

COMMENTS

Brownian-Diffusion Viscosity Measurement in a Thermal Gradient*

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Experiments performed by Gaeta, Migliardo, and Wanderlingh indicated the existence of a large viscosity anisotropy in fluids in the presence of a thermal gradient. We measure the diffusion constant of small ($0.19\ \mu\text{m}$) Brownian particles in a thermal gradient. The viscosity was determined with the Stokes-Einstein relation. No anomalous increase is observed in the presence of a thermal gradient.

In a recent Letter, Gaeta, Migliardo, and Wanderlingh¹ (GMW) measured a significant increase in the viscosity of several fluids in a thermal gradient. They found a 0.9-cP increase in viscosity for a thermal gradient of $23^\circ\text{C}/\text{cm}$ for all fluids studied, when the velocity and thermal gradients were parallel, and no increase when the gradients were perpendicular. The dependence of the viscosity anomaly was approximately linear with the thermal gradient. For one fluid, aniline, a rotating-disk viscometer was used, while for the other three fluids, water, formamide, and ethyl cinnamate, a vibrating-wire viscometer was used, which indicates that the effect may not be apparatus dependent. There has been no published theoretical explanation of these results.

We investigated these results by measuring the diffusion constant of particles undergoing Brownian motion, using light-scattering techniques. The intensity-intensity autocorrelation function of light scattered from the Brownian particles was measured. The autocorrelation function is an exponential with a decay time related to the diffusion constant, D , of the Brownian particles by²

$$t_{\text{decay}} = 1/Dq^2, \quad (1)$$

where $q = (4\pi n/\lambda) \sin \frac{1}{2}\theta$, and where n is the index of refraction of the medium, λ is the wavelength of the light, and θ is the scattering angle. One can determine the viscosity from the diffusion constant by using the Stokes-Einstein relation

$$D = kT/6\pi\eta a, \quad (2)$$

where η is the viscosity of the fluid, a is the ra-

dius of the diffusing particle, T is the absolute temperature, and k is the Boltzmann constant. GMW's experiment suggests that the fluid is anisotropic. If so, what would be the effective viscosity derived from the diffusion constant associated with the Brownian particles? To answer this question accurately, one would have to derive the Stokes drag on a spherical particle in a fluid with an anisotropic viscosity. However, we may estimate the effect by averaging over the three independent directions the velocity gradient will have for a spherical particle moving through a fluid. Such reasoning, in conjunction with GMW's data, leads to a predicted increase in the effective viscosity seen by a Brownian particle of approximately 30% in water when $|\nabla T| = 23^\circ\text{C}/\text{cm}$.

Figure 1 shows the configuration of the light-

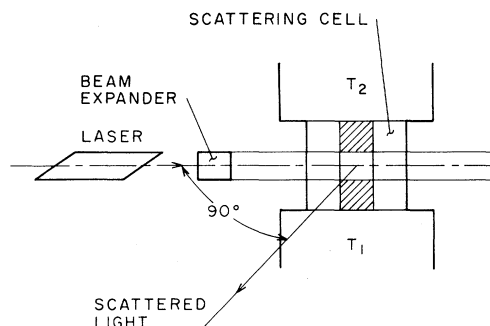


FIG. 1. A schematic representation of the light-scattering experiment. A vertical thermal gradient was established in the scattering cell by heat baths labeled T_1 and T_2 , where $T_2 > T_1$. The scattering plane is normal to the thermal gradient.

scattering experiment. An argon-ion laser was used operating at a wavelength of 5145 Å. The beam was expanded to a collimated beam of 1 cm diam which uniformly illuminated the sample. The beam was expanded to minimize any possible local heating effects by the incident light which might alter the thermal gradient in the region of the light-scattering particles. The incident light power was never more than 30 mW. The light scattered at 90° was collected by an aperture which views a 1-mm horizontal zone of the fluid. The temperature gradient was maintained normal to this viewed region. The light then passes through a pinhole and falls on the cathode of an FW130 photomultiplier tube. The pulses from the photomultiplier tube, corresponding to individual photons striking the photocathode, are processed by an autocorrelator which produces a spectrum of the intensity-intensity autocorrelation function of the light scattered by the diffusing Brownian particles.

The scattering cell was a rectangular solid made of clear, thermally insulating Plexiglass walls 1.25 cm thick, and top and bottom stainless-steel end plugs spaced 1 cm from each other. The volume was approximately 3.6 cm³. The stainless-steel end plugs were kept in good thermal contact with large, temperature-controlled heat baths, the lower bath being the cooler to avoid thermal convection. The bath temperatures were controlled to $\pm 0.3^\circ\text{C}$. Calculations of typical experimental conditions show that a uniform thermal gradient is established on this cell. The Brownian particles were Ludox (SiO₂) particles approximately 0.19 μm in diameter. They were suspended in water at a concentration of 1:10⁴ by volume. Water was used because it showed the largest increase in viscosity in GMW's experiment. The diffusion constant was measured with and without a thermal gradient and the viscosity was calibrated to the nonthermal gradient case. The temperature of the region viewed by the phototube was determined from the known temperatures of the end plugs, their separation, and the position of the viewing aperture relative to the end plugs.

The data for two experimental runs are shown in Table I. In Table I, T (beam) is the calculated temperature at the region viewed by the phototube, η (meas) is the viscosity derived from the measured diffusion constant of the particles, η (tables) is the value of the viscosity at the temperature T (beam) for no thermal gradient as found in standard tables,³ and the last column is

TABLE I. Results for the shear viscosity of water at two different temperatures, T (beam), and for two different thermal gradients. η (meas) are the shear viscosities extracted from the measured diffusion constants, η (tables) are the handbook values of η for the corresponding values of T (beam), and $\Delta\eta/\eta_t$ is the percentage deviation of the measured and the handbook (η_t) viscosities.

grad T (°C/cm)	T (beam) (°C)	η (meas) (cP)	η (tables) (cP)	$\Delta\eta/\eta_t$ (%)
18.6	11.3 ± 0.9	1.235 ± 0.016	1.26 ± 0.03	-2.1
29.1	14.7 ± 1.9	1.12 ± 0.03	1.13 ± 0.05	-0.9

the percentage deviation of the measured and tabulated viscosities. The major sources of error were in the measurement of the viewing position, T (beam), and in the measurement of the decay time of the intensity-intensity autocorrelation function of the scattered light. The viscosities in the thermal gradients computed from the Stokes-Einstein relation (1) agree with the tabulated viscosities from standard tables³ within our experimental error. Thus, we find that a thermal gradient has no effect on the viscosity seen by a Brownian particle to within $\pm 5\%$.

Our results for diffusing Brownian particles are consistent with the theoretical predictions of Mazo.⁴ He has presented theoretical arguments to show that for Brownian motion in a thermal gradient one does not expect a change in the diffusion constant. He does show that a thermal gradient would produce a force on the particles with an effect similar to the effect of the force of gravity. This Soret-type motion would not be detected in our light-scattering experiments. However, his investigation does not predict the anisotropy in the viscosity as seen by GMW, either. While an exact calculation of the effect of an anisotropic viscosity on the diffusion constant is needed to determine if the effect is smaller than 5% as in the case of water, it does not appear in the light of the large effect observed by GMW that the anisotropy is observed on the size scale of our Brownian particles.

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¹F. S. Gaeta, P. Migliardo, and F. Wanderlingh, Phys. Rev. Lett. **31**, 1181 (1973).

²K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A **10**, 393 (1974).

³*Handbook of Chemistry and Physics*, edited by C. D.

Hodgman (Chemical Rubber Publishing Co., Cleveland, Ohio, 1973-1974), 54th ed., p. F45.

⁴R. M. Mazo, J. Statist. Phys. **1**, 101 (1969).

Bond-Orbital Model and the Properties of Tetrahedrally Coordinated Solids

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The recent application of tight-binding models of the Coulson-Hall type to semiconductors by Harrison and co-workers is discussed critically.

Several years ago Van Vechten and I developed an algebraically simple yet numerically very accurate ($\sim 1\%$) model of chemical bonding in $A^N B^{8-N}$ compounds, including specifically the tetrahedrally coordinated semiconductors.¹ The obvious qualitative trends in properties have, over the years, tempted many authors to propose specific quantitative models of binary bonds, but most of them have had little success. For this reason I took some care to review in detail¹ what I regarded as the two models (Pauling and Coulson) which, prior to our model, had been most successful (errors of order 10%). In the review I attempted to identify, insofar as possible, the differences between the three theories. The chemical theories of Pauling and Coulson concentrate primarily on the energies of charge transfer between cation A and anion B , which were estimated either from Pauling's famous table of elemental electronegativities, where the parameters were derived in turn from heats of formation, or in Coulson's case from atomic ionization energies (Mulliken's definition of electronegativities).

By contrast, our theory derives its parameters from chemical trends in the dielectric constants of $A^N B^{8-N}$ compounds. That the dielectric constants could actually contain information of this kind was no doubt unexpected. Traditionally, oscillator strengths were thought to be very difficult to calculate from quantum mechanics, and the large variations in calculated values in small molecules suggested that the oscillator strengths might be sensitive to many factors. However, those who had studied the fundamental optical spectra of semiconductors in some detail² noticed that conventional chemical trends were qualitatively evident in many features of the spectra, notably the energy of the largest peak (conven-

tionally denoted by E_2) in $\epsilon_2(\omega)$, the imaginary part of the frequency-dependent dielectric constant. This led to discovery of the relation for isoelectronic sequences (e.g., diamond, cubic BN, BeO, or Ge, GaAs, ZnSe) that $[\epsilon_1(0) - 1]^{-1}$ was proportional to E_g^{-2} , i.e., to $a + b(4 - N)^2$ in all cases.³ The appearance of the valence number N is what makes possible the development of a chemical theory; this relation is as basic to the success of the dielectric theory of chemical bonding as the fact that most heats of formation depend quadratically on electronegativity differences is to Pauling's approach.⁴

Harrison and co-workers, in a series of recent papers,^{5,6} have attempted to marry dielectric theory to an atomic-orbital model of the Coulson-Hall type. However, it is well known that atomic orbitals yield very poor conduction bands. This is recognized by Harrison, who omits the conduction levels altogether from his energy-band plots. (In fact, the tight-binding models make the conduction band much narrower than the valence band, whereas it should be at least as wide.) For many applications (e.g., to dangling- and back-bond surface states with energies near or below the top of the valence band⁷), the tight-binding method can give results of even quantitative value, provided one is interested in the valence band *only*. However, the dielectric constant involves valence and conduction bands symmetrically, and a method which is good for valence bands and poor for conduction bands cannot derive satisfactory values for chemical parameters from the starting point of dielectric constants. In particular, the valence dependence of $[\epsilon_1(0) - 1]^{-1}$, which is the cornerstone of the dielectric theory, is not explained by Harrison's model, which gives instead of $a + b(4 - N)^2$ an en-