Vol 18 No 9, September 2009
1674-1056/2009/18(09)/3918-04

Chinese Physics B

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and IOP Publishing Ltd

Direct measurement of the surface dynamics of supercooled liquid-glycerol by optical scanning a film*

Zhang Fang(张 芳), Zhang Guo-Feng(张国峰), Dong Shuang-Li(董双丽),
Sun Jian-Hu(孙建虎), Chen Rui-Yun(陈瑞云), Xiao Lian-Tuan(肖连团)†, and Jia Suo-Tang(贾锁堂)

State Key Laboratory of Quantum Optics and Quantum Optics Devices, College of Physics and Electronics Engineering, Shanxi University, Taiyuan 030006, China

(Received 18 February 2009; revised manuscript received 13 April 2009)

The surface dynamics of supercooled liquid-glycerol is studied by scanning the thickness of the glycerol film with single photon detection. Measurements are performed at room temperature well above the glycerol's glass transition temperature. It is shown that the surface dynamics of the glycerol film is very sensitive to the temperature. The linear relationship between the thickness of the film and the viscosity predicted by the Vogel–Fulcher–Tammann–Hesse (VFTH) law is also presented experimentally.

Keywords: supercooled liquids, surface dynamics, viscosity, single photon detection
PACC: 6140K, 6825, 6220D, 0670D

1. Introduction

Liquids at temperatures below their melting points are called supercooled liquids (SCL).[1−3] Because of the disordered structure and rich phenomenology, the dynamics of SCL is one of the most important characteristics, yet thoroughly unsolved.[4] The past decade has been one of tremendous vitality for the study of SCL.[5,6] Much of the excitement and interest is due to the enormous progress made in increasing the power of relevant experimental tools, in which the most efficient way for detecting the dynamics inside SCL is single-molecule spectroscopy[7] which is used to follow the orientation of a single probe molecule in SCL in real time.[8] These experiments yield the characteristic timescale of the fluorophore's rotational diffusion and thereby probe the relaxation dynamics inside the SCL.[9] In addition, the surface dynamics of SCL has been evaluated by several groups.[10,11] It has been shown that SCL surfaces fluctuate with thermally induced height fluctuation, called capillary waves, which play an important part in surface dynamics. Scattering methods such as x-ray photon correlation spectroscopy are used in these groups noninvasively to measure the overdamped surface capillary waves relaxation on the SCL, where the surface dynamics are obtained through normalized intensity–intensity autocorrelation,[12] which also provides a means to study the entanglement effects in the capillary waves on the SCL films.[13]

Here, we present a new optical method to probe the surface dynamics of SCL by scanning the thickness of the glycerol film at room temperature which is well above the glycerol's glass transition temperature (192 K). In this way, capillary waves are visible in the scanning images. In order to achieve better sensitivity, superior spatial resolution and the absence of the so-called classical dead zones,[14] we employ photon counting with single photon detection.

2. Experimental section

The experimental setup is a common confocal scanning microscopy system as shown in Ref.[15]. Glycerol is coated on a cover glass (20 mm×60 mm×160 μm) by a 3000 rotation/minute spin coater. The laser light from a CW diode laser of $\lambda = 690$ nm (TCLDM9) is led to an inversion microscope (Nikon ECLIPSE TE2000-U) by a single mode polarization maintain fibre. An oil immersion objective (Nikon, 100×, 1.3 NA) is used for both focusing

*Project supported by the Natural Science Foundation of China (Grant No 10674086), 973 Program of China (Grant Nos 2006CB921603, 2006CB921102 and 2008CB317103), 863 Program of China (Grant No 2009AA01Z319), NCET-06-0259, the Shanxi Provincial Foundation for Leaders of Disciplines in Science, the Natural Science Foundation of Shanxi province, China (Grant No 2007011006) and Shanxi Province Foundation for Returned scholars of China.
†Corresponding author. E-mail: xlt@sxu.edu.cn

laser light onto the film and collecting the reflected laser. Then, the laser is focused onto a 100 μm pinhole for spatial filtering to reject out-of-focus photons. Subsequently, the laser is focused by lenses and collected by a single photon detector (APD SPCM-AQR-15). Images are acquired by scanning the glycerol film using a closed-looped piezoelectric scan stage (Tritor 200/20 SG) mounted on the inversion microscope whose position can be changed in three dimensions with nanometer precision by modulating the voltage imposed on it. Here, its position along the z-axis is modulated by a sawtooth wave voltage. When the waist of the laser is approaching the lower surface (the interface between the cover glass and glycerol) or the upper surface (the interface between glycerol and air) of the film, the intensity of the scattered light collected by the microscope becomes larger, and the maximum is reached when the laser is just focused on each surface. The light intensity decreases as the waist leaves the surface. So when the waist goes through the glycerol film, firstly, the lower surface and then the upper surface of the film will be probed optically. Therefore, the thickness information can be obtained by the light intensity peaks due to the surface scattering. After getting the two peaks of a position, we move to another position by changing the modulation voltage along the x axis and y axis, which triggers the next scanning along the z axis. Repeating the above action 400 times, the total thickness data of a plane can be obtained. On the x–y plane, along both the x axis and y axis, the step sizes are 1 μm, and the scanning numbers are 20. A LabVIEW program is used to control the scanning process and carry out data analysis.

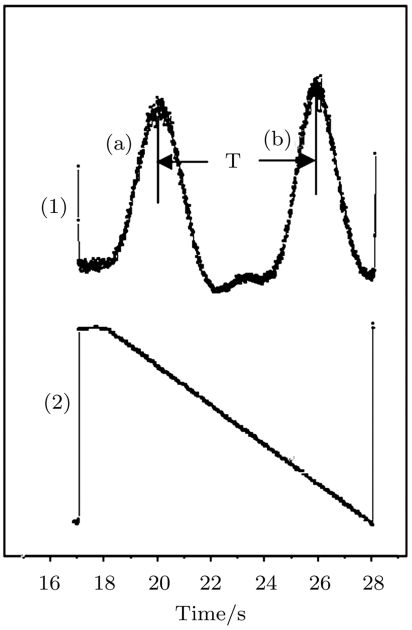


Fig.1. (1) is the scanning trace of light intensity with single photon detection when a position of the glycerol film is scanned along the z axis. Peaks in (a), (b) attribute to scattered light from the lower surface and the upper surface of the glycerol film, respectively. The modulation voltage along the z axis imposed on the piezo-scan table is shown in (2).

3. Results and discussion

The arriving time of two peaks can be acquired from the light intensity trace, and the thickness is calculated as $d = T \times V$. T is the time difference between two peaks, V is the calibrated scanning velocity and $V = 0.52$ μm/s here. The typical time-trace of the film optically scanned is shown in Fig.1. At room temperature, the vibration amplitude of the cover glass is estimated to be 0.014 nm in Ref.[16], far beyond our experiment's resolution (10 nm). So the thickness data only reflect the information about the film itself.

Two scanned images (a) and (c) are shown in Fig.2, where the capillary waves are intuitionistic. The repeatability of the scanning position of the piezoelectric scan stage is 15.8 nm along the x axis or y axis, which is much smaller than the dimension of the spot size determined by the laser wavelength (690 nm). So the effect of repeatability can be ignored. By comparing (a) with (c) it can be found that the surface of the glycerol film is not static. In addition, statistics on the thicknesses of the 400 positions of the surface in (a) and (c) are made in (b) and (d), respectively, to study the fluctuation of the film surface. The statistic distribution is fit by a Gaussian curve (black line) here. When the surface is in equilibrium, the distribution of the thicknesses on the surface submits to Gaussian distribution and the standard deviation of the 400 data should be consistent with the standard deviation of the fit curve. Once the condition changes, the thickness distribution of the studied plane will change, and the standard deviation will depart from the standard deviation of its Gaussian fit curve before it reaches a new equilibrium. A χ^2 test[17] is used and when Eq.(1) or Eq.(2) is satisfied, the thickness distribution of the surface has departed from equilibrium, which indicates the fluctuation of the surface.

$$(n-1)s^2/\sigma_0^2 \geq \chi^2_{\alpha/2}(n-1), \quad (1)$$

$$(n-1)s^2/\sigma_0^2 \leq \chi^2_{1-\alpha/2}(n-1). \quad (2)$$

Here χ^2 is the familiar distribution function. n is the test times, α is the error probability and here $n = 400$, $\alpha = 0.05$. σ_0 is the standard deviation of the Gaussian fit curve, s is the standard deviation of the 400 data of the plane. Based on this criterion, the standard deviation of the thickness in Fig.2(a) is far from that of the Gaussian fit curve, which implies fluctuation of the film surface. In contrast, the film surface shown in Fig.2(c) is in equilibrium.

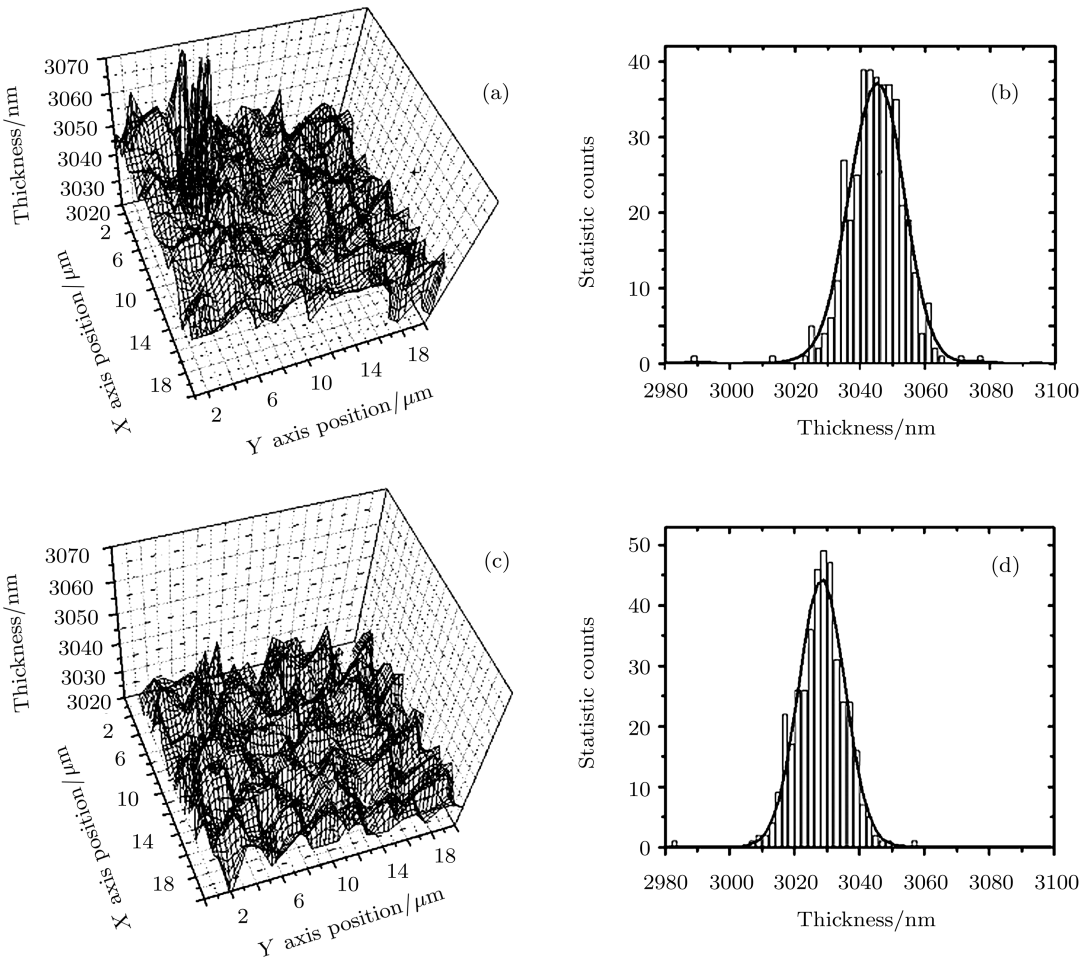


Fig.2. Scanned images showing the fluctuation of the glycerol film surface. (a), (c) are made by measuring the thicknesses of 400 positions of the x–y plane (20 μm×20 μm). (b), (d) are statistic distributions of their left scanning images, respectively. In (b), the standard deviation of the distribution s is 0.152 μm, the standard deviation of the Gaussian fit curve σ_0 is 0.015 μm. The standard deviation of the distribution s in (d) is 0.008 μm, and the counterpart of the Gaussian fit curve σ_0 is 0.014 μm.

The exact temperature dependence of the viscosity of glycerol η can be approximated by the Vogel–Fulcher–Tammann–Hesse (VFTH) law:

$$\eta = \eta_0 10^{\left(\frac{B}{T-T_0}\right)} \tag{3}$$

with below 283 K, $\eta_0 = 7.9 \times 10^{-8}$ Pa·s, $B = 1260$ K, $T_0 = 118$ K, and above 283 K, $\eta_0 = 3.54 \times 10^{-6}$ Pa·s, $B = 780$ K, $T_0 = 153$ K. All of the reference parameters presented are from Ref.[18].

The room temperature is about 295 K, and the change range is 2 K or so. The relation between viscosity predicted by the VFTH law and temperature is nearly linear. We obtain the viscosity dependence of thickness as seen in Fig.3. It is shown that the relationship between viscosity and thickness is linear, with the slope 0.703 μm/(Pa·s). So the main factor bringing about the fluctuation of the thickness is thermal induced viscosity change. When the viscosity

changes about 0.1 Pa·s, the thickness of the glycerol film changes about 70 nm.

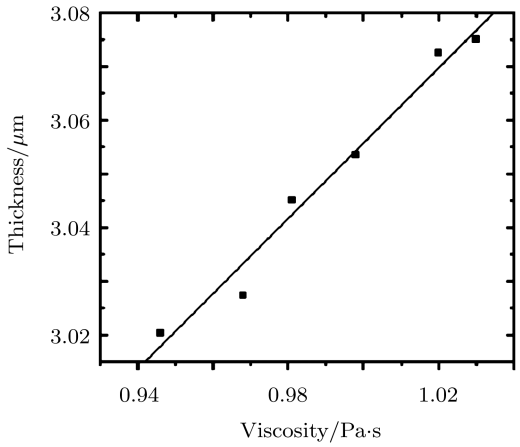


Fig.3. Viscosity dependence of the glycerol film thickness.

4. Conclusion

The surface dynamics of glycerol is probed by an optical scanning film. It is found that the scanned images make the capillary waves on glycerol film visible. Statistical distributions prove the fluctuation of glycerol film quantitatively. When the room temperature is just about 295 K, the thickness of the film surface is linear to viscosity. Though the variation range of room temperature is just 2 K, the change of glycerol film thickness can be measured exactly, which shows that the glycerol film could be a sensitive probe to temperature. Furthermore, we present that the thickness of the glycerol film linearly changes with viscosity predicted by the VFTH law near room temperature.

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