transition as T is lowered (we assume the nucleating solid to be in the bcc phase for $T > 1.464$ K because this is the natural phase in this T region; neutron scattering studies[3] are needed to clarify this point), the associated increase in $n_{sM}(T)$ would cause the experimental data to double back from point A to point B in Fig. 3 and then to continue downward along the curve. This effect was not observed, from which we conclude that the solid film in the run for $N = 0.2976$ most probably remained in the metastable bcc phase for $T < 1.464$ K.

It had been anticipated at the outset of the experiment that evidence of layer-by-layer deposition of the solid would be observed. This was not the case, perhaps because of the quantum nature of He^4 as well as thermal motion, effects which would tend to smear out evidence of such a local phenomenon.[12,13]

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[1] The qualitative nature of the effect of surface on the solidification of He^3 is discussed by M. Cederbaum and J. Landau, Phys. Lett. 55A, 265 (1975).

[2] GTA grade of Grafoil R, produced by Union Carbide, Carbon Products Division, Parma, Ohio. Some physical properties of Grafoil as well as details of the adsorption of He^4 from the vapor phase are discussed by M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. Vilches, Phys. Rev. A 8, 1589 (1973). See also G. J. Coellner, J. G. Daunt, and E. Lerner, J. Low Temp. Phys. 21, 347 (1975).

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[9] This form is a simple interpolation between the short range z^{-3} behavior and the long range z^{-4} behavior of van der Waals potentials. See the classic paper of E. S. Sabisky and C. H. Anderson [Phys. Rev. A 7, 790 (1973)] for many experimental and theoretical details.

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Soret-Type Motion of Macromolecules in Solution*

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We show that by using a simple optical method, thermodiffusion processes can be exploited for an accurate, reasonably fast determination of the diffusion coefficient D for various macromolecules in solution. As a byproduct, reliable values for the thermal-diffusion ratio k_T are also derived. Furthermore, we report experimental evidence of a new type of convective instability generated in a dilute solution of macromolecules heated from above.

Although it is not widely known, a temperature gradient can make macromolecules sediment from a solution in very much the same way as a centrifugal field does. This is due to the Soret effect or thermodiffusion,[1] a physical process particularly well studied in the case of solutions of electrolytes, mixtures of liquids, and mixtures of gases.[2,3] Much less work has been done in the field of solutions of macromolecules and most studies have been mainly concerned with the investigation of steady-state properties.[4] One exception is the work of Meyerhoff and Nachtigall[5] who performed an optical study of the dynamics of the Soret effect in solutions of polymers in toluene and derived a set of values for the diffusion coefficient D. In spite of their accurate work, thermal diffusion never became a well-established technique for the determination of diffusion coefficients of macromolecules. Partial explanation of this situation lies in the fact that the technique used in Ref. 5 is rather time consuming.

In this Letter we show that by using a very simple optical method employing a laser-beam deflection technique, thermal diffusion can indeed become a relevant, accurate, reasonably fast technique for the determination of D for macromolecules in solution. We also show that its range of applicability is probably quite large. Indeed, we present data for various macromolecular species, including polymers, micelles, and proteins. Values for the thermal-diffusion ratio k_T are also presented. Finally, we discuss the special case of macromolecules that, rather exceptionally, migrate to the hot plate. This situation can generate a new type of convective instability even if the sample is heated from above. Direct evidence of this instability will be presented.

The experimental setup and optical technique are identical to those described in a previous article.[6] The index-of-refraction gradient (dn/dz) is measured by determining the angular deflection $\Theta = l(dn/dz)$ of a laser beam, mildly focused in the midplane of a thin sample confined between two horizontal metallic plates. The length of the fluid samples was $l = 20$ mm, and thicknesses of 0.5 and 1 mm were used.

Measurements were taken according to the following procedure. Each sample was left to thermalize inside the temperature controller until the temperature of the two plates became equal and the transmitted-beam angular position was stationary. A temperature difference ΔT, typically less than 0.7°C, was then suddenly applied between the plates (heating was done from above). Such a temperature could be maintained over a few hours to better than ±0.2 mdeg. Measurements of Θ were made every minute after the temperature difference had been applied. Typical data for Θ versus time t are shown in Fig. 1. Notice that Θ undergoes first a very rapid variation, followed then by a very slow one. Indeed, dn/dz is the sum of two contributions:

$$\frac{dn}{dz} = \frac{\partial n}{\partial T}\frac{dT}{dz} + \frac{\partial n}{\partial c}\frac{dc}{dz}. \tag{1}$$

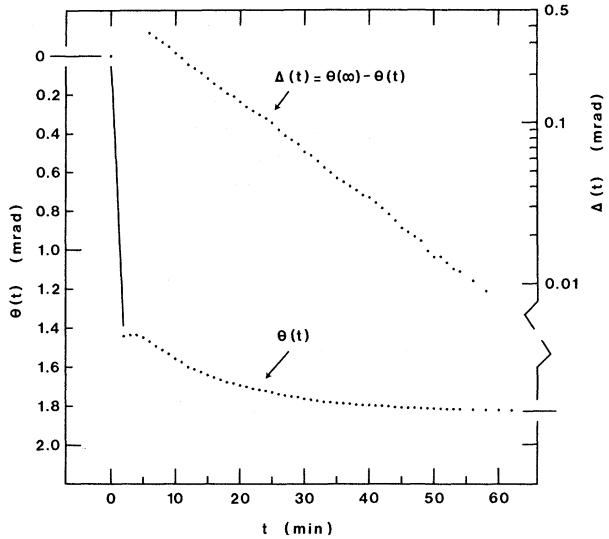

FIG. 1. Typical time evolution of the beam deflection $\Theta(t)$ and $\Delta(t) = \Theta(\infty) - \Theta(t)$ for a 1% mass fraction aqueous solution of sodium dodecyl sulfate. Salt concentration was 0.1M NaCl, $\Delta T = 0.658$°C, sample thickness $a = 1$ mm. Data for $\Delta(t)$ are presented on a semilog plot.

The first contribution is due to the thermal expansion of the sample and sets in almost instantaneously. The second contribution is the interesting one, since it is due to the buildup of the thermally induced concentration gradients.

According to the theory,[7] the time evolution of dc/dz estimated in the center of the cell is given by

$$\frac{dc}{dz} = -\frac{\Delta T}{a}\frac{k_T}{T}\left[1 - \frac{4}{\pi}\exp\left(\frac{-t}{\tau}\right)\right]. \tag{2}$$

This expression is valid for $t > \tau/3$, where $\tau = a^2/\pi^2 D$, and a is the samples thickness. Incidentally we would like to point out that the square bracket in Eq. (2) is identical to the expression one obtains for dc/dz in the case of a thin sample placed in a (small) uniform acceleration field.[8] According to Eq. (2) dc/dz should decay as a pure exponential characterized by the time constant τ, at least for $t > \tau/3$, while for $t < \tau/3$ higher-order terms come into play. These terms account for the initial rounding observed in the plot Θ versus t. The agreement between Eq. (2) and the experimental data can be judged from Fig. 1 where data for $\Delta(t) = \Theta(\infty) - \Theta(t)$ are reported in a semilog scale. From the slope of this plot we derive the value of the diffusion coefficient.[9]

Values for the thermal diffusion coefficient, $D_{\text{th diff}}$, and k_T for different macromolecules are

TABLE I. Thermal diffusion ratio k_T and diffusion coefficient D for various macromolecules in solution. All the data are taken at, or corrected for, $T = 25$ °C. Water was used as a solvent for all samples, except polystyrene, which was dissolved in toluene. The salt content is $0.1M$ NaCl for sodium dodecyl sulfate solutions. The lysozyme sample is prepared at $pH = 4.2$ using a $0.1M$ sodium acetate–acetic acid buffer. The bovine serum albumin sample is prepared at $pH = 6.9$ using a $0.5M$ KCl buffer.

	c (wt.%)	k_T	$D_{\text{th diff}}$ (10^{-7} cm^2/sec^{-1})	D_{ref} (10^{-7} cm^2/sec^{-1})
Triton X-100	1.0	+0.210	5.82	5.80[a]
Sodium dodecyl sulfate	0.5	+0.048	10.8	10.30[b] 10.2[c]
Sodium dodecyl sulfate	1.0	+0.096	11.5	11.10[b] 9.01[c]
Polyvinyl alcohol[d]	0.7	−0.113	2.01	1.35[b,e]
Polystyrene[f]	1.0	+0.531	5.55	5.58[b]
Lysozyme	1.0	+0.061	11.3	11.9[g]
Bovine serum albumin	3.0	+0.168	6.78	6.7[h]

[a] M. Corti and V. Degiorgio, Opt. Commun. 14, 358 (1975).

[b] Light scattering values kindly determined by M. Corti on the same samples we have used.

[c] D. H. McQueen and J. J. Hermans, J. Colloid Interface Sci. 39, 389 (1972).

[d] The sample is highly polydisperse.

[e] Z average value.

[f] The sample is a mondisperse standard $M_w/M_n = 1.0$, $M_w = 110\,000$.

[g] S. B. Dubin, Ph.D. thesis, Massachusetts Institute of Technology, 1970 (unpublished).

[h] S. B. Dubin, J. H. Lunacek, and G. B. Benedek, Proc. Nat. Acad. Sci. 57, 1164 (1967).

reported in Table I together with reference values, D_{ref}. Typical accuracy for $D_{\text{th diff}}$ is better than ± 1% for the polystyrene sample and drops to ± 5% for lysozyme. Good agreement is found with D_{ref} except for polyvinyl alcohol, which was a highly polydisperse sample. A discussion of the meaning of $D_{\text{th diff}}$ in polydisperse systems will be given in a forthcoming paper.[10] These results show that indeed dynamic thermodiffusion measurements allow precise determination of the diffusion coefficient of macromolecules, and that they can be a valid, useful alternative to classical techniques like free diffusion[11] or dynamical studies performed with analytical centrifuges.[8] Light-scattering self-beating spectroscopy,[12] the most modern technique for the determination of D, is possibly more accurate and less time consuming than thermodiffusion, expecially in the fairly high molecular weight range. It should be said, however, that due to the fact that a laser beam can be focused down to a small diameter, operation with a 0.2-mm-thick sample is quite feasible (conventional techniques like those described in Refs. 5 and 9 could not work properly with such a reduced fluid height). Incidentally, with a 0.2-mm-thick sample, measurements of the type shown in Fig. 1 would take less than 3 min. One subtle, but practical advantage of thermodiffusion is that this technique is quite insensitive to dust problems (centrifuge studies also benefit from this advantage). All the samples we have studied required no filtering.

We would like to make here some remarks on the analogy between thermodiffusion and centrifuging. Although the time evolution obeys the same laws, the magnitude of the steady-state concentration gradient depends, in the two cases, on two different physical quantities. For a given centrifugal field it is proportional to $\partial c/\partial \mu \propto M$, where M is the molecular weight.[11] On the contrary, k_T (and therefore the steady-state concentration gradient) is proportional[1,2] to the product $(\partial c/\partial \mu)S^*$, where S^* is the net entropy of transfer. S^* is related to the order that a macromolecule imposes on the surrounding solvent molecules. If the order is high, S^* is large and positive. In highly structured liquids, like water, it can happen that a macromolecule induces less order in the neighboring solvent molecules than is usually found in the bulk, pure-solvent phase. In this case S^* is negative. Our measurements indicate that k_T is usually quite large and can be determined quite accurately (the steady-state concentration gradient reported in Fig. 1 has the same magnitude one would obtain by spinning the same sample to 1020g). We suggest that by combining thermodiffusion with light-scattering intensity measurements (which give $\partial c/\partial\mu$), one could determine S^*. It is likely that such a combined measurement could give useful information especially in connection with aqueous solutions.

Finally we point out that if $k_T < 0$, macromolecules migrate to the hot plate. Such a situation can lead to a convective instability even if heating is done from above.[13,14] For a pure-fluid layer of thickness a, convective instabilities develop only when heating is done from below and if the temperature difference ΔT is large enough to make the Rayleigh number $R = ga^3\alpha\Delta T/\chi\nu = 1708$ [g is the acceleration due to gravity, $\alpha = -(1/\rho)(\partial\rho/\partial T)$, ν is the kinematic viscosity, and χ is the thermal diffusivity]. Typically, for a 1-mm-high sample of water $\Delta T_{\mathrm{crit}} \simeq 88°\mathrm{C}$. For mixtures and solutions the situation is quite different. Heating from above now, the critical temperature difference is given by the relation[14]

$$\tilde{R} = R(\chi/D)(\beta k_T/\alpha T) = 720, \tag{3}$$

where β is $(1/\rho)(\partial\rho/\partial c)$. Since $\chi \sim 10^{-3}$ cm^2/sec and $D \sim 10^{-6}$–10^{-7} cm^2/sec, Eq. (3) indicates that the critical temperature difference is drastically lower than for pure fluids. We present, for the first time, direct evidence of this instability. Measurements have been taken on two samples of polyvinyl alcohol 0.5 and 1.0 mm high, and the results are presented in Fig. 2. The temperature difference for the 0.5-mm cell was 0.214°C. The data for this cell (curve a) are similar to those reported in Fig. 1. The only difference is that the beam now moves upward during the slow diffusive motion, thus indicating that the macromolecules are migrating upwards, and therefore k_T is negative. The temperature difference for the 1-mm cell was 0.672°C. In this case $\tilde{R}$ is roughly 25 times larger than for the 0.5-mm cell. The data (curve b) are, at the beginning, similar to those of curve a. We notice the rapid downward movement, followed by the slow upward displacement. The process goes on for a while, but then, after roughly 90 min, convection sets in, and after a heavily damped oscillating transient, the concentration gradient in the midplane of the cell is almost entirely destroyed by the convected flux.

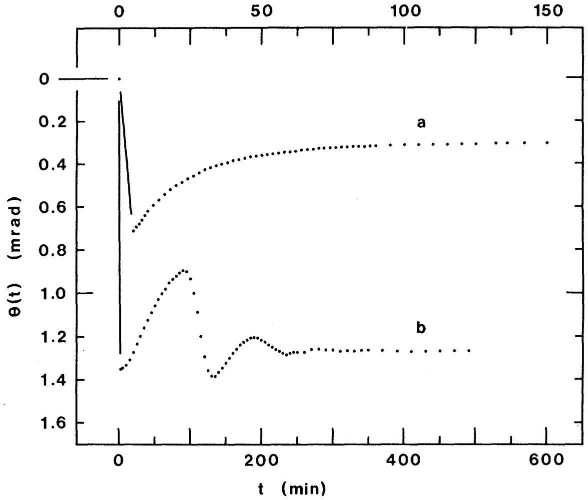

FIG. 2. Time evolution of $\Theta(t)$ for a 0.7% mass fraction aqueous solution of polyvinyl alcohol (highly polydisperse). Curve a, cell thickness 0.5 mm, $\Delta T = 0.214$ °C; curve b, cell thickness 1 mm, $\Delta T = 0.672$°C. Data for curve a are presented on a time scale which has been expanded by a factor of 4 (top scale).

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Validity of Using Lattice Statics at All Temperatures*

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It is shown that zero-point and thermal vibrations change the vacancy formation volume calculated from classical lattice statistics by usually no more than 10^{-3} at all temperatures. In view of the recent interest in relating the temperature variation of the vacancy formation volume to Arrhenius plot curvature, the validity of lattice statics, as a tool for the calculation of temperature-dependent defect properties, is established.

As the name of the method implies, lattice statics (LS) is a technique used for calculating atomic relaxation displacements due to the presence of a defect in a nonvibrating, static lattice; that is, the usual formulation of LS[1-3] calculates the relaxation volume, ΔV_R^{stat}, hence the defect (for our purposes, the vacancy) volume of formation, $\Delta V_F^{\text{stat}} = \Omega + \Delta V_R^{\text{stat}}$ (Ω is the atomic volume), at 0°K in the absence of zero-point vibrations.

It has recently been shown by Gilder and Lazarus[4] that Arrhenius-plot curvature can be explained in terms of a vacancylike defect, in which the anharmonicity of the lattice modes gives rise to a large thermal coefficient of expansion associated with the vacancy activation volume of diffusion, $\Delta V = \Delta V_F + \Delta V_M$ (ΔV_M is the vacancy migration volume). As their analysis is based on the experimental result for zinc[5] and cadmium[6] that the activated-vacancy thermal coefficient of expansion $\beta_v = \Delta V^{-1}(\partial \Delta V/\partial T)_p = T^{-1} \approx 15\beta_0$ (β_0 is the thermal coefficient of expansion of the perfect lattice), the logical question that arises is whether a calculation of the thermal coefficient of expansion associated with the vacancy formation volume, $\beta_F = \Delta V_F^{-1}(\partial \Delta V_F/\partial T)_p$, in the absence of calculated or measured values of β_M (the thermal coefficient of expansion associated with the vacancy migration volume), would yield values comparable to the large experimental values of β_v necessary to make their explanation plausible from a theoretical point of view.

Since there are now, for the simple metals, reliable pseudopotential-derived interionic potentials[7] which have an intrinsic temperature dependence due to the variation of electronic charge density with lattice parameter or temperature, it is evident that a relaxation volume based on such a potential would exhibit a temperature dependence. But this volume would be the result, at each temperature, of the transformation of a portion of the discrete interionic, pairwise potential energy of the crystal to continuous elastic energy stored in the vacancy relaxation volume. However, we know that at all temperatures there exist both zero-point and thermal vibrations that can channel energy into the elastic deformation that represents the vacancy relaxation volume. The obvious question, then, is whether LS, in ignoring both zero-point and thermal vibrations as possible sources of energy available to the elastic deformation, introduces negligible errors in the calculation of $\Delta V_R(T)$, or whether these sources of energy change the calculated value of $\Delta V_R^{\text{stat}}(T)$ significantly.

It is the purpose, then, of this Letter to explore the influence of both zero-point and thermal vibrations on the LS calculated value of $\Delta V_R(T)$. We herein evaluate their contribution, ΔV_F^{vib}, to