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Dendritic solidification of krypton

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We have measured the tip growth velocity v_{tip} and the tip radius R of krypton dendrites growing into a supercooled melt in the supercooling range $0.005 < \Delta T < 0.25$ K. The experimental results can be fitted by $v_{tip} = 3.1 \times 10^{-2} \Delta T^{1.73}$ cm/s and $R = 6.7 \times 10^{-4} \Delta T^{-0.68}$ cm which is compatible with $v_{tip} R \propto \Delta T$. Our experimental data do not confirm the stability hypothesis according to which $v_{tip} R^2 =$ const. The dendrites show four fins equal in shape and size in the dendrite tip region, indicating anisotropic attachment kinetics and corresponding influence on the growth rate.

Early experiments on ice dendrites have been reported by several authors and summarized by Sekerka.[1] Glicksman, Schaefer, and Ayers[2] introduced the so-called capillary injection technique to obtain data on growth kinetics of succinonitrile dendrites. In this method a seed crystal is growing out of a capillary into a volume of a homogeneously supercooled melt. Temperature distributions at the dendrite surface and in the bulk melt can be calculated, at least in principle, invoking diffusion of heat and continuity conditions so that it is not necessary to measure the temperature at the dendrite surface. For a review, see Ref. 3. Dendritic solidification of pure substances has also been studied using pivalic acid[4] and helium.[5]

Here we report on tip-velocity and tip-radius measurements on krypton dendrites as a function of supercooling. Krypton has been chosen because it forms a simple liquid similar to alkali metals, which makes it a favorite for the study of the liquid-solid transition because the short-range correlation of the liquid structure does not have to undergo a profound change prior to solidification. On the other hand, it is known that even in the case of globular organic molecules such as CCl_4 the short-range structure in the liquid is different from that in the solid.[6] This is one reason why structured organic liquids often can be highly supercooled.

The krypton gas with a purity of 99.997% was supplied by Messer-Griesheim. The main impurities O_2, N_2, and H_2O were extracted to less than 0.1 vpm (volume per million) by a rare-gas purifier each time before an experiment was started. The sample cell depicted in Fig. 1 had an outer diameter of 48 mm and a volume of about 100 cm^3. It was placed in a liquid bath in a Dewar-type double-wall glass vessel surrounded by liquid nitrogen. As a thermostating liquid, 1-butene was chosen because of its wide temperature range between melting point (−185.35 °C) and boiling point (−6.3 °C). The capillary was capable of being turned around its axis and had an inner diameter of 0.47 mm [outside diameter (o.d.) 0.59 mm] at the tip. A seed crystal was nucleated in the closed upper end by lowering the pressure above the surrounding liquid krypton. To isolate this cold spot thermally from the liquid bulk krypton phase, it was contained in a double-wall glass tube around the capillary top end. The cooling power was adjustable according to the sublimation temperature-pressure relationship of solid krypton. Once a seed crystal was nucleated, it grew down the capillary and entered the supercooled melt.

A propeller driven from outside the cryostat stirred the 1-butene bath to provide temperature homogeneity. The temperature of the bath was measured and controlled by a Tinsley 5840 ac resistance thermometer bridge with a deviation output connected to a TS-510 PID temperature

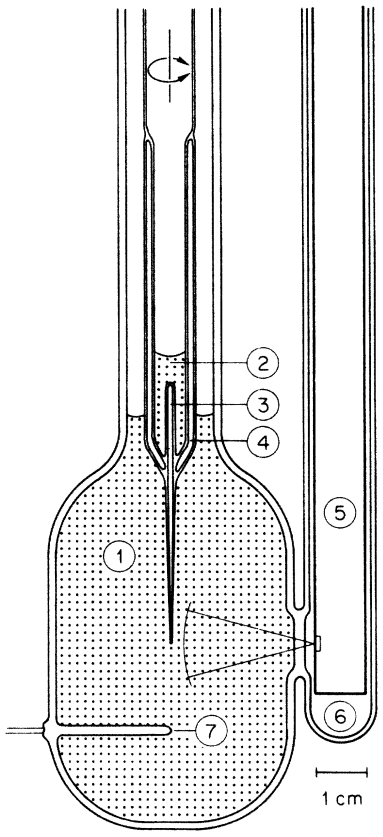

FIG. 1. Sample cell: (1) liquid krypton; (2) liquid krypton for cooling of the capillary; (3) closed top end of the capillary wherein nucleation occurs; (4) double-wall glass tube for thermal insulation; (5) boreskope with an angle of sight of 30°; (6) helium atmosphere; (7) fused-in platinum resistor (100 Ω at 0 °C).

controller (RV-Elektroniikka Oy). The vacuum between the vessel walls was adjusted to a counterheater power dissipation of about 4 W.

The temperature in the sample cell was measured directly by a fused-in-platinum resistor and a Tinsley Senator ac resistance thermometer bridge with 10^{-5} Ω resolution and a measurement current of 0.5 mA. Absolute calibration was achieved by comparison with the triple-point temperature $T_t = 115.7639$ K and pressure $P_t = 0.7312$ bar of krypton.[7] Errors in supercooling are estimated to be less than ± 0.0005 K including contributions of long-time drift in the measurement of the triple-point temperature over the period of half a year. The temperature of the liquid krypton was constant within a range of ± 0.0002 K during an experiment lasting typically 8 h.

The dendrites were imaged on a CCD video camera (aqua SM 72) with 576×384 pixels and a sensitivity of 0.005 lx by a boreskope (Olympus B-100-037-090-30) with an optical resolution of about 10 μm. The area to be observed in the image plane of the optical system could be selected by moving the camera parallel to the image plane. Thus optimum resolution of a dendrite tip region could be obtained. Illumination was provided from outside the cryostat by a cold light source opposite to the boreskope. The growth process was continuously recorded by a commercial videotape recorder combined with a time-date-stopwatch generator. Individual pictures could be selected and printed by a video printer. The optical magnification of this system was calibrated with a 0.5-mm grating on a glass plate which was dipped into the growth cell in place of the capillary under standard experimental conditions. The evaluated magnification factor on the video prints was 96.8 ± 1. At the beginning of an experiment the liquid krypton was thermally equilibrated at the operating temperature $T_t - \Delta T$. Then a seed crystal was nucleated. The growth of the crystal through the capillary took some minutes to hours depending on ΔT. Crystal growth in the capillary did not significantly influence the temperature field in the liquid krypton because of the very small volume of the capillary. After five main dendrite stems (four in a plane perpendicular to the capillary or slightly inclined, the fifth pointing downwards perpendicular to the plane of the four) were sufficiently large to have reached their steady-state tip growth velocity, the capillary was turned so that one dendrite stem (usually the one pointing downwards) came to lie in the calibrated object plane. For slowly growing dendrites ($\Delta T < 0.05$ K) the velocity was determined by measuring the position of the tip on successive video prints. Faster growing dendrites required an additional movement of the CCD camera with a constant, calibrated velocity to follow the dendrite tip. Tip radius measurements were carried out by comparing the video prints with standard parabolas of known curvature. The estimated error of the velocity measurements is about $\pm 5\%$. The accuracy of the radius measurements is about $\pm 10\%$, and sometimes limited by low contrast of the video prints. Figure 2 shows a typical dendrite tip with a fourfold symmetry and fins reaching almost to the tip. The four fins are equal in size and shape in the dendrite tip region. Regular sidearm spacing is observed at each fin. The sidearm spacing showed perfect agreement for the four directions. For $\Delta T > 0.02$ K dendrites scale with a factor depending on ΔT. For very low supercooling, $\Delta T \leq 0.02$ K, the tip becomes rounder in a manner to resemble more a paraboloid of revolution, as is expected for a crystal with an isotropic solid-liquid interface free energy (Fig. 3). Broughton and Gilmer[8] have shown that the solid-liquid interface free energy of a rare-gas solid is isotropic. This indicates that the appearance of the four fins at the dendrite tip is due to anisotropic attachment kinetics and that solidification rates are influenced by this. Krypton dendrites show increasing tip velocity and decreasing tip radius with increasing supercooling. Our measurements cover supercooling, ranging from 0.005 to 0.25 K, corresponding to a variation of the tip velocity by a factor of about 1000. Velocity and tip-radius data are shown in Figs. 4 and Fig. 5. The straight line in both plots represents a least-squares fit and leads to the relations

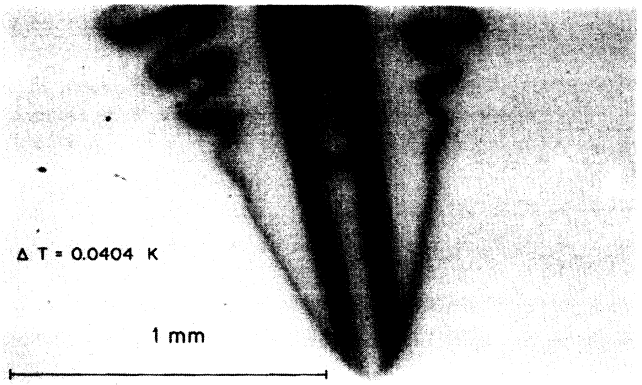

FIG. 2. Krypton dendrite showing four fins reaching almost to the tip.

$$v_{\text{tip}} = (3.12 \pm 0.09) 10^{-2} \Delta T^{(1.729 \pm 0.007)} , \quad (1)$$

$$R = (6.70 \pm 0.29) 10^{-4} \Delta T^{(-0.683 \pm 0.010)} , \quad (2)$$

where v_{tip} is in cm/s, R in cm, and ΔT in K. The combination of these equations leads to $v_{\text{tip}} \propto \Delta T$. This propor-

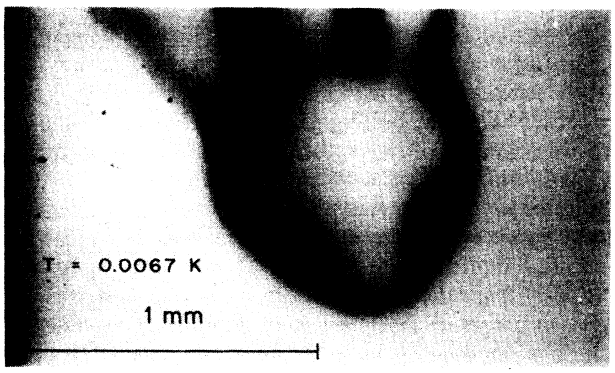

FIG. 3. Krypton dendrite at low supercooling showing a smoother tip shape resembling more a paraboloid of revolution.

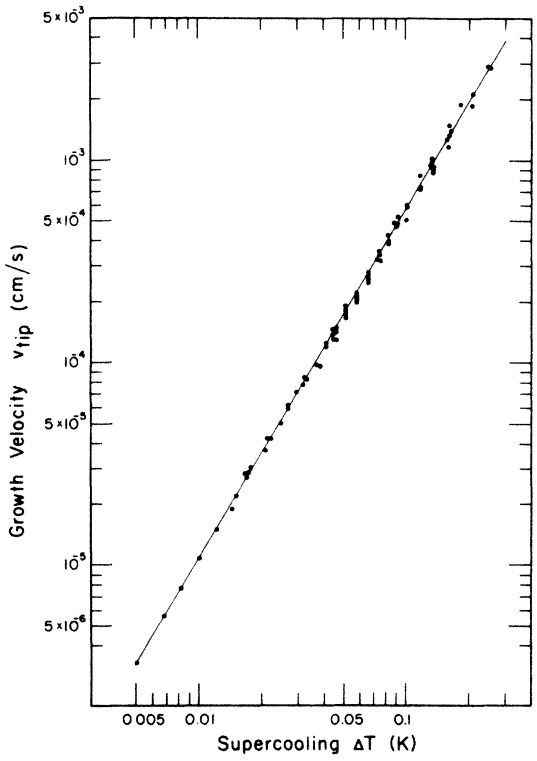

FIG. 4. Tip growth velocity as a function of supercooling.

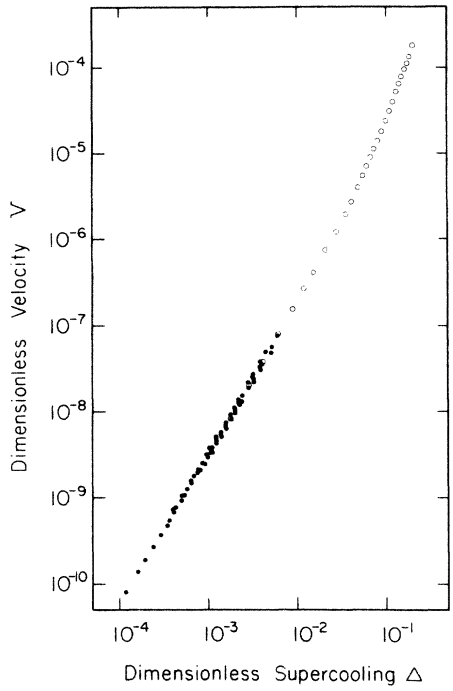

FIG. 6. Dimensionless tip growth velocity $V=v_{tip}d_0/2a$ is plotted as a function of dimensionless supercooling $\Delta=\Delta TC_p/L$ for succinonitrile (○) and krypton (●). For succinonitrile properties see Ref. 2, for krypton, Ref. 10: $L(s)=54.6$ J/cm^3, $c_p(1)=1.25$ J/cm^{3}K, $a(1)=7.24\times10^{-4}$ cm^2/s, $d_0=4.4$ Å. L is the latent heat per unit volume of the solid, c_p and a are the specific heat and the thermal diffusivity of the melt, respectively, and d_0 is the capillary length.

tionality has been deduced by Horvay and Cahn[9] for the so-called Ivantsov solution at low supercooling. In Fig. 6 we compare the growth rates measured for succinonitrile[2] with the growth rates of krypton dendrites. We use dimensionless supercooling and find excellent agreement. It has been argued that small growth rates are affected by convection. The four fins at the dendrite tip region are equal in size and shape. The sidearm spacings for the four directions are exactly equal. It is hard to believe that convection is reproducible for all supercoolings, for the five dendrite orientations, for two different substances, and the different experimental geometries used in the experiments with krypton and succinonitrile. To obtain more information about the conditions inside the krypton vessel we have monitored the temperature in the liquid krypton. No change of the temperature was found within instrumental resolution for small to medium supercooling. A convection should cause mixing in the whole volume. At the highest supercooling of $\Delta T=0.25$ K an increase in temperature of a few mK was detected during the experiment. Such an increase is compatible with diffusive heat flow. The overall dimensions of our dendrites at small supercooling are small compared to the diameter of the growth vessel. It can be shown by solving the equation of heat diffusion in spherical coordinates that the dendritic growth is not influenced by the walls of the growth vessel. At high supercooling the dimensions of our dendrites grow up to several mm. In this case the calculations of Ivantsov (references to this work can be found in Ref. 3) show that the distance between the dendrite tip and the wall of the growth vessel has to be large compared to the radius of curvature of the dendrite tip. Thus in all our experiments the dendrites grow into the same environment as they would do if the growth vessel would have infinite extension. This is confirmed by the fact that succinonitrile data and krypton data can be scaled by units which have been deduced under the assumption that the latent heat is

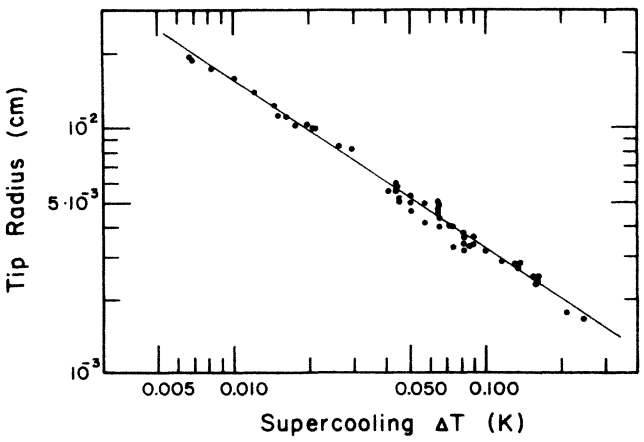

FIG. 5. Tip radius as a function of supercooling.

transported away from the dendrite by diffusion into an infinite volume of a supercooled melt (Ref. 9). Effects of convection or influences of the finite size of the growth vessel can be neglected. The experimental data do not confirm the stability hypothesis according to which $v_{tip}R^2 = \text{const}$. $v_{tip}R^2$ increases with increasing supercooling indicating that attachment kinetics play an important role in the rate of dendrite growth and that the volume solidified per time increases with increasing supercooling.

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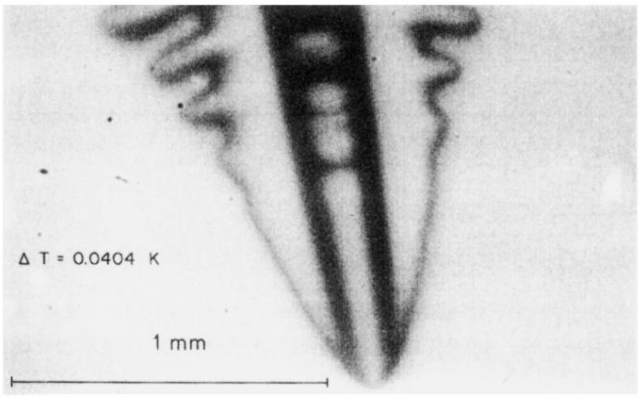

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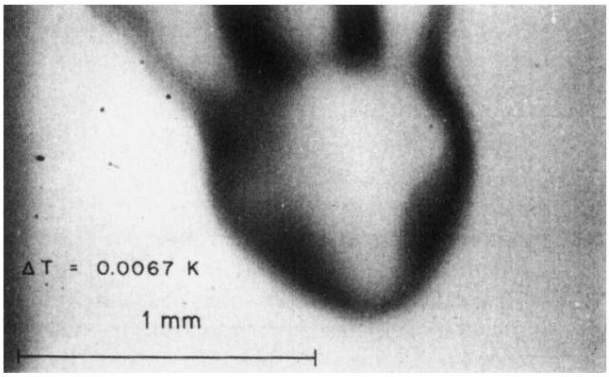

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