on *in situ* x-ray reflectivity measurements of the surface roughness of supercooled glass forming polymers in a temperature range from 190 to 330 K. The experimentally determined rms roughness has been found to obey the capillary wave model of a single liquid/vapor interface over the entire temperature range. An expression for the surface roughness below the bulk glass transition ($T_G \approx 200$ K) is deduced from the viscoelastic theory of surface fluctuations; however, no indication of a frozen-in surface roughness has been observed in the experiment. Additionally, it is shown that precise values of the surface tension of highly viscous liquids in the supercooled state can be determined by x-ray reflectivity.

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I. INTRODUCTION

The transition from a liquid to a glass in the bulk is characterized by an exponential increase of the viscosity as the glass transition temperature is approached, and the question arises how surface properties are affected by this strong change of the viscosity. Of special interest is whether the glass transition at the free surface differs from that of the bulk. A number of studies have addressed this question for thin polymer films. For example, a change of the glass transition temperature was observed when the film thicknesses were decreased below a certain limit [1–5]. This phenomenon was explained by an increase of the ratio of mobile polymer chain segments near the free surface to those less mobile ones in the bulk with decreasing film thickness. A different approach attempted to use the embedding process of small metal clusters into the polymer as a marker to gain information about surface properties [6–8].

The dynamic surface properties are closely related to the glass transition at the surface. Until now these properties of free surfaces in the supercooled region and at the glass transition have not been in the focus of investigations. A liquid surface is subject to thermally excited capillary wave fluctuations. X-ray scattering experiments showed typical static fingerprints of such fluctuations like a resolution dependent rms roughness or a power-law behavior of the diffuse scattering [9–13]. Capillary waves may be either propagating or over-damped depending on viscosity, surface tension, density, and wave vector. Dynamic light scattering has been the standard method to study dynamic properties of liquids [14]. In addition, the application of correlation spectroscopy with coherent x rays (XPCS) to liquid surfaces has emerged as a new technique [15] and recently the transition between propagating and overdamped capillary waves has been investigated by XPCS [16]. However, for the moment the methods that directly probe dynamical properties of liquid surfaces cannot reach molecular length scales, and hence information about the behavior on such small length scales is only accessible via time-averaged quantities, such as the rms roughness measured by x-ray reflectivity.

In thermal equilibrium the surface roughness depends only on the cost of energy for deforming the surface, which is given by the surface tension [17]. Therefore, the viscosity should have no effect on the surface roughness as determined by x-ray reflectivity experiments as long as the sample is in thermal equilibrium. However, a glass is not in thermal equilibrium and its state depends on the thermal history of the sample. Effects of this nonequilibrium condition on the surface roughness of glass forming liquids are of interest. It has been shown by viscoelastic theory that surface fluctuations of highly viscous liquids close to the glass transition become very slow and are finally “frozen in” [18]. In addition, it has been shown, by taking a frequency dependent kinematic viscosity into account, that the spectrum of surface fluctuations becomes richer close to the glass transition, with the appearance of elastic Rayleigh surface waves and a continuum of bulk elastic shear waves.

A recent x-ray reflectivity study of the temperature dependence of the surface roughness of the glass forming liquid glycerol revealed discrepancies between the roughness expected from the capillary wave theory of a simple liquid and the measured values [19]. The decrease of the surface roughness with decreasing temperature was found to exceed the theoretical predictions, thus revealing a surface smoother than predicted. In addition, it has been found that the surface roughness of glycerol stays almost constant with decreasing temperature for temperatures below $T \approx 250$ K, i.e., the roughness is already frozen in at temperatures well above the bulk glass transition temperature ($T_{G,C_3H_8O_3} \approx 186$ K).

In order to determine whether such a temperature dependence of the surface roughness is a common feature of glass formers, we have investigated glass forming melts of propylene glycol (PPG) with different molecular weights in a temperature range from 190 to 330 K by x-ray reflectivity. Compared to glycerol, PPG has the main advantage that no crystallization occurs in the supercooled state. This enables the measurement of x-ray reflectivities over a large range of wave vector transfers at constant temperature for the full

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temperature range. This behavior differs from the fragile glass former glycerol, which crystallizes in the region from 240 K down to its glass transition temperature if cooling rates smaller than 1.5 K per minute are applied.

The paper is organized as follows. In Sec. II we present the details of the experimental apparatus including the sample preparation. Section III contains a theoretical description of the surface roughness of glass forming liquids. The experimental results of the reflectivity measurements including the determined surface roughness as a function of temperature are presented in Sec. IV, which is followed by a discussion in Sec. V. Section VI contains a summary and the conclusions.

II. EXPERIMENT

The x-ray measurements were performed at the Harvard/BNL liquid surface spectrometer at the NSLS beamline X22B. A Ge(111) steering crystal was used to deflect the monochromatic x-ray beam with a wavelength of $\lambda = 1.576$ Å downward onto the horizontal liquid surface. A vertical slit size of 0.05 mm and a horizontal slit size of 1.6 mm were used to define the incident beam. The predetector slit was opened to $2\ \text{mm} \times 2\ \text{mm}$ resulting in an angular resolution $\Delta\alpha = 3.4$ mrad in the scattering plane. All measured reflectivities were normalized to the incoming beam intensity. The background signal arising from bulk scattering was subtracted from the specularly reflected intensity by performing scans out of the scattering plane with a constant angular detector offset of 0.4°. A typical x-ray reflectivity measurement was recorded within 3–4 h. No indication for beam damage such as visible lines on the surface or a strong increase of the diffusely scattered intensity was detected during the measurements.

Samples of PPG with average molecular weights of 425 and 4000 g/mol were purchased from Sigma-Aldrich (product numbers 202304 and 202355). At room temperature PPG-425 and PPG-4000 are viscous liquids with viscosities of 0.08 and 1.3 Pa s [20], respectively, and a surface tension of 0.031 N/m. The melting point of the two liquids is $T_M \approx 330$ K and the bulk glass transition is $T_G \approx 200$ K, slightly depending on molecular weight and thermal history. PPG can be considered a supercooled liquid between T_M and T_G. Recently, a microscopic picture of the surface structure of liquid PPG at ambient conditions was obtained by vibrational spectroscopy, revealing a surface mostly covered by methyl groups [21].

To perform these x-ray reflectivity experiments liquid samples with large flat surfaces have to be prepared and cooled homogeneously toward the glass transition. Additionally, the samples have to be deep enough to avoid any influence of a substrate. The sample environment used in this experiment has been described in detail elsewhere [22]. The x-ray beam penetrates the sample chamber through Kapton windows of 25 μm thickness and the liquid is kept in an aluminum trough of 140 mm diameter and 4 mm depth. The samples were prepared by filling the trough with liquid PPG until the surface of the liquid was above the rim. This is possible since a meniscus with positive curvature is formed due to the surface tension. After the filling procedure of the sample, the chamber is evacuated to pressures of better than 10 mbar. During the pumping procedure residual solvents in the liquid are removed. Cooling of the sample is achieved via evaporating liquid nitrogen in a heat exchanger underneath the sample chamber. A flow meter ensures a constant flow rate of cold nitrogen vapor through the exhaust of the exchanger. Heating is achieved by the use of a Kapton embedded resistive heating foil beneath the heat exchanger, and the temperature is measured by two ceramic coated platinum resistor sensors dipped into the liquid sample. The whole setup is controlled by a Lakeshore temperature controller and covers a temperature range from 180 to 340 K with a temperature stability better than ±0.01 K. The volume of PPG is reduced significantly during cooling due to the large value of the thermal expansion coefficient $\kappa \sim 8 \times 10^{-4}\ \text{K}^{-1}$. At low temperatures this results in a meniscus with negative curvature of the sample surface and makes the region around the critical inaccessible. This effect complicates x-ray reflectivity measurements and analysis over large temperature ranges.

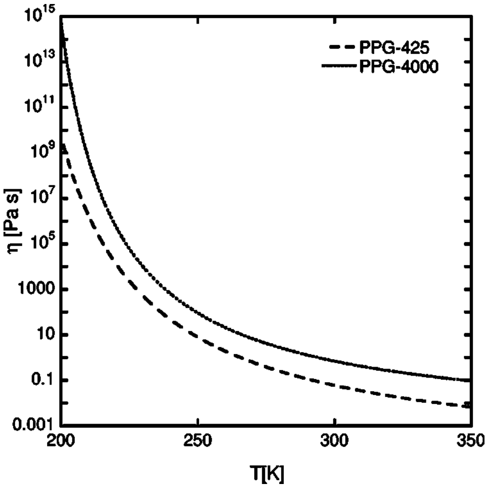

FIG. 1. The temperature dependent viscosities of both investigated PPG samples [20].

III. SURFACE DYNAMICS AND SURFACE ROUGHNESS

By cooling a glass former from the liquid state to the glass transition the viscosity increases several orders of magnitude. Figure 1 displays results obtained by Cochrane concerning the two investigated PPG samples [20]. Upon cooling from 350 to 200 K the viscosities of both polymers increase by about 10 orders of magnitude. The question of how this increasing viscosity affects the surface roughness can be answered on the basis of the dynamic susceptibility $\chi(q,\omega,T)$ of the surface fluctuations. Using the fluctuation dissipation theorem the spectrum of the capillary waves $S(q,\omega,T)$ is determined by the imaginary part of the dynamic susceptibility $\chi''(q,\omega,T)$ via $S(q,\omega,T) = 2k_B T \chi''(q,\omega,T)/\omega$. The static part of the spectrum $S(q)$ is then determined by the static susceptibility $S(q,T) = k_B T \chi(q,\omega=0,T)$.

An expression for the dynamic susceptibility of liquid surfaces based on the linear response theory was given by Bouchiat and Meunier [23] and by Loudon [24]:

$$\chi(q,\omega,T) = \frac{q/\rho(T)}{-\omega^2 + \omega_s^2(q,T) - i\omega\Gamma(q,\omega,T)}, \tag{1}$$

where ρ is the density and γ the surface tension. $\omega_s(q,T) = \sqrt{\gamma q^3/\rho}$ denotes the capillary wave frequency and $\Gamma(q,\omega,T)$ is a frequency dependent damping function

$$\Gamma(q,\omega,T) = 4\nu q^2 + \frac{i}{\omega}(2\nu q^2)^2\left[1 - \left(1 - \frac{i\omega}{\nu q^2}\right)^{1/2}\right], \tag{2}$$

which depends on the kinematic viscosity ν. $\Gamma(q,\omega)$ and $\omega_s(q)$ are temperature dependent via the density, the surface tension, and the viscosity.

The mean square surface displacement can be obtained by integrating the static part $S(q,T)$ over the experimentally accessible q values:

$$\sigma^2(T) = \sigma_0^2 + \int_{q_l}^{q_u} dq \frac{q}{2\pi} S(q,T), \tag{3}$$

where q_l is a lower wave vector cutoff and q_u an upper cutoff. The magnitude of the upper cutoff is commonly assumed to be on the order of π/r_M with the molecular radius r_M. The lower cutoff q_l is given by the experimentally determined resolution of the diffractometer via $q_l = q_z\Delta\alpha/2$, where $\Delta\alpha$ is the measured angular acceptance of the detector. The intrinsic roughness σ_0 represents the intrinsic interface width in the absence of capillary waves and is on the order of $\sigma \sim 1$ Å[11]. Both the upper cutoff and the intrinsic width are expected to depend only weakly on the temperature.

In thermal equilibrium Eq. (1) gives the static susceptibility $\chi(q,\omega=0)=1/\gamma q^2$, which is independent of the viscosity ν. By inserting the static susceptibility into Eq. (3) and neglecting the phenomenological parameter σ_0 the usual expression for the measured roughness σ of a liquid surface broadened by capillary waves is obtained

$$\sigma^2(T) = \frac{k_B T}{2\pi\gamma(T)} \ln\left(\frac{q_u}{q_l}\right). \tag{4}$$

Jäckle and Kawasaki [18] describe the supercooled liquid near the glass transition as an incompressible viscoelastic medium with a frequency dependent viscosity $\nu(\omega)$ given by a simple Maxwell-Debye model and a single relaxation time τ,

$$\nu(\omega) = \frac{\nu_0}{1 - i\omega\tau}. \tag{5}$$

$\nu_0(T)$ is the low-frequency hydrodynamic value of the viscosity and τ is given by $\tau = \nu_0(T)\rho/G(\infty)$, with the high-frequency shear modulus $G(\infty)$. Jäckle and Kawasaki argue that below the glass transition at T_G the average shear stress relaxation time τ exceeds the experimental time scale and the quasielastic part of the fluctuation spectrum is frozen in. By inserting Eq. (5) in Eq. (1) an expression for the structure factor of the frozen-in fluctuations is obtained

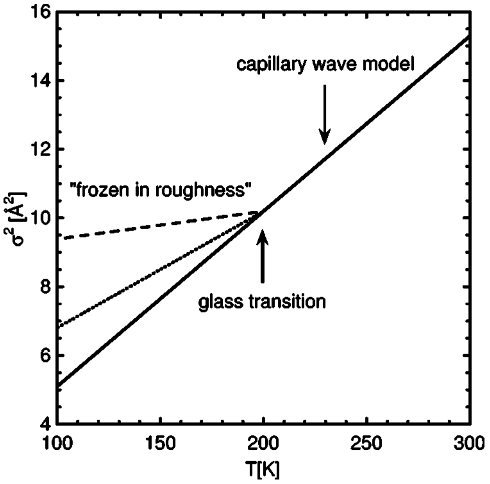

FIG. 2. Schematic temperature dependence of the square of the surface roughness along the glass transition according to viscoelastic theory. The solid line shows the usual prediction for the capillary wave model (i.e., no glass transition). Below the glass transition temperature predictions for different values of l_0 are displayed: the dashed line for $l_0=10$ Å and the dotted line for $l_0=500$ Å.

$$S(q)_{frozen} = \frac{k_B T_G}{\gamma(T_g) q^2[1 + q l_0(T_G)]} \tag{6}$$

with the length scale parameter of the transition $l_0 = \gamma/G(\infty)$. Thus the following expression for the surface roughness below T_G is obtained:

$$\sigma^2(T) = \frac{k_B T_G}{2\pi\gamma} \ln\left(\frac{q_u(l_0 q_l + 2)}{q_l(l_0 q_u + 2)}\right) + \sigma'^2(T), \tag{7}$$

where $\sigma'(T)$ accounts for the surface roughness due to the Rayleigh surface waves and bulk elastic shear waves. Typical values of the elastic shear modulus are on the order of gigapascals. As an example, Fig. 2 shows the temperature dependence of the surface roughness according to Eq. (4). In addition, for temperatures below a $T_G = 200$ K the behavior of the roughness for frozen-in surface fluctuations [Eq. (7)] is shown for two different values of l_0 (dashed line, $l_0=10$ Å and dotted line, $l_0=500$ Å). For reasons of simplicity a constant surface tension has been used. Since only the contributions from the elastic parts of the spectrum are still temperature dependent the surface roughness according to Eq. (7) decreases less strongly with temperature.

IV. RESULTS

The temperature dependent x-ray reflectivity $R(q_z,T)$ of a liquid/vapor interface is given by [10]

$$R(q_z,T) = R_F(q_z)\exp[-q_z^2\sigma^2(q_z,T)], \tag{8}$$

where R_F is the Fresnel reflectivity of an ideally smooth surface, $q_z=(4\pi/\lambda)\sin(\alpha_i)$ is the vertical wave vector transfer with α_i denoting the incident angle of the radiation with respect to the surface, and $\sigma^2(q_z,T)$ is the surface roughness, which depends on temperature and wave vector transfer. According to Eq. (4) the surface roughness of a liquid is

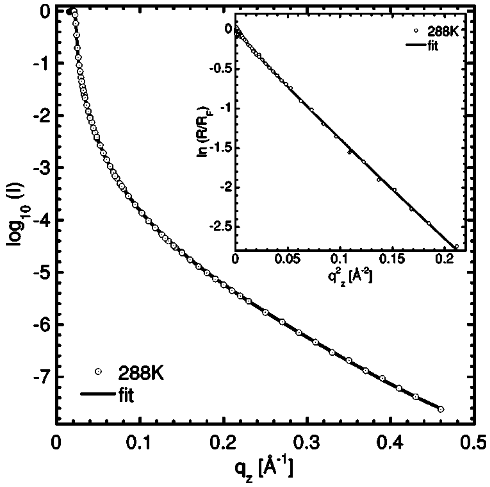

FIG. 3. X-ray reflectivity of PPG-425 at $T=288$ K. The inset shows the natural logarithm of the same data normalized to the Fresnel reflectivity $\ln(R/R_F)$ as a function of q_z^2.

$$\sigma^2(q_z,T)=\frac{k_BT}{2\pi\gamma(T)}\ln\left(\frac{q_u}{q_z\Delta\alpha/2}\right). \tag{9}$$

The data have been analyzed in two stages. In the first stage the reflectivities were fitted according to Eq. (8) with a q_z independent effective roughness $\sigma_{\text{eff}}(T)$. This is a good approximation since the q_z dependence of $\sigma^2(q_z,T)$ is weak. Hence, the natural logarithm of the data normalized to the Fresnel reflectivity $\ln(R/R_F)$ is plotted as a function of q_z^2. According to Eq. (8) this results in a straight line with slope $-\sigma^2(T)$. In a second refinement step the q_z dependence via Eq. (9) is taken into account and the surface tension becomes the sole fit parameter.

Figure 3 displays a typical x-ray reflectivity measurement of PPG-425 as a function of q_z at $T=288$ K. The circles show the data taken with the scintillation detector after background subtraction while the solid line is a fit with a Fresnel reflectivity according to Eq. (8). The inset shows the natural logarithm of the same data normalized to the corresponding Fresnel reflectivity $\ln(R/R_F)$ as a function of q_z^2. Here the solid line is a linear fit with slope $-\sigma_{\text{eff}}^2(T)$. The weak q_z dependence of σ_{eff} is not visible in the limited region of the wavevector transfer.

Figure 4 shows the natural logarithm of six reflectivities normalized to the corresponding Fresnel reflectivities as a function of q_z^2 for each of the two PPG samples. The top panel displays measurements of PPG-425 at temperatures from 188 to 318 K and the lower panel shows data sets of PPG-4000 at temperatures from 188 to 332 K. For the sake of clarity four additional measurements in the temperature interval for each of the two polymers are not shown in the figure. All data sets of the two polymers show simple Fresnel reflectivities in the entire temperature region. The data could be modeled very well with a linear fit with slope $-\sigma_{\text{eff}}^2(T)$. In contrast to the previous study of the surface roughness of liquid glycerol, where deviations from a linear behavior were observed at higher temperatures [19], no indication of a layer formation at the surface is observed in this case.

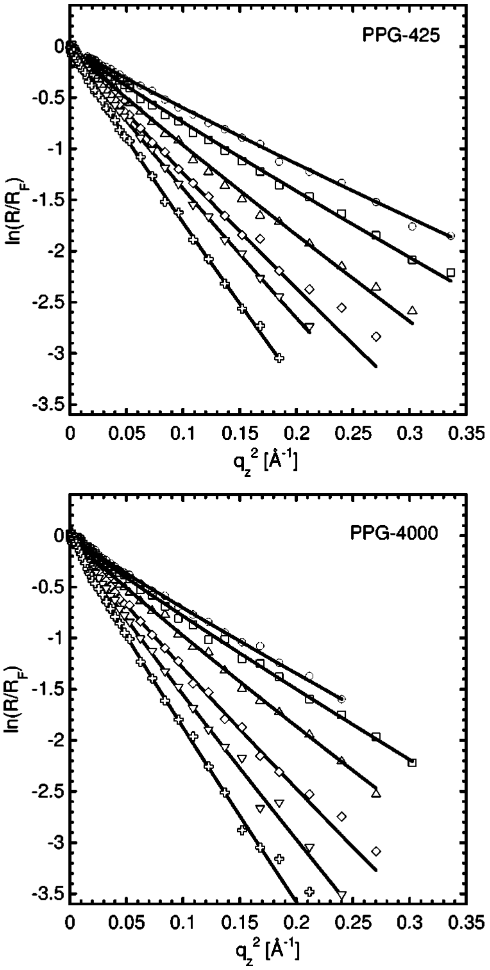

FIG. 4. The natural logarithm of the reflectivity data normalized to the Fresnel reflectivity $\ln(R/R_F)$ versus q_z^2. The upper panel displays data sets of PPG-425 (temperatures from bottom to top, 318 K, 288 K, 273 K, 243 K, 213 K, and 188 K) and the lower panel shows data sets for PPG-4000 (temperatures from bottom to top, 332 K, 300 K, 273 K, 233 K, 202 K, and 188 K).

The resulting surface roughnesses as functions of temperature for the PPG-425 and PPG-4000 samples are shown in Fig. 5. Again the results for the PPG-425 sample are shown in the top panel and the results for PPG-4000 in the lower one. The surface roughnesses of both samples decrease with decreasing temperature.

The observed behavior of the surface roughness can be modeled by a temperature dependent surface tension $\gamma(T)=\gamma_0-a(T-T_0)$ with $T_0=273.15$ K. The solid line in the two panels of Fig. 5 represents a fit according to $\sigma^2(T)=cT/\gamma(T)$. The known value of the surface tension at room temperature is used as reference to evaluate the constant factor c. It is possible to model the data very well with this simple model and we obtained values of $\gamma_0=3.8\times10^{-2}$ N/m, $a=1.57\times10^{-4}$ N/m K for PPG-425 and $\gamma_0=3.6\times10^{-2}$ N/m, $a=1.3\times10^{-4}$ N/m K for PPG-4000. The additional lines shown in both panels of Fig. 5 indicate the theoretical temperature dependence of the surface roughness below the glass transition according to Eq. (7) for $l_0=10$ Å and $l_0=500$ Å, respectively. Due to limitations of our experi-

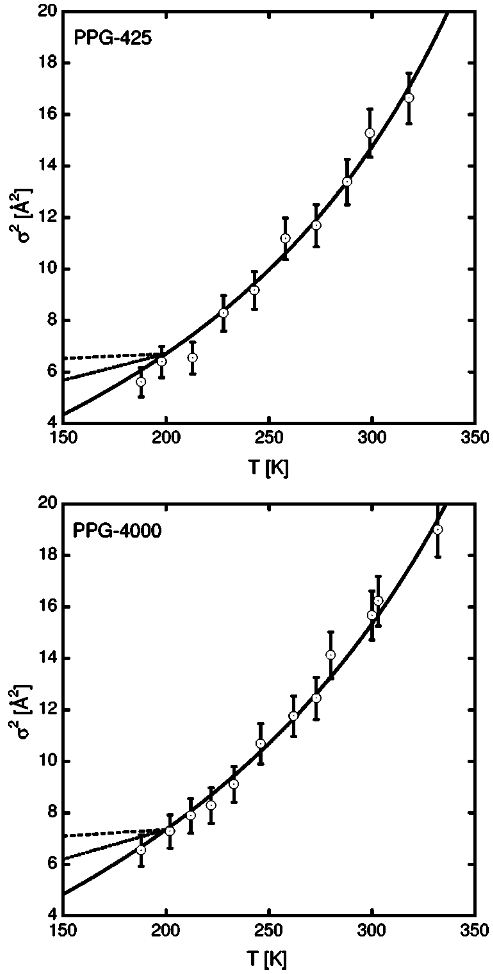

FIG. 5. Temperature dependence of the estimated surface roughness (top, data for PPG-425; bottom, data for PPG-4000). The solid lines are fits according to $\sigma(T)^2 = cT/\gamma(T)$. The dashed and dotted lines are calculations according to Eq. (7) for $l_0 = 10$ and 500 Å, respectively. The bulk glass transition temperature is around $T_G \approx 200$ K.

mental setup only a few data points below the bulk glass transition temperature could be investigated and within the error bars no indication of a freezing in of the surface roughness near the bulk glass transition temperature around 200 K can be observed. More importantly, the data also show that the increase of the viscosity by ten orders of magnitude upon cooling (see Fig. 1) does not have any influence on the static picture of the capillary wave induced roughness for these polymers.

Knowing that the surface roughness can be described by the capillary wave model of a single liquid/gas interface, we refined the model to describe the data in a second stage by taking the q_z dependence of the surface roughness into account, i.e., we refined the reflectivity data according to Eq. (8) with the surface tension $\gamma(T)$ as single fit parameter. The resulting values of the surface tension are shown in Fig. 6. The values of the surface tension of the two polymers show a linear increase with decreasing temperature, the surface tension of PPG-425 being larger than that of PPG-4000.

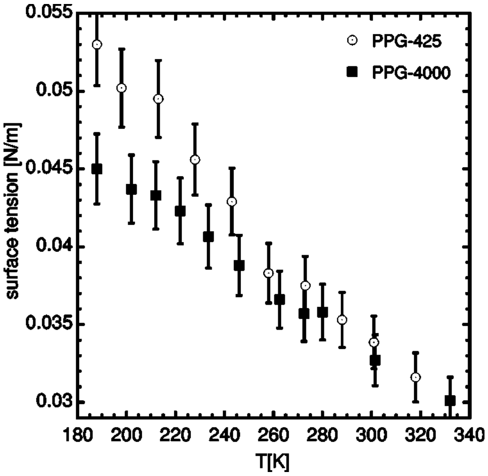

FIG. 6. The temperature dependence of the surface tension of PPG-425 and PPG-4000 as obtained from the analysis of the x-ray reflectivity data.

V. DISCUSSION

Our experiment addresses two questions: whether surface fluctuations freeze in when a supercooled liquid is cooled toward its glass transition, and whether the capillary wave model of a single liquid/gas interface is still valid to describe surfaces which are undercooled by more than 110 K, even if the bulk liquid undergoes a glass transition.

While a recent study of the rms roughness of the surface of liquid glycerol revealed strong discrepancies between the capillary wave theory and experiment, this is not the case in the present study. Our experiment shows that surface fluctuations of PPG behave like those of a simple liquid all the way toward the bulk glass transition temperature. The surface roughness of the glass forming polymers PPG-425 and PPG-4000 was found to obey the capillary wave model of a single liquid/vapor interface in the entire temperature region. It is shown that the exponential increase of the viscosity of about ten orders of magnitude in the investigated temperature interval has no influence on the time-averaged picture of the surface fluctuations. Thus, the surface fluctuations behave as if they were in thermal equilibrium with the heat bath. Additionally, no molecular surface layer forms for the two PPG samples, and no crossover of the temperature dependence of the surface roughness is indicated near the bulk glass transition temperature.

We show that x-ray reflectivity experiments can be useful to measure the surface tension in otherwise inaccessible temperature regions. Even though progress has been made in the determination of precise values of the surface tension of highly viscous liquids with the development of the micro-Wilhelmy plate technique [25,26], this technique is still limited when the surface tension near a glass transition is to be measured. However, the error of the estimated value for the surface tension obtained by x-ray reflectivity is larger as determined by standard technique due to the uncertainty of the roughness, which is of the order of 5% at the low temperatures. On the other side, there is no upper viscosity limit for this technique and the behavior as a function of temperature is quite accurate. Thus a combination of standard techniques with x-ray reflectivity measurements can obtain a more complete picture.

VI. SUMMARY AND CONCLUSION

The surface roughness of strongly undercooled polymers has been studied by means of x-ray reflectivity experiments. The temperature region covered in the experiment ranged from above room temperature to values below the temperature of the bulk glass transition near 200 K. Within this temperature range the viscosity of the liquids increases by ten orders of magnitude. However, all data sets have been found to be in good agreement with the model of a single liquid/vapor interface broadened by capillary waves. The temperature dependent behavior of the rms roughness showed no clear indication of a frozen-in surface roughness due to capillary waves or of a surface glass transition. In addition, no evidence for layer formation has been found.

Thus we find, that the surface of PPG behaves like a single liquid/gas interface even 110 K below the bulk melting point. Our findings show that x-ray reflectivity experiments allow for a precise *in situ* determination of the surface tension of highly viscous liquids. Using standard techniques this is often a difficult task due to high viscosity and long relaxation times.

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