Dilute solution theory is in accordance with the given quasi-static treatment[5,6]. The same holds for the theory of networks containing cross-links of finite lifetimes[7]. The given reduction (equations (3) and (4)), however, is only meaningful so long as one can speak of separate macro-molecules. The same holds for any relationship between E and β. From Zimm's theory for dilute solution, perfectly flexible macromolecules at low values of q, Peterlin has shown that

$$E = \varepsilon\beta^2 \qquad (6)$$

with ε between 0·136 for impermeable coils and 0·267 for freely draining coils[6]. In actual fact, ε can take these values only in the case of linear polymers of very narrow molecular weight distribution. For other linear materials ε should, according to dilute solution theory, rapidly increase with the broadness of the distribution[1,8].

In Fig. 1 a plot according to equation (6) is presented on a double logarithmic scale. The data were obtained from a series of anionic polystyrenes of different molecular weights. The high molecular weight samples were investigated in monobromo-benzene as a solvent and at a temperature of 25° C (ref. 9). The sample of the lowest molecular weights was investigated in bulk at a temperature of 196° C (ref. 10). The purpose of this graph is to show that the proposed reduction covers pronounced differences in molecular weight, concentration and temperature. Apparently it is valid even for the melt. For ε, a value of 0·27 is obtained. This is practically within the limits given previously.

It can be concluded from this rather surprising result that even in the melt the polymer molecules behave like separate molecules. The interaction with the neighbour molecules seems to be satisfactorily described by an effective friction factor. The value of this factor is irrelevant when the normal stresses are related to the shear stress.

The coincidence of reduced results shown here is, however, not always found. Concentrated solutions apparently show a more complicated behaviour than dilute solutions or melts, and their E-values are comparatively higher at corresponding β-values. The results shown in Fig. 1 were obtained for polymer samples which possess a very narrow distribution of molecular weights. With broader distributions coincidence is sometimes obtained for results on dilute solutions and on the melt.
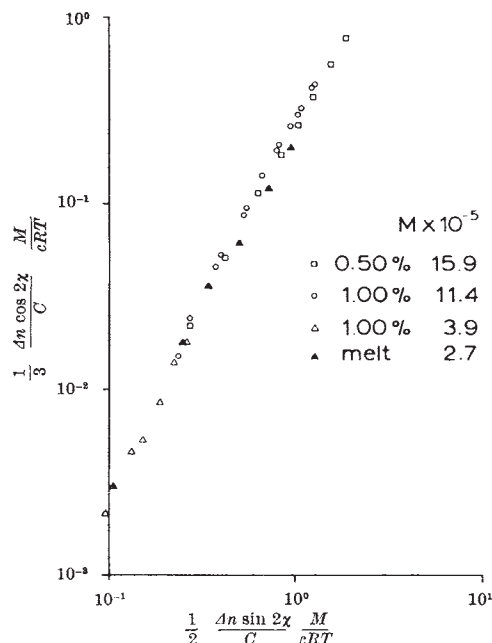

Fig. 1. Double logarithmic plot of the reduced flow birefringence data, obtained on various anionic polystyrenes. The molecular weights are indicated in the graph. Solutions in monobromo-benzene were measured at 25° C, melt measurements were carried out at 196° C.

This matter will be an important point for future investigations. In fact, some theories[11] for the determination of molecular weight distributions are based on the concept of the effective friction factor and on the simple additivity of the contributions of each molecular species to the properties of the bulk.

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A Moving Body must "appear" Cool

LANDSBERG has recently suggested[1] replacing Einstein's law $T_{\text{lab}} = T_{\text{cm}} (1 - w^2/c^2)^{1/2}$ with the law $T_{\text{lab}} = T_{\text{cm}}$, where T_{lab} is the temperature of a body as measured in laboratory co-ordinates, T_{cm} is the temperature of the body measured in its rest frame, and w is the velocity of the body relative to the laboratory. The word "appear" was placed in quotation marks in the title becasue T_{lab} may not be the temperature as observed by the casual laboratory observer at all, just as the Lorentz contraction is not seen by a laboratory observer under ordinary visual inspection, no matter how large it is, but is replaced by a rotation[2]. A black body at some temperature T_{cm} will emit a black body spectrum appropriate to T_{cm} in its rest frame, which will be seen Doppler-shifted to another temperature by other observers. An observer in front will see a blue-shift and one behind will see a red-shift, in neither case by a factor $(1 - w^2/c^2)^{1/2}$.

To see what is the proper definition of T_{lab} one may proceed either via general principles as Einstein did, or via simple hypothetical experiments. The elegance and generality of the former technique evidently are compensated by some vagueness or appearance of arbitrariness, as evidenced by the fact of Landsberg's objection. Thus a simple experiment is desired. It is impossible, however, to carry on the sort of quasi-static variations and transfers of energy demanded by "thermodynamics" (sometimes called "thermostatics") between two bodies that are moving rapidly together or apart. The only relevant experiment is one where the relative velocity is transverse to the line of centres of the two objects; then the distance remains constant. Consideration of such a hypothetical experiment leads at once to the conclusion that Einstein's definition is the only one consistent with the zero'th and second laws of thermodynamics. [By the zero'th law is meant that there exists a unique function, called temperature (or a one-to-one function thereof), such that two bodies in thermal contact remain in their initial states if and only if they have the same temperature.]

Consider, then, the following experiment: place a black body B_1 at one temperature T_0 at the centre of a revolving turntable, and place another B_2 at laboratory temperature T_{lab} on the rim, so as to move with constant velocity w. Allow radiative transfer between the two through a narrow radial tube. Unless the spectrum radiated by B_2 as seen at B_1 is a black body spectrum of temperature T_0 and that of B_1 as seen at B_2 is a similar spectrum of temperature T_{cm}, net radiative transfer will occur, causing one to get hotter and the other cooler. Thus one must define $T_{\text{lab}} = T_0$ when the above spectral conditions hold, and only then. Any other definition leads to a viola-

tion of the second law of thermodynamics. But photons from B_2 suffer a transverse Doppler shift toward the red by a factor $(1-w^2/c^2)^{1/2}$ as seen at B_1. Thus $T_{cm}(1-w^2/c^2)^{1/2} = T_{lab}$. For consistency, one should verify that photons from B_1 are seen blue-shifted by the factor $(1-w^2/c^2)^{-1/2}$ as seen at B_2. The transverse Doppler shift formula may not be used directly to find out how things are seen by B_2 as it is in accelerated motion, but one may use either of two arguments to solve the problem, First, one may note that the shift already found is because clocks at B_2 would run slower than those at B_1 by a factor $(1-w^2/c^2)^{1/2}$; applying this in reverse, one finds the proper blue-shift of B_1's spectrum as seen at B_2. Second, one can replace the special-relativistic discussion by one that depends on the equivalence principle, and use rotating co-ordinates in which B_2 is still. Then the spectral shifts are gravitational in origin, because of the gravitational potential $-\dfrac{1}{2}r^2\omega^2$.

This ensures reciprocity between the spectral shifts of each body as seen at the other. These shifts have been verified in the laboratory[3], which verifies Einstein's law.

Landsberg's concern about the properties of bodies initially at rest and put into motion does not seem to fall within the scope of this discussion. The results depend on how they are set moving; does one keep the proper volume or the volume as seen in the laboratory constant during the acceleration? Furthermore, deformations must occur, since rigid bodies cannot accelerate, according to the special theory of relativity[4]. The transformation of temperature under consideration is valid only for different observers looking at the same body, or for finding T_{lab} for bodies the rest-temperature of which is known by other means, such as by knowledge of their volume, pressure and composition.

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Temperature of a Moving Body

RECENTLY Landsberg[1] suggested that the "true" value of the temperature of a body moving at relativistic speeds will appear the same as the temperature measured by an observer moving with the body itself. This conclusion is reached by re-defining temperature in terms of entropy and internal energy.

Fremlin[2] suggests that some physical concept of temperature must be introduced before the mathematics becomes valid, and shows that if the temperature is defined on a kinetic model (that is relating the temperature to the random velocities of the molecules) then the body appears cooler to any observer relative to whom it has a uniform velocity. He states that the apparent component of velocity in the direction of motion is reduced by a factor β^2, where as usual

$$\beta = \left(1 - \frac{V^2}{c^2}\right)^{-\frac{1}{2}}$$

and V the velocity of the whole body relative to the observer, while the velocity components perpendicular to the direction of motion are reduced by a factor β.

The apparent reductions in the velocity components are, however, greater than those that Fremlin has calculated. Let the body have speed V relative to an observer A. If an observer at rest relative to the body, B, measures the velocity component of an average molecule in the direction

of relative motion as u, then the observer A measures this speed as

$$u' = \frac{u+V}{1+\dfrac{uV}{c^2}}$$

(See, for example, McCrea[3] for a derivation of this.)

As the body has velocity V, observer A estimates the molecule speed relative to the body as

$$\frac{u+V}{1+\dfrac{uV}{c^2}} - V = \frac{u}{\beta^2\left(1+\dfrac{uV}{c^2}\right)} \tag{1}$$

This expression reduces the apparent speed by the further factor

$$\left(1+\frac{uV}{c^2}\right)$$

over what Fremlin obtained.

A velocity component v in a direction perpendicular to the motion of the body, as measured by B, is measured by A as

$$\frac{v}{\beta\left(1+\dfrac{uV}{c^2}\right)} \tag{2}$$

This again is smaller than the Fremlin result by the same factor

$$\left(1+\frac{uV}{c^2}\right)$$

Thus if the temperature is defined in terms of the random velocities of molecules, the temperature of a moving body will appear cooler. The amount of apparent cooling is, however, greater than deduced by Fremlin, though for most temperature ranges expressions (1) and (2) will reduce to those obtained by Fremlin as u will be much less than the velocity of light c.

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CHEMISTRY

Hydrazine Synthesis in the Silent Electrical Discharge

THE synthesis of hydrazine from ammonia in the silent discharge was first reported by Besson[1]. Subsequent investigations by other workers on flowing systems[2,3] only led to both low conversion and very low hydrazine yields being obtained. The yields are normally expressed as grams of hydrazine per kilowatt hour of energy dissipated in the actual discharge. More recent work claims substantially increased yields by withdrawal from the discharge of the desired product in an absorbent[4]. A reasonable working explanation for the increase in yield reported in this case could well be as follows. The reactions in the discharge are undoubtedly of a very complex nature probably consisting of a series of competing formation and degradation reactions for any particular species in the discharge. The use of an absorbent is equivalent to reducing the residence time of the chemical species in the discharge, that is, it reduces the possibility of its decomposition by either further electron bombardment or other collision phenomena. Ideally, the absorbent would be selective only for the product and allow the activation reactions to take place virtually unhindered by its presence. Furthermore, if the effect of the absorbent is assumed to be entirely physical in nature, it follows that any method of reducing the residence time of the product