Pressure–Volume–Temperature Measurements on Atactic Polystyrene. A Thermodynamic View†

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ABSTRACT: It is shown by P–V–T measurements that the glassy solidification of atactic polystyrene can be described in a first approximation as a freezing-in process of only one internal parameter ξ and that this process cannot be a genuine second-order transformation. The equations of the pressure dependence of the glass transition temperature T_g are critically analyzed together with the Ehrenfest equations which hold for second-order transformations. In this connection will be discussed the idea that the second-order transformation postulated by the Gibbs–DiMarzio theory at the temperature T_2, which cannot be proved experimentally, should be the lowest possible glass temperature. According to the here reported freezing-in model precise instructions are given for the experimental determination of the terms in the considered equations. At 1 bar and 295 K we observed strong volume retardations of densified polystyrene. This must be taken into account for the construction of the equilibrium volume curve below T_g according to Breuer and Rehage.[4] In a molecular interpretation it is attempted to connect the model of the ξ parameters with certain fluctuations of physical cross-links.

Introduction

Atactic polystyrene is a polymer, which undergoes a glassy solidification without showing any crystallinity when it is cooled down isobarically from the melt. Together with the favorable temperature range of the glass transition this material is especially suited to serve as a model substance for studying the glassy solidification. P–V–T measurements are an important instrument to examine theoretical statements on the vitrification process.

There is a general agreement that the glass transition should be regarded as a kinetically controlled process, as it was first stated by Simon.[1] Concerning the background of the kinetical phenomenon, however, different views are under discussion. In the theory of Gibbs and DiMarzio (GD), a second-order transformation is postulated, which should occur at an infinitely slow cooling rate at about 50 K below the glass temperature T_g.[2,3] This transformation is regarded as the underlying cause of the glass transition at normal cooling rates. In agreement with other publications, however, we regard the glass transition as a freezing-in process without any connection to stability criteria as it ought to be for genuine transformations.[4–7]

In connection with this discussion the Ehrenfest equations take an important part:

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{\Delta\alpha^*}{\Delta\varkappa^*} \tag{1a}$$

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{\Delta c_p^*}{T \cdot \Delta\alpha^*} \tag{1b}$$

These equations connect the slope of the transformation line $(dP/dT)_{tr}$ for second-order transformations in the pressure (P)–temperature (T) diagram with the steps in the specific volume expansion coefficient $\alpha^* = (\partial\tilde{V}/\partial T)_P$, ($\tilde{V}$ = specific volume), the specific compressibility $\varkappa^* = -(\partial\tilde{V}/\partial P)_T$, and the specific heat c_p^*.

From the validity or invalidity of one or both of eq 1 arguments for and against the GD or freezing-in theory were deduced. We want to examine the meaning of these equations. From this we will get precise instructions for the measurement of the experimental quantities which appear in (1). The experimental results will be discussed in the context of some existing glass theories.

† Dedicated to Professor Maurice L. Huggins on the occasion of his 80th birthday.

Theory

The meaning of the Ehrenfest equations is first of all a formal one, because they result from only a mathematical standpoint: If the first derivatives of the free enthalpy G with respect to pressure and temperature, namely the volume V and the entropy S, of an equilibrium system show a bend at the same point (P,T) in their isothermal pressure and isobaric temperature dependence, then the influence of the pressure on the bend point will be described by eq 1.

Second-order transformations as the appearance of superconductivity fulfill these formal prescriptions. Therefore the pressure dependence of such transformations will be described by the Ehrenfest equations. This fact, however, must not lead to the conclusion that all bended volume and entropy curves which fit eq 1 ought to be second-order transformations.

This will become more evident by the following considerations: Volume and entropy curves with bends can also be explained by the freezing-in model. Several papers have been published on this subject.[4–8] All agree in the point that a freezing-in process is a transition from an equilibrium to a nonequilibrium state. One or more additional internal parameters ξ_i serve as variables to describe this process. These parameters are unambiguous functions of pressure and temperature in the equilibrium state, and according to the model they become constant in the nonequilibrium state. A thermodynamic treatment of this model results in rather complicated equations.[7] Only in the case that only one ξ parameter is sufficient to describe the freezing-in process does one get the simple function.[4]

$$\left(\frac{dP}{dT}\right)_g = \frac{\Delta\alpha^*}{\Delta\varkappa^*} - \frac{1}{\Delta\varkappa^*} \cdot \left(\frac{\partial\tilde{V}}{\partial\xi}\right)_{T,P} \cdot \left(\frac{d\xi}{dT}\right)_g \tag{2a}$$

$$\left(\frac{dP}{dT}\right)_g = \frac{\Delta c_p^*}{T \cdot \Delta\alpha^*} - \frac{1}{\Delta\alpha^*} \left(\frac{\partial\tilde{S}}{\partial\xi}\right)_{T,P} \cdot \left(\frac{d\xi}{dT}\right)_g \tag{2b}$$

$$\frac{\Delta\alpha^*}{\Delta\varkappa^*} = \frac{\Delta c_p^*}{T \cdot \Delta\alpha^*} \tag{3}$$

Equations 2 and 1 become identical, if $(d\xi/dT)_g$ vanishes, that means, if along the transition line (index g) ξ becomes constant. Such a freezing-in process at constant order surely does not represent a second-order transformation for kinetic reasons, although the Ehrenfest equations are formally valid. Thus these equations are not able to define second-order transformations, they are only a necessary condition. In the case of

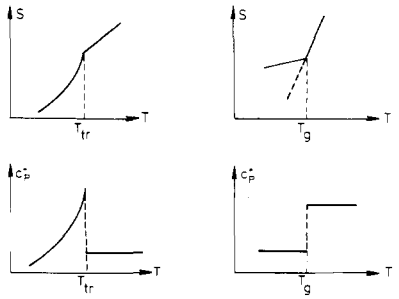

Figure 1. Specific heat c_p^* and entropy S as a function of temperature T for a genuine second-order transformation at T_{tr} (left) and a freezing-in process at T_g (right).

$$\left(\frac{\partial \tilde{V}}{\partial \xi}\right)_{T,P} = 0; \left(\frac{\partial \tilde{S}}{\partial \xi}\right)_{T,P} \neq 0 \tag{4}$$

or

$$\left(\frac{\partial \tilde{V}}{\partial \xi}\right)_{T,P} \neq 0; \left(\frac{\partial \tilde{S}}{\partial \xi}\right)_{T,P} = 0 \tag{5}$$

it would be possible that only one of the two eq 2 becomes identical with the corresponding Ehrenfest equation. In ref 4 it was shown that the constellation (4) cannot exist. In this case the step values $\Delta\alpha^*$ and $\Delta\varkappa^*$ would vanish, and therefore undefined terms would appear in eq 1 and 2. An analogous proof holds for (5). Thus for one single ξ parameter only both eq 2 are valid or none of them. With $(d\xi/dT)_g = 0$ this assertion also holds for the Ehrenfest eq 1. Already from their thermodynamic background these equations can be valid or not only simultaneously. The case that both volume and entropy do not depend on ξ does not meet the freezing-in model. If one still observes a bend in the $V(T)$ and $S(T)$ curves this should be an indication for a second-order transformation.

In the following we will quote some distinctive marks of genuine second-order transformations and freezing-in processes with $(d\xi/dT)_g = 0$: For freezing-in processes the states on one side (high-temperature side) of the freezing-in line should be path independent and on the other side (low-temperature side) path dependent. For equilibrium transformations the states must be independent of the history. In addition to this, the jumps of c_p^* and $\varkappa^*$ take opposite directions for second-order transformations and freezing-in processes. While c_p^* and $\varkappa^*$ of the frozen-in state are always smaller than those of the equilibrium state in the environments of the freezing-in line, the low-temperature state of a genuine second-order transformation has greater values of c_p^* and $\varkappa^*$ than the high-temperature state near the transformation line according to Landau's theory for second-order transformations.[36-38]

In Figure 1 these facts are reproduced together with the corresponding course of the entropy. It is to be seen that below the freezing-in temperature T_g the entropy always will be greater than it would be without any freezing. For second-order transformations the very opposite is true. Finally, rate effects exert a different influence on the position of the freezing-in temperature and on the transformation temperature, respectively. Rapid processes shift the freezing-in temperature to higher values and enlarge the probability of the freezing-in. Genuine transformations, however, only shift, if at all, to lower values for kinetic reasons.

Freezing-in processes with more than one internal parameter cannot be reduced to a formal description by simple equations. As it was shown by Meixner and a little bit later by Davies and Jones, only the following inequality can be stated:[6,9]

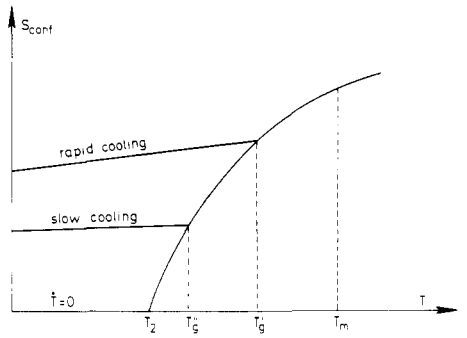

Figure 2. Conformation entropy S_{conf} as a function of temperature at various cooling rates $\dot{T}$ (T_m = crystallization temperature, T_g',T_g'' = glass transition temperatures, T_2 = transformation temperature of the GD theory).

$$\frac{\Delta\alpha^*}{\Delta\varkappa^*} < \frac{\Delta c_p^*}{T\Delta\alpha^*} \tag{6}$$

Thus eq 3 and 6 yield a possibility to distinguish between freezing-in processes with one and more ξ parameters. In connection with this an interesting publication of DiMarzio should be mentioned, where he pointed out that eq 3 and 6 are not able to distinguish between one or more parameters, because in the sense of the freezing-in model (3) always must hold, no matter how many ξ parameters freeze-in simultaneously.[10] This statement was rejected in a replique by Goldstein, however, as we will show later, by unsuited arguments.[11] The main point of the proof in DiMarzio's publication is the statement that the existence of a continuous freezing-in line demands a number of coupling equations between the ξ_i, that at least only one indepent ξ parameter remains whereas all others are dependent linearly.

We believe, however, that the freezing-in line is described by $(d\xi/dt)$ (t = time) rather than by the ξ_i as functions of T and P. Therefore it is possible that here two different properties, the time dependence and the P,T dependence, will be compared. At this time, however, we cannot say definitely whether a simultaneous freezing-in of several ξ parameters along a line in the $\tilde{V}$–T–P space causes a coupling between these parameters.

The glass transition obeys practically all the above mentioned criteria of a freezing-in process. Therefore it cannot be a transformation in a thermodynamic sense. At the first sight, here is a contradiction to ideas of Gibbs and DiMarzio, who showed in a recent paper that the pressure dependence of their postulated second-order transformation at T_2 obeys the Ehrenfest eq 1.[12] According to the authors this statement should also hold for $T_g(P)$, principally.

This contradiction can be solved. The authors conclude from the fact that there is a bend in the course of the entropy at T_2 with corresponding jumps in α^*, $\varkappa^*$, and c_p^* that here a "second-order transformation in the sense of Ehrenfest" or generally a "second-order transformation" is present. As we have shown above, this could be a genuine thermodynamic transformation or a freezing-in process with $(d\xi/dT)_g = 0$. It is our opinion that there are no objections considering the second-order transformation of the GD theory at T_2 as a glass transition at the lowest possible temperature corresponding to an infinitely slow cooling rate. Thus, at T_2, a freezing-in process would also take place, and the configurational entropy S_{conf} of the GD theory would change its course and become zero as it is shown in Figure 2.

This suggestion removes some discrepancies in the theory concerning the sign of the step values $\Delta\varkappa^*$ and Δc_p^*. The GD theory predicts positive jumps as it must be for a freezing-in

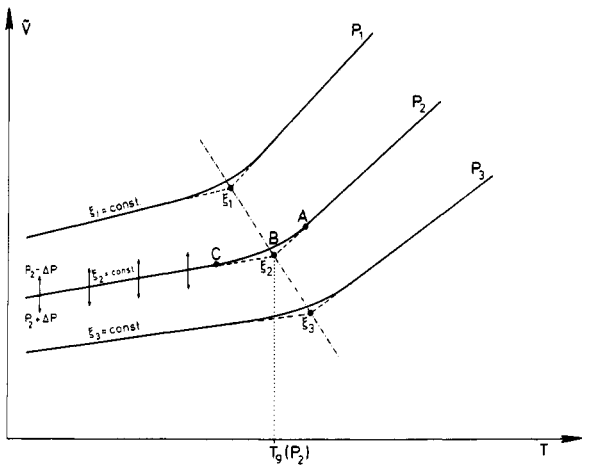

Figure 3. Isobaric vitrification process described by one internal parameter (see text).

process and not negative jumps as it ought to be for a second-order transformation according to Landau.[36-38]

Unfortunately there is no possibility for an experimental proof of these questions because the condition $\dot{T} = 0$ cannot be realized experimentally. We shall return to an indirect method in the discussion. However, the theoretical statements on the vitrification as a freezing-in process at normal cooling rates can be proved experimentally. For this some principles must be paid attention to because the freezing-in model only describes a certain ideal state and not the reality.

In Figure 3 the isobaric cooling curves at different pressures of a vitrifying polymer are reproduced in a V–T diagram together with the idealized curves which are required by the freezing-in model. The experimental curves show a broad transition range from the equilibrium to the nonequilibrium state without any bend. The usual construction for finding the glass temperature T_g by an extrapolation of the linear parts of the volume curves, however, meets the requirements of the freezing-in model. That is why it seems to be reasonable to consider the connecting line of all intersection points B at various pressures as the freezing-in line, later on to be called "glass transition line". The position of the points B is rate dependent. Therefore this line only makes sense if all points B were determined at the same time scale. The slope of the glass transition line in the P–T plane yields the value $(dP/dT)_g$. If one wants to compare this quantity with the step values of α^*, $\varkappa^*$, and c_p^* according to eq 1 or 2, these values must be found by the same way of cooling and the same extrapolation method. Otherwise glasses with different histories and different freezing-in lines, that is glasses with different sets of frozen ξ parameters, would be compared.

Hence $\Delta\alpha^*(P_2)$ can be found easily from the difference of the slopes of the lines $\overline{AB}$ and $\overline{BC}$. For the determination of $\Delta\varkappa^*(P_2)$ the isothermal compressibility should be measured at various temperatures during the isobaric cooling process. Such measurements are combined with a certain variation of pressure. Therefore some caution must be used to keep the history of the sample identical with the $\Delta\alpha^*$ measurement. This was the reason that the following procedure was obeyed:

After the usual measurement of the isobaric cooling down of the volume the compressibility $\varkappa^*$ was measured by slight pressure variations at certain temperatures in the glassy region, as it is illustrated by the arrows in Figure 3. For temperatures below the end of the freezing-in process (point C) one gets the temperature dependence of the specific compressibility of the glass $\varkappa_g^*(T)$ with the same isobaric history as in the case of the $\Delta\alpha^*(P_2)$ determination, that means with the same ξ_2 value. For temperatures above the beginning of the freeze-in the compressibility $\varkappa_l^*(T)$ of the melt can be determined in an analogous way or by isothermal measurements. The latter can be done because the thermodynamic properties do not show any path dependences in the liquid region. The freezing region $\overline{ABC}$ is omitted on purpose to avoid irreversible volume retardations. By an extrapolation of $\varkappa_g^*(T)$ and $\varkappa_l^*(T)$ to the corresponding $T_g(P_2)$ one gets the wanted step value $\Delta\varkappa^*(P_2)$ (see Figure 9). The measurements of Δc_p^*, too, should be performed in an analogous way on the same sample having an identical history of a similar extrapolation method.

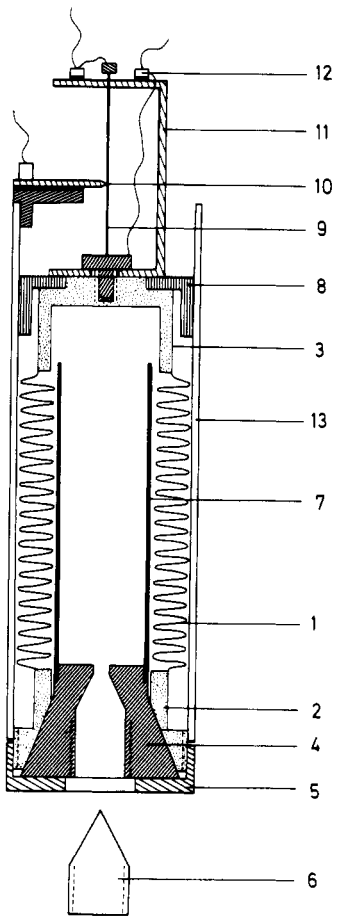

Figure 4. Diagram of pressure piezometer: (1) metal bellows; (2) conical end piece; (3) closed end piece; (4) tapered plug; (5) clamp; (6) sealing screw; (7) inside tube; (8) sliding cap; (9) sliding wire; (10) sliding contact; (11) mounting bow; (12) binding post; (13) guiding tube.

These extrapolations show why Goldstein's criticism of DiMarzio's argumentation is contestable.[10,11] In the opinion of Goldstein the following equations of the DiMarzio paper

$$S_l(T_g) - S_g(T_g) = 0 \quad V_l(T_g) - V_g(T_g) = 0$$

(index l = melt, g = glass)

cannot be right in all cases: Taking advantage of the path dependence of physical properties of glasses it is really possible to produce entropy and volume jumps at T_g. Surely this possibility exists but it does not meet the freezing-in model. A thermodynamic treatment of freezing-in processes is only possible under constant conditions, that means, path and time scale of the freezing-in process must be fixed unambiguously.

Experimental Section

The P–V–T measurements were performed with a metal bellows piezometer of the Bridgman-type[13] similar to the equipment de-

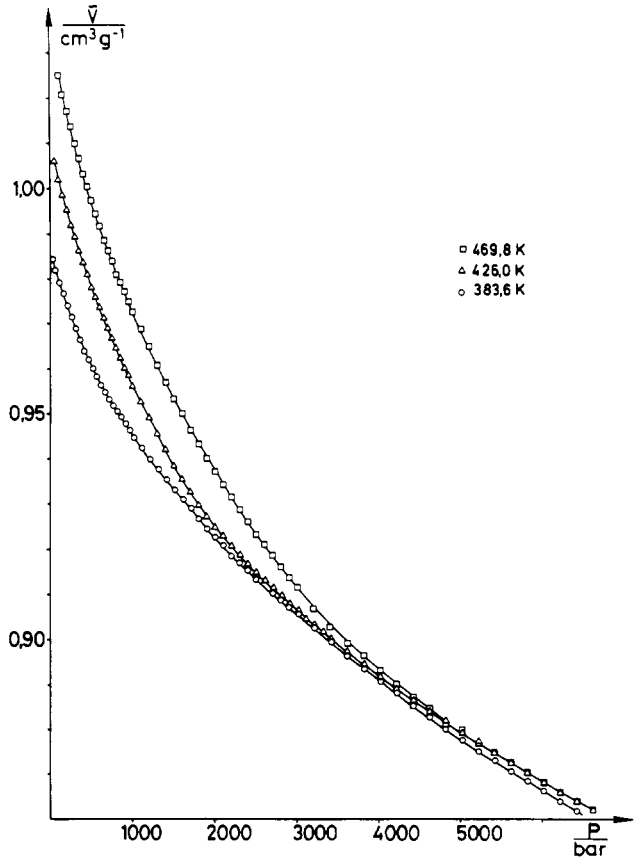

Figure 5. Volume–pressure plot of atactic polystyrene at various temperatures.

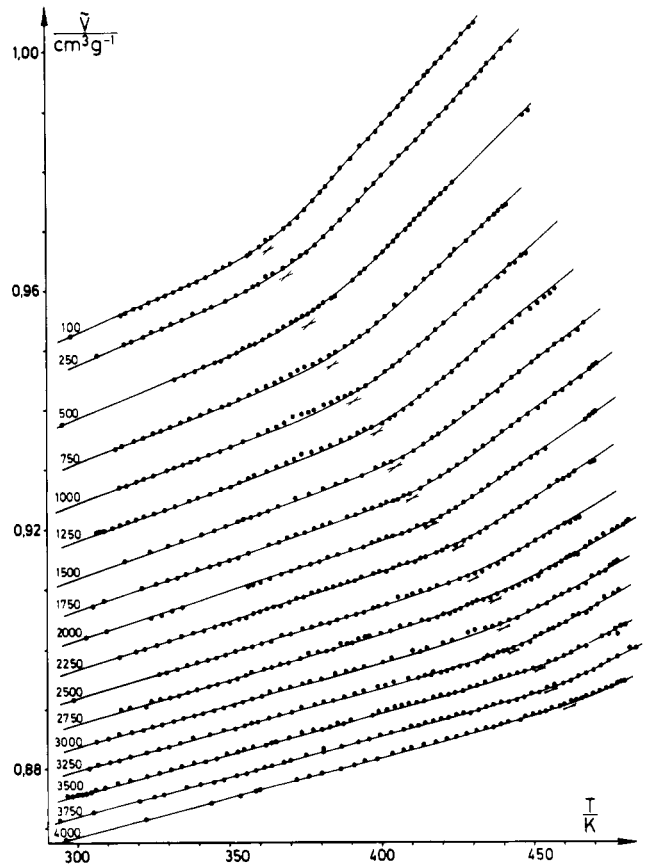

Figure 6. Volume–temperature plot of atactic polystyrene at various pressures.

scribed by Quach and Simha.[16,22] A diagram of the high-pressure piezometer is shown in Figure 4. The bellows 1 (Metallschlauchfabrik Pforzheim, GFR) is made of a 0.1 mm thin stainless steel with an outside diameter of 22 mm, an inside diameter of 14 mm, and a convolution length of 40 mm. The top of the bellows is welded to a closed end piece (3) and the bottom to an open conical end piece (2). The opening is closed by a tapered plug (4), a small hole passing through the plug being sealed by a screw (6). The plug is held in place by the clamp (5). The inside tube (7) is stuck on the plug (4) and is filled up rather completely by the (not shown) sample. Having mounted the tube with the sample and the plug inside the bellows, the whole device is filled with mercury under vacuum and sealed by the screw (6). The filled bellows then is fitted up with the sliding cap (8) and the sliding wire device (9, 11, and 12) and mounted inside the guiding tube (13). From the change of the electric potentials at the sliding contact (10) the elongation of the bellows can be calculated.

A calibration of the device was performed under room conditions measuring the mercury volume pushed out from the bellows into a capillary by defined elongation changes of the bellows. The sliding wire (0.3 mm diameter, 20 mm length, 17% Cr, 83% Ni) was calibrated by defined displacements with a micrometer slide. The influence of pressure and temperature on the dimensions of the metal bellows and the sliding wire has been calculated from material data. The volume change of the enclosed mercury has been calculated, too, by an equation quoted by Bett, Weale, and Newitt.[14]

Some difficulties arose in guaranteeing strict hydrostatic conditions for the sample. At last the sample was covered with a Teflon foil and brought into a capsule of thin sheet iron (30 μm). Over this, the tube (7) was supplied with a lot of bores.

The complete piezometer was put in a turned position into an oil-filled pressure vessel. This vessel is supplied with four electric isolated leads and an installed thermocouple for measuring the temperature of the inside bore of the vessel. The temperature of the vessel is regulated by a jacket flown through by a temperature controlled fluid. The accuracy of the temperature measurement was estimated to be ±0.1 K at room temperature and ±0.5 K at 470 K.

The hydrostatic oil pressure was produced by a device with an oil pump driven by compressed air and an intensifier. The hydraulicum was a 1:1 mixture of oil (Shell Diala D) and petroleum. An additional automatic precision control of the pressure was allowed by an electrically driven screw plunger pump being coupled to the pressure gauge. Thus isobaric long-time experiments could be performed at various temperatures. The pressure was read on a precision Heise gauge (Heise Bourdon Tube Co., Inc., Newton, Conn.) with a pressure range of 1–7000 bar. The accuracy of the gauge is 0.1% full scale. The accuracy of the volume measurements was estimated to be 15×10^{-4}.

The sample material was an atactic polystyrene of the Pressure Chemical Corp. with a low molecular weight (M_w = 20.400 g mol^{-1}) and a narrow distribution (M_w/M_n = 1.06).

The powdery material was molten into bars at 448 K under vacuum (10^{-7} bar) and then cooled down slowly (−18 K/h). In their final form the samples had a diameter of 11 mm and a length of 40 mm. The specific volume at 1 bar and 293 K was found to be 0.9550 cm^3 g^{-1} by means of the buoyancy method in butanediol.

All isobaric measurements were performed at a cooling rate of −18 K/h. In each case the sample was compressed to 1000 bar at room temperature and then heated up to such temperatures which guaranteed a liquid state of the sample at the pressure to be adjusted later on. Having reached a certain constancy of temperature the wanted pressure was adjusted and 1 h later the temperature program was switched on. The isothermal measurements were performed with an average rate of 1000 bar/h with pressure jumps of 50 bar (below 1000 bar), 100 bar (below 3000 bar), and 200 bar (else). For experimental reasons the measurements could only be evaluated at pressures above 50 bar.

Results and Discussion

In the temperature range from 370 to 470 K ten isothermal volume curves were measured. For reasons of a better survey only three of them are shown in Figure 5. At high pressures the curves approach each other without any intersecting. This finding is new, because all the isothermal measurements on atactic polystyrene published up to now show intersections of the curves in the glassy region.[15–18] At an earlier state of our experimental work we also measured intersections of the volume curves in the glassy state. After certain improvements

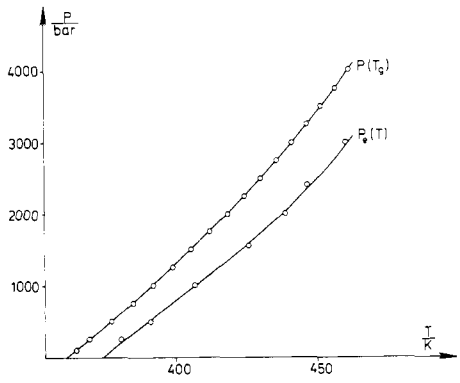

Figure 7. Temperature dependence of the pressure at the beginning of the freezing-in $P_e(T)$ and pressure dependence of the glass transition temperature T_g.

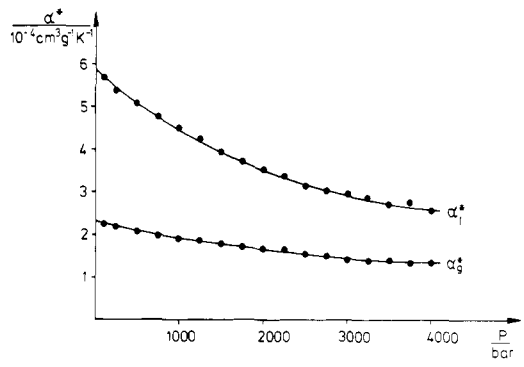

Figure 8. Specific thermal expansion coefficient α^* as a function of pressure (l = liquid state, g = glassy state).

concerning the hydrostatic conditions described in the "Experimental Section" the published volume curves were found.[13]

In the monotonous course of the volume curves no bend is to be seen where the glass transition takes place. The slopes of the curves, namely the specific compressibility $\kappa^*(P)$, show a sharp bend at the beginning of the vitrification, corresponding to point A in Figure 3. Figure 6 shows the result of the isobaric volume measurements in the pressure range of 100–4000 bar. Within the frame of accuracy one gets linear $\tilde{V}(T)$ curves, changing their slope in the glass transition range. The intersection points of the extrapolated linear parts of the curves yield the position of the glass temperature T_g. T_g shifts with increasing pressure to higher values.

In Figure 7 the change of T_g with pressure is plotted as curve $P(T_g)$ together with the change of the pressure of the beginning vitrification with the temperature $P_e(T)$. (The latter values can be found from the above-mentioned $\kappa^*(P)$ curves.) As it is to be seen, one gets different freezing-in lines being shifted to one another and having slightly different courses.

The specific expansion coefficient α^* was calculated from the slopes of the linear part of the volume curves in Figure 6. The result for the various pressures is shown in Figure 8. The expansion coefficient of the melt α_l^* decreases much more with the pressure than the expansion coefficient of the glass α_g^*. Therefore $\Delta\alpha^* = \alpha_l^* - \alpha_g^*$ also decreases with increasing pressure. At higher pressures, however, a certain levelling can be observed. The value of $\Delta\alpha^* = 3.5 \times 10^{-4}$ cm^3 g^{-1} K^{-1} at 1 bar and 361 K is a little bit greater than the value $\Delta\alpha^* = 3.4 \times 10^{-4}$ cm^3 g^{-1} K^{-1} at 1 bar and 360 K quoted by Richardson for the same material.[19] The discrepancies may be caused by different fitting processes of the volume curves. Richardson

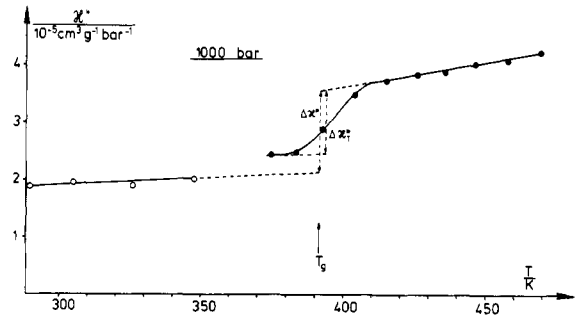

Figure 9. Construction for the determination of $\Delta\kappa^*$ at 1000 bar (see text).

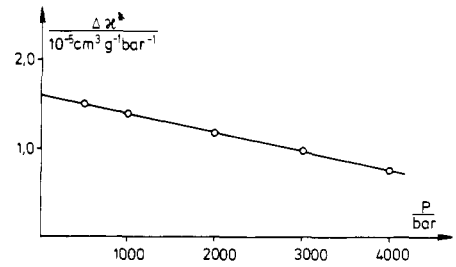

Figure 10. Variation of the step value $\Delta\kappa^*$ of the specific isothermal compressibility with the pressure.

used a quadratic equation in opposition to our linear approximation.

For the determination of the corresponding $\Delta\kappa^*$ values we made use of the procedure which was described in the theoretical section. The method is illustrated in Figure 9 where the result of the construction at 1000 bar is plotted together with the complete $\kappa^*(T)$ curve being obtained from measurements on a sample with an isothermal history. We note from the figure that the different histories do not change the κ^* values in the liquid region. Below the beginning of the freezing-in process, however, there are great differences resulting in a smaller step value $\Delta\kappa_T^*$ in the case of an isothermal history.

Figure 10 shows the pressure dependence of the constructed $\Delta\kappa^*$ values corresponding to an isobaric history. $\Delta\kappa^*$ decreases linearly with the pressure as it was found earlier by Rehage and Breuer for the pressure of the beginning freeze-in.[18,34] Up to now no comparable measurements of $\Delta\kappa^*$ on the same material have been published. Therefore our value of $\Delta\kappa^* = 1.60 \times 10^{-5}$ cm^3 g^{-1} bar^{-1} at 1 bar and 361 K cannot be compared with any parallel results. The published data for other products are widely scattered. These discrepancies are not only caused by experimental errors and product specifications but also by the evaluation method. An example for this is the measurements of Hellwege et al.[15] The authors found a $\Delta\kappa^*$ value of 0.8×10^{-5} cm^3 g^{-1} bar^{-1}, while a new evaluation of the same data by Gee yields a value of $\Delta\kappa^* = 2.0 \times 10^{-5}$ cm^3 g^{-1} bar^{-1}.[20]

The specific heat could only be measured at 1 bar by means of a Perkin-Elmer DSC-2 apparatus.[39] The course of $c_p^*(T)$ in the liquid and the glassy region was extrapolated linearly to the corresponding transition temperature. The resulting Δc_p^* value showed only little dependence on the cooling rate. An extrapolation to the usual cooling rate of 18 K/h yielded $\Delta c_p^* = 0.30$ J g^{-1} K^{-1}. On the same material Richardson measured a somewhat greater value of $\Delta c_p^* = 0.313$ J g^{-1} K^{-1}.[21,40] Δc_p^* should decrease with increasing pressure, but an estimation was not possible.

In Figure 11 all terms of the Ehrenfest equations, $\Delta\alpha^*/\Delta\kappa^*$, $\Delta c_p^*/T\Delta\alpha^*$, and $(dP/dT)_g$, are compared. It is to be seen that

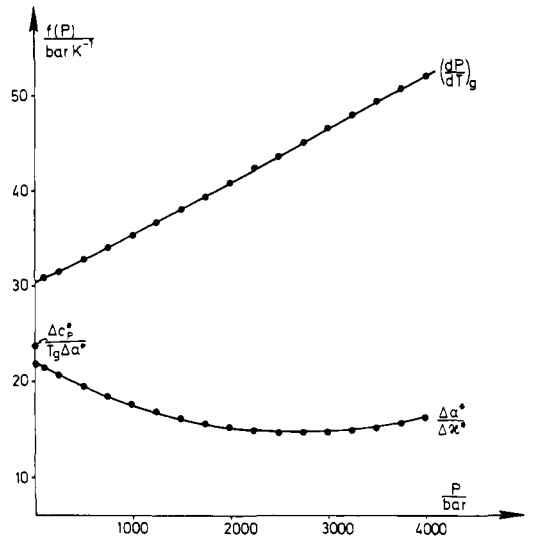

Figure 11. Examination of the Ehrenfest equations (see text).

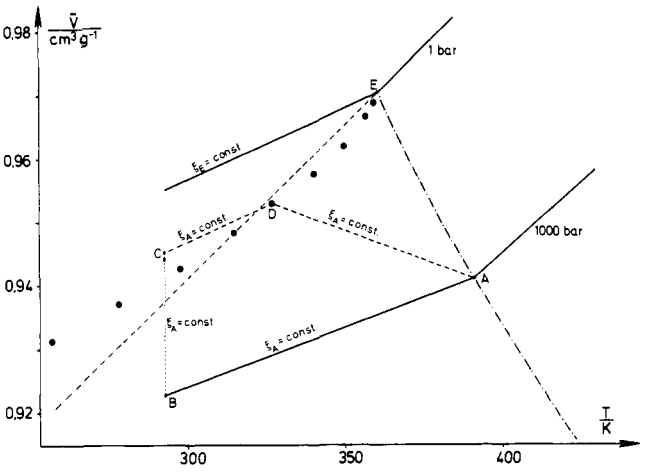

Figure 12. Volume–temperature plot of atactic polystyrene for the construction of the equilibrium curve of infinitely slow cooling (see text).

the equations do not hold. Beyond any experimental error the $(dP/dT)_g$ values are always greater than $\Delta\alpha^*/\Delta\kappa^*$ and $\Delta c_p^*/T \cdot \Delta\alpha^*$. With increasing pressure this finding gets even more strongly marked for the $\Delta\alpha^*/\Delta\kappa^*$ values. Because of missing $\Delta c_p^*(P)$ values this tendency cannot be checked by $\Delta c_p^*/T \cdot \Delta\alpha^*$.

This finding is similar to a result given by Breuer and Rehage[4] but it contrasts with most of the other publications reporting a validity of eq 1b whereas the right side of eq 1a was found to be approximately twice as small as the left side.[20,22–24] To our opinion three main points can be taken into consideration for these discrepancies: First, our measurements were performed under strict hydrostatic conditions in opposition to other measurements. Second, our method to determine the physical properties was adapted to the freezing-in nature of the glass transition being the same for all quantities. That means especially the strict observance of path and time dependencies. Third, all measurements were performed on one and the same material.

A striking point is the rather good validity of eq 3 as it was found earlier only by Breuer and Rehage.[4] That means in the sense of DiMarzio's statement that the freezing-in model and the reality of the glass transition are consistent.[10] Moreover, it can be concluded that the glass transition line can be described by the freezing-in of only one ordering parameter ξ. Provided that eq 3 holds also at higher pressures it is possible to calculate the pressure dependence of Δc_p^*. Naturally, with these calculated values eq 1b would be congruent with the lower curve in Figure 11.

The GD theory only gives unambiguous statements for the postulated second-order transformation at $T_2 < T_g$ and not for the glass transition itself. Therefore our results cannot invalidate this theory. Some doubts, however, remain, as quoted in the theoretical section.

Therefore we will try by an indirect method to construct the course of the equilibrium volume curve at 1 bar below T_g for the hypothetical case of an infinitely slow cooling rate. For this purpose we make use of a construction being described first by Breuer and Rehage;[4] a further explanation is given in ref 5. The method is based on the freezing-in model with only one internal ξ parameter, and it shall be briefly explained by means of Figure 12. The figure shows two isobaric volume curves being measured with the same cooling rate at pressures of 1 and 1000 bar. According to the freezing-in model, the transition range has been idealized to a sharp bend. Hence the internal order ξ_A of the point A remains constant along $\overline{AB}$ left to the dash-dotted glass transition line; on the right side it always takes its equilibrium value. Naturally at every point of the freezing-in line another value of ξ will freeze-in; for instance at one bar the value ξ_E. Because the model does not allow any change of ξ in the glassy region, the value ξ_A should remain constant during the isobaric cooling to room temperature (point B) as well as during the following isothermal pressure release to 1 bar (point C). This should be the case too for the isobaric heating process of the densified volume C at 1 bar to D. At D the line $\overline{CD}$ intersects the line $\overline{AD}$ the latter having the slope (index ξ_A = at constant ξ_A)

$$m = \left(\frac{d\bar{V}}{dT}\right)_{\xi_A} = \alpha_g^*(1000) - \kappa_g^*(1000) \cdot \frac{\Delta\alpha^*}{\Delta\kappa^*} \qquad (7)$$

That means $\overline{AD}$ is the geometrical locus of all volumes being just still in an equilibrium state at constant ξ_A.[4,5] At D the values for the internal ordering parameter (ξ_A), the temperature, and the volume of both lines are the same. Therefore the pressures must also be equal, i.e., 1 bar. Thus the volume where the internal order ξ_A exists in its equilibrium at 1 bar is represented by D. For details regarding eq 7 and Figure 12 see ref 4 and 5.

This construction can be performed for any pressure. The connecting line of the resulting intersection points D then represents the equilibrium volume curve at 1 bar below T_g at an infinitely slow cooling rate.

These model calculations are only reasonable if the internal order, once frozen-in, does not change its value in the glassy region. For this some doubts are justified especially concerning the pressure release from B to C.

Figure 13 shows the time dependence of the volume at 1 bar and 295 K of polystyrene being densified previously by an isobaric cooling procedure from the melt at the quoted pressure. Especially at higher densifications considerable time dependencies are to be seen. A very extreme behavior is revealed by the sample being densified at 5000 bar: the initially great densification of 1.8% is reduced to 0.8% after 1 week thus being smaller than the densification of a sample with a 1000-bar history.

Weitz and Wunderlich also observed volume retardations of densified glassy polystyrene.[25] They assume that polymers being frozen-in at high pressures and temperatures are highly stressed systems after the pressure release in the glassy state. The reduction of the stresses than causes the observed retardations. But this assumption alone can hardly explain the observed crossing-over of the retardation curves. It may be possible that at greater jumps of the pressure release the in-

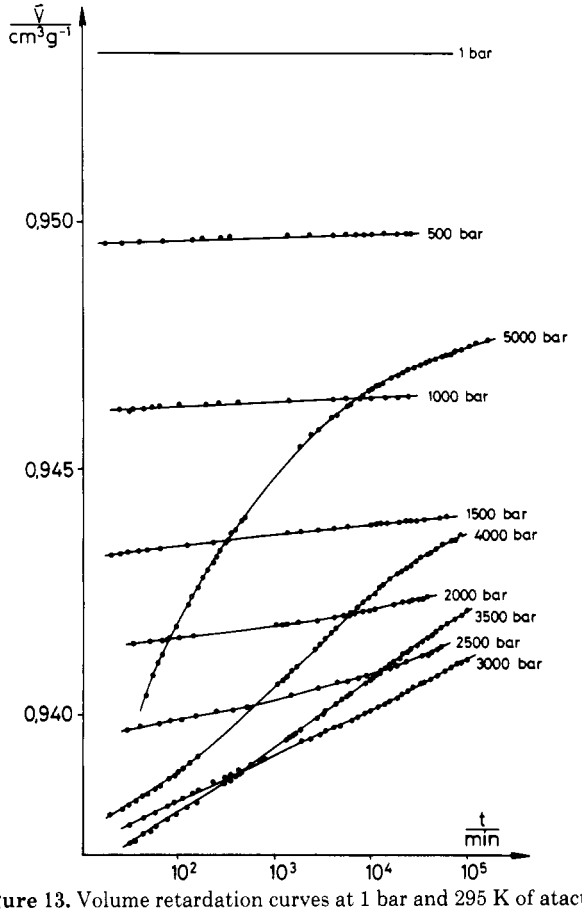

Figure 13. Volume retardation curves at 1 bar and 295 K of atactic polystyrene being densified previously by isobaric cooling from the melt at the quoted pressure.

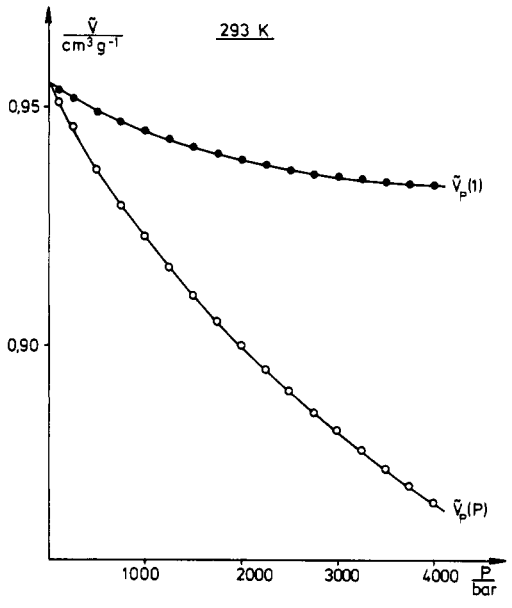

Figure 14. Specific volume of atactic polystyrene being densified previously by isobaric cooling from the melt at the pressure P. $\tilde{V}_p(P)$: at 293 K and P bar. $\tilde{V}_p(1)$: at 293 K and 1 bar (calcd).

ternal stresses exceed some limiting value and thus initiate certain yield processes.

Altogether these results make it plain that the *experimentally* gained densified volume at point C (in Figure 12) exhibits a time dependent and not a constant internal order ξ. Therefore we *calculated* the volume jump during the pressure release from B to C for a temperature of 293 K from our compressibility data. The result is plotted in Figure 14, the curve $\tilde{V}_p(P)$ representing the starting volume B, the curve $\tilde{V}_p(1)$ the final unretarded volumes C. It is to be seen that there is no saturation effect of the densification at 2000 bar, contrary to former measurements.[4,25] Even at higher pressures, say 3000 or 4000 bar, the densification increases. Therefore we must assume that retardation effects during and after the pressure release had affected the experimentally determined volumes. These calculations can also be carried out for higher temperatures making possible the determination of the slope of the line $\overline{CD}$. Together with the lines $\overline{AD}$ calculated from eq 7 one gets the equilibrium volume curve as represented by the filled points in Figure 12. Below T_g (point E) this curve at first follows approximately the extrapolated straight line of the liquid. At lower temperatures the points deviate in a weak rounding without any necessity to assume a transformation point with a sharp bend. On the whole this result meets the findings in ref 4. With reference to the volume retardations, however, one gets a somewhat weaker rounding of the equilibrium curve compared to the earlier measurements.[4] By a quite different method Smith calculated a similar volume curve.[26] The author applied the hole model of Hirai and Eyring to volume data for liquid polystyrene published in ref 15.

Apparently there are various possibilities in extrapolating thermodynamic data of the liquid state to lower temperatures beyond T_g. Only the linear method by Kauzman and Gibbs–DiMarzio leads to a sharp bend in the entropy and volume curves. This fact has been noted, too, by Gutzow who finds in his theory a widely curved course of the conformation entropy without any bend.[27]

In a recent paper published by Gordon et al. these geometric arguments are interpreted controversially.[35] The authors argue that the existence of a second-order Ehrenfest transition is not predicted on an absolutely sharp kink. The separation of two essentially linear portions of a thermal expansion curve by a rounded portion could be extrapolated linearly to a kink point, too, and thus exhibiting the characteristics of a second-order transformation.

As we discussed in the theoretical section the difference between a freezing-in process and a genuine second-order transformation is not a geometric problem but rather a problem of thermodynamics. To our opinion there is no doubt that at T_2, in the limit, and even more at T_g a freezing-in process takes place.

The introduction of ξ-parameters does not lead to statements about the molecular processes, which freeze in at T_g. Also the existing hole theories are not able to describe the underlying molecular processes connected to the glass transition.[28,29] While Nose assumes a total freezing-in of the hole fraction at T_g, McKinney and Simha derive directly from experiment a further decrease of the hole fraction h even below T_g, though to a lower extent.[30,31] In connection with the presence of secondary dispersion processes in the glassy state (β, γ mechanisms) we have to discuss the possibility that at T_g and at certain temperatures below T_g a successive freezing-in takes place (see also ref 32). Hence further transition temperatures T_β, T_γ exist which may be described by the freezing-in of internal parameters ξ_β or ξ_γ. According to this conception, at T_g the total internal ordering state does not freeze but only that part being described by ξ_α. The remaining parameters ξ_β, ξ_γ are still able to reach their equilibrium values within the time scale at temperatures below T_g under the limiting condition of a constant ξ_α. Then, at T_β the parameter ξ_β freezes in. Below T_β only ξ_γ can equilibrate under the limiting condition of frozen ξ_α and ξ_β, etc. Thus we guess that every freezing-in process could be described formally by the freezing of only one parameter. In this case for each freezing-in line eq 2 and 3 should hold.

Hence, the glassy *state* surely cannot be described by only one ξ parameter; the glass *transition*, however, being characterized by a T_g from an extrapolation method, can be represented approximately by the one-parameter model, at least in the case of atactic PS.

These aspects allow a new interpretation of the findings of McKinney and Simha for PVAC. Apparently the hole fraction h does not freeze-in completely at T_g but only a part of it. At lower temperatures the remaining holes take their equilibrium values under certain restraint conditions. In ref 33 Goldbach and Rehage propose the following molecular interpretation for the glass transition of PS: The interaction forces between neighbored phenyl groups of different polystyrene molecules work as fluctuating physical cross-links. Above T_g the frequency of the interchange of places is very high allowing the polymer chains to take their equilibrium positions within the time scale. At T_g a critical frequency of place interchanging is attained preventing the chains to glide off each other, the substance vitrifies. At lower temperatures only a part of the phenyl groups can move freely, under restraint conditions. At T_β all remaining phenyl groups loose their mobility causing a further restriction of the chain mobility. A correlation of the chain mobility to the hole fraction h of the Simha theory shows that h must not be constant at T_g.

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References and Notes

(1) F. E. Simon, *Ergeb. Exakten Naturwiss.*, **9**, 244 (1930).
(2) J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
(3) G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).
(4) H. Breuer and G. Rehage, *Kolloid Z. Z. Polym.*, **216**, 159 (1967).
(5) G. Rehage and W. Borchard, "The Physics of Glassy Polymers", R. N. Haward, Ed., Applied Science Publishers Ltd., Barking, 1973, Chapter I.
(6) R. O. Davies and G. O. Jones, *Proc. R. Soc. London, Ser. A*, **217**, 26 (1953).
(7) A. J. Staverman, *Rheol. Acta*, **5**, 283 (1966).
(8) J. Prigogine and R. Defay, "Chemical Thermodynamics", translated by D. H. Everett, Longmans, Green and Co. Ltd., London, 1954.
(9) J. Meixner, "Changements des Phases", Société de Chimie Physique, Paris, 1952, p 432.
(10) E. A. DiMarzio, *J. Appl. Phys.*, **45**, 4143 (1974).
(11) M. Goldstein, *J. Appl. Phys.*, **46**, 4153 (1975).
(12) E. A. DiMarzio, J. H. Gibbs, P. D. Fleming, and J. C. Sanchez, *Macromolecules*, **9**, 763 (1976).
(13) H.-J. Oels, Thesis, Clausthal, 1977.
(14) K. E. Bett, K. E. Weale, and D. M. Newitt, *Br. J. Appl. Phys.*, **5**, 243 (1954).
(15) K.-H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid Z. Z. Polym.*, **183**, 110 (1963).
(16) A. Quach, Thesis, Cleveland, 1970.
(17) P. Zoller, P. Bolli, E. Hersche, and U. Foppa, *Kunststoffe*, **66**, 363 (1976).
(18) H. Breuer, Thesis, Aachen, 1965.
(19) M. J. Richardson and N. G. Saville, *Polymer*, **18**, 3 (1977).
(20) G. Gee, *Polymer*, **7**, 177 (1966).
(21) M. J. Richardson, private communication.
(22) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).
(23) G. Gee, *Contemp. Phys.*, **11**, 313 (1970).
(24) S. Ishihara, A. Komatsu, Y. Tsujita, T. Nose, and T. Hata, *Polym. J.*, **2**, 530 (1971).
(25) A. Weitz and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2473 (1974).
(26) R. P. Smith, *J. Polym. Sci., Part A-2*, **8**, 1337 (1970).
(27) I. Gutzow, "The Physics of Non-Crystalline Solids", Fourth International Conference, Clausthal, 1976.
(28) T. Somcynsky and R. Simha, *J. Appl. Phys.*, **42**, 4545 (1971).
(29) T. Nose, *Polym. J.*, **2**, 124, 427, 437, 445 (1971).
(30) J. E. McKinney and R. Simha, *Macromolecules*, **7**, 894 (1974).
(31) J. E. McKinney and R. Simha, *Macromolecules*, **9**, 430 (1976).
(32) S. Manabe, N. Kobayashii, K. Imada, and M. Takayanagi, *Kogyo Kagaku Zasshi*, **73**, 1557 (1970).
(33) G. Goldbach and G. Rehage, *Kolloid Z. Z. Polym.*, **216**, 56 (1967).
(34) G. Rehage and H. Breuer, Forschungsbericht des Landes Nordrhein-Westfalen Nr. 1839, Köln und Opladen, 1967.
(35) M. Gordon, P. Kapadia, and A. Malakis, *J. Phys. A: Math. Nucl. Gen.*, **9**, 751 (1976).
(36) L. D. Landau and E. M. Lifschitz, "Lehrbuch der Theoretischen Physik", Vol. V, Akademie-Verlag, Berlin, 1966, p 467.
(37) G. Falk, "Theoretische Physik", Vol. II, Springer Verlag, Berlin, 1968, p 197.
(38) H. Stumpf and A. Rieckers, "Thermodynamik I", Vieweg & Sohn, Braunschweig, 1976, p 291.
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Possible Role of the Inertia of the Liquid in the Intrinsic Viscosity of Rodlike Particles

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ABSTRACT: In Burgers' formulation a suspended particle contributes to the viscosity of the suspension through the forces which the particle exerts on the liquid. For bodies in the form of a rod, it is convenient to distinguish between the radial forces (in the direction of the axis of the rod) and the tangential forces (perpendicular to the axis). The radial force is determined entirely by the velocity gradient, and its Fourier time transform has negligible high-frequency components. It is found that the radial contribution to the viscosity is not affected by the inertia of the liquid. The tangential force, however, is determined also by the rapidly fluctuating rotational Brownian motion, the Fourier time transform of which does contain components of quite high frequency. In these rapidly changing velocities and forces the inertia of the liquid plays an important role. The analysis is made for a rigid dumbbell, and although no explicit final answers for the intrinsic viscosity are obtained, the results in the limit of low and of high frequencies suggest that the tangential contribution to the viscosity is substantially reduced by the inertia of the liquid.

As early as 1938 Huggins[1] published a theory of the intrinsic viscosity of rigid rods, and it seems appropriate in a paper which pays tribute to his numerous contributions to science to discuss the possible effect of the inertia of the liquid. The model used by Huggins was a linear array of beads, used also in theories by Kuhn[2] and, later, by Kirkwood;[3-6] the rigid

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