

Structural Relaxation in Dense Hard-Sphere Fluids

Anthony J. C. Ladd,¹ W. Edward Alley,¹ and Berni J. Alder¹

Received April 21, 1987

The long-time decay of the shear-stress autocorrelation function is shown to be quantitatively related to the decay of correlations between the orientation of "bonds" connecting colliding pairs of particles. Within computational uncertainties, we find that orientational correlations in high-density fluids decay as a "stretched" exponential in time, with an exponent that is independent of density. However, at low densities the decay is exponential. In two-dimensional systems the decay is exponential, even at high density.

KEY WORDS: Structural relaxation; stretched exponential.

This article, dedicated to Prof. I. Prigogine, is concerned with correlation or memory effects in an irreversible phenomena that so far has defied theoretical analysis. There seem to be only two prominent memory effects in simple fluids. The one associated with diffusion results from a positive feedback of the momentum of a particle via vortex formation in the surrounding fluid, and is well characterized.⁽¹⁾ A hydrodynamic analysis led to a universal power-law decay of the velocity correlations, with a power that depended only on dimensionality. The memory effect associated with the slow decay of the shear-stress autocorrelation function at high density, which leads to viscoelastic behavior and ultimately to glass formation, is not well understood. We have undertaken some computer experiments to delineate the nature of this memory effect, to help define the physical processes involved, and in particular to establish whether this phenomena has any universal characteristics. We have previously shown that the mechanism for the slow decay of the potential contributions to the shear viscosity differs from the hydrodynamic effects that cause the long-time tails in kinetic correlation functions.⁽²⁾ The slowly decaying potential

¹ Lawrence Livermore National Laboratory, Livermore, California 94550.

contribution to the shear-stress autocorrelation function has been called the "molasses" tail,⁽³⁾ to differentiate it from the hydrodynamic origin of the kinetic tails, and to emphasize its relation to the highly viscous glassy state. It is limited to high-density fluids close to the solid-liquid transition. Our approach to understanding the glass transition focuses on the rapidly increasing time scale for the decay of angular xy correlations in high-density liquids close to the glass transition point. Other work has focused on the growth of higher order angular correlations in supercooled monatomic liquids.^(4,5)

A quantitative relationship between the decay of the collisional contributions to the shear stress and the orientational (xy) correlations of "bonds" linking colliding pairs of particles has been established at long times and high densities.⁽²⁾ The transverse momentum current J_{xy} (equal to minus the product of the shear stress and the volume) in a hard-sphere fluid of particles of mass m contained in a volume V can be written as a sum of kinetic and potential contributions,

$$J_{xy}^K = \sum_i m \dot{x}_i \dot{y}_i \quad (1)$$

$$J_{xy}^P = \sum_c (-m \mathbf{r}_{ij} \cdot \mathbf{v}_{ij}) \frac{x_{ij} y_{ij}}{r_{ij}^2} \delta(t - t_c) \quad (2)$$

The potential contribution occurs only at the collision times t_c , because of the impulsive hard-sphere interaction. The vector \mathbf{r}_{ij} connects the centers of the colliding pair, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity before collision. It is known that the correlation function of the normal momentum transfer decays rapidly,⁽⁶⁾ so that beyond about three mean collision times ($-m \mathbf{r}_{ij} \cdot \mathbf{v}_{ij}$) can be replaced by its average value, $(\pi m k T \sigma^2)^{1/2}$, where k is Boltzmann's constant, T is the temperature, and σ is the collision diameter. This leads to a factorization in Eq. (2), and implies that a quantitative relationship exists, at long times, between the shear-stress autocorrelation function and orientational correlations between colliding pairs of particles, i.e.,

$$\langle J_{xy}^P(t) J_{xy}^P(0) \rangle = \pi m k T \sigma^2 \langle K_{xy}(t) K_{xy}(0) \rangle \quad (3)$$

where the orientational factor K_{xy} is given by

$$K_{xy} = \sum_c \frac{x_{ij} y_{ij}}{r_{ij}^2} \delta(t - t_c) \quad (4)$$

The factorization assumption has been verified over a range of high-density liquid states by comparing the left- and right-hand sides of Eq. (3). A

typical result is shown in Fig. 1 at $V/V_0 = 1.6$, where V_0 is the volume at close packing. As expected, the correlation functions in Eq. (3) are statistically indistinguishable after about ten mean collision times. This is strong evidence that the “molasses” tail is structural rather than hydrodynamic in origin. The factorization of the cross correlation between the kinetic and potential contributions, namely

$$\langle J_{xy}^K(t) J_{xy}^P(0) \rangle = (\pi mkT\sigma^2)^{1/2} \langle J_{xy}^K(t) K_{xy}(0) \rangle \tag{5}$$

was also found to hold, within statistical accuracy, beyond about ten mean collision times. Factorization holds at densities up to about $V/V_0 = 2$, beyond which the “molasses” tail is too weak to be measured. It is most clearly established at the highest densities where the tail is strongest.

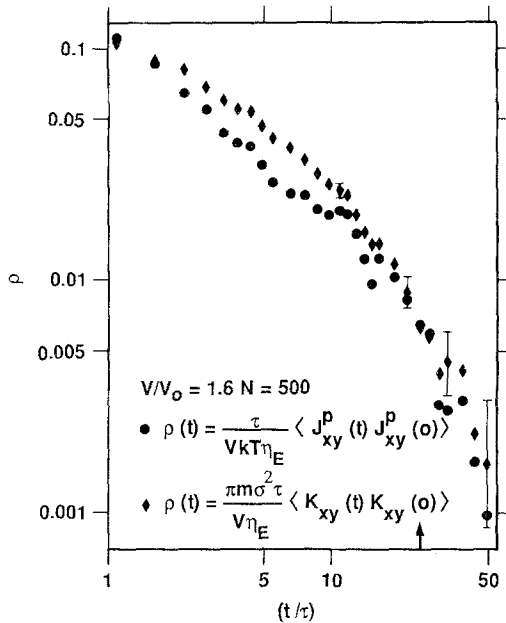


Fig. 1. Comparison of the collisional shear stress and orientation autocorrelation functions at $V/V_0 = 1.6$. The logarithms of the correlation functions $\langle J_{xy}^P(t) J_{xy}^P(0) \rangle$ and $(\pi mkT\sigma^2) \langle K_{xy}(t) K_{xy}(0) \rangle$ plotted against the logarithm of the time are shown for 500 hard spheres after 10^8 collisions. The time is measured in units of the mean collision time $\tau = 0.0321(m\sigma^2/kT)^{1/2}$, and $\eta_E = 2.63(mkT)^{1/2}/\sigma^2$ is the Enskog shear viscosity. The viscosity obtained from integrating the total shear-stress autocorrelation function $\langle J_{xy}(t) J_{xy}(0) \rangle$ out to 25 mean collision times is $1.44\eta_E$, in good agreement with earlier results.^(6,7) The error bars, indicated by vertical lines, are comparable for both correlation functions. The vertical arrow indicates the sound-wave traversal time.

The very slow structural relaxation in glasses has recently been investigated using the concept of "hierarchically constrained dynamics."⁽⁸⁾ The orientation of a pair of particles at high density is locked (grid-locked) until an appropriate arrangement of neighbors is achieved. Local structural relaxation is expected to be slowest, because the unlocking of a large orientationally ordered cluster starts at the outside and proceeds inward toward the center. This idea can be tested in detail by molecular dynamics. One such test is the nature of the decay of the autocorrelation function. The model predicts a "stretched" exponential form for the relaxation, $\exp[-(t/t_0)^\alpha]$, which is often used to represent dielectric and viscous relaxation in dense liquids.^(9,10) The data in Fig. 1 can be fitted quite well, though not uniquely, by this same functional form.

A stringent test for "stretched" exponential behavior is to plot the data as shown in Fig. 2. For a "stretched" exponential the quantity $-t\dot{\rho}/\rho$, the normalized decay rate, is proportional to t^α , so that the logarithm of that quantity plotted versus the logarithm of the time has a slope α , that is, the value of the "stretched" exponent. The question is then whether this slope can be readily distinguished from a power-law decay of the correlation function, in which case the slope would be zero, or a purely exponential decay of the correlation function, in which case the slope would be unity.

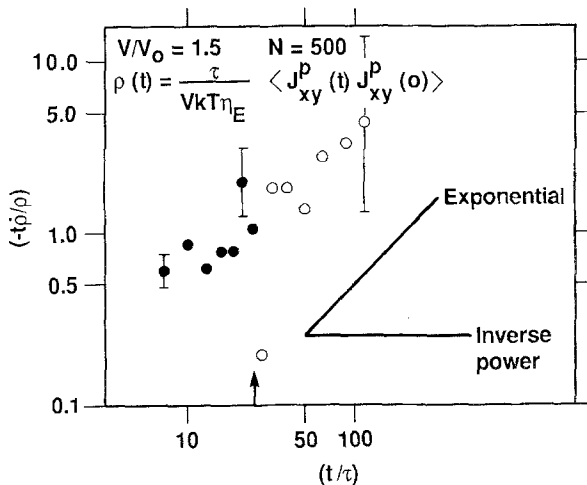


Fig. 2. Collisional contribution to the shear-stress autocorrelation function at $V/V_0 = 1.5$. The logarithm of the normalized decay rate $(-t\dot{\rho}/\rho)$ plotted against the logarithm of the time is shown for 500 hard spheres after 10^8 collisions. The slopes for exponentially and algebraically decaying functions are indicated in the lower right-hand corner. The sound traversal time is indicated by the vertical arrow, and data points occurring after this time are shown by open circles.

These slopes are indicated in Fig. 2. Even after an extensive run just below the freezing density where the "molasses" tail is most pronounced, the statistical errors are large, magnified, especially at long times, by the added differentiation. Moreover, the correlations are perturbed by effects, so far unanalyzed, arising from the propagation of sound waves across the periodic cell. Thus we cannot rule out an exponential decay, as predicted by extended mode-coupling theories,^(11,12) or even a power-law decay for times prior to the sound traversal time.

Although Fig. 2 gives weak indication of "stretched" exponential behavior, more definitive results were sought by decomposing the four-particle correlation function $\langle K_{xy}(t) K_{xy}(0) \rangle$ into pair, triplet, and quadruplet contributions, as had been done previously for the dipole-induced-dipole correlation function.^(13,14) In that case, the individual pair, triplet, and quadruplet contributions were an order of magnitude larger than the total, both in amplitude and in relaxation time. Symmetry arguments led to near cancellation of the three individual terms in the formation of the sum that represents the total autocorrelation function. Furthermore, extensive analysis of experimental data suggest that the decay of angular correlations in dielectric and viscous relaxation are similar.^(10,15) A similarity has also been noted in comparisons, by computer simulation, of the dipole-induced-dipole and shear-stress autocorrelation functions.⁽¹⁶⁾ Indeed, the decomposition of the orientation autocorrelation function was found to be quite analogous to the depolarized light scattering simulations and thus advantage could be taken of the long relaxation time of the individual contributions to establish the functional form of the relaxation, as shown in Fig. 3. Pair correlations can be followed for times corresponding to a decay of more than three orders of magnitude and are essentially exactly factorizable, in the manner of Eq. (3), over that time span. The orientational pair correlation function is defined as

$$\rho_2(t) = \frac{\pi m \sigma^2 \tau}{V \eta_E} \left\langle \sum_{i>j} K_{xy}^i(t) K_{xy}^j(0) \right\rangle \quad (6)$$

where K_{xy}^i is the contribution to K_{xy} arising solely from collisions between the ij pair. To be consistent with the local structural arguments presented before, the pair correlation should have a much longer relaxation time than the total, and should not be sensitive to the size of the system. Both of these hypotheses are substantiated. Most importantly, the pair correlation gives a strong indication of being neither exponential nor algebraic (power law), but a "stretched" exponential, $\exp[-(t/t_2)^\alpha]$, with a least squares "stretched" exponent of $\alpha = 0.73$.

Furthermore, for other high-density fluid states, the pair correlations yielded the same "stretched" exponent, within the statistical error bars,

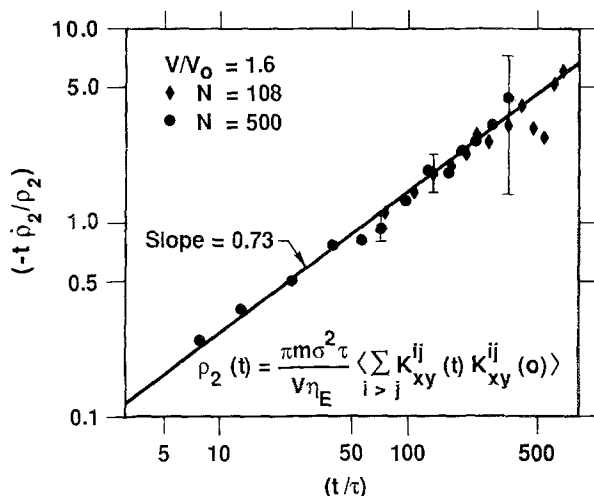


Fig. 3. Pair orientation autocorrelation function at $V/V_0 = 1.6$. The logarithm of the normalized decay rate $(-t\dot{\rho}_2/\rho_2)$ plotted against the logarithm of the time are shown for 108 and 500 hard spheres. The “stretched” exponent $\alpha = 0.73$ and relaxation time $t_2 = 41.0\tau$ were determined by least squares fitting.

when plotted in a manner similar to Fig. 3, i.e., $\alpha = 0.73 \pm 0.03$. No systematic variation of the “stretched” exponent could be established for densities above $V/V_0 = 2$, although the relaxation times t_2 vary by an order of magnitude over this density range. The insensitivity of the “stretched” exponent is shown in Fig. 4 by using a universal value of $\alpha = 0.73$ in plotting $-t_2\dot{\rho}_2/\alpha\rho_2$ versus $(t/t_2)^{\alpha-1}$ over a range of high-density states. Conformity to a single “stretched” exponent is indicated by the fit to the straight line that passes through the origin with a slope of one. Considering that the data at the longest times have statistical uncertainties larger than the deviations from this straight line, the universality of the “stretched” exponent is a tentatively acceptable hypothesis.

Moreover, the decay of the self-correlation function, which is a combination of pair and triplet correlations,⁽¹⁴⁾

$$\rho_s(t) = \frac{\pi m \sigma^2 \tau}{V \eta_E} \left\langle \sum_{i, j, k \neq i} K_{xy}^{ij}(t) K_{xy}^{ik}(0) \right\rangle \quad (7)$$

is also consistent with the same “stretched” exponent at several high densities, as shown in Fig. 5. The results are more scattered than in the pair case because the cancellation of pair and triplet correlations increases the statistical errors, but not to the same extent as in the total. This

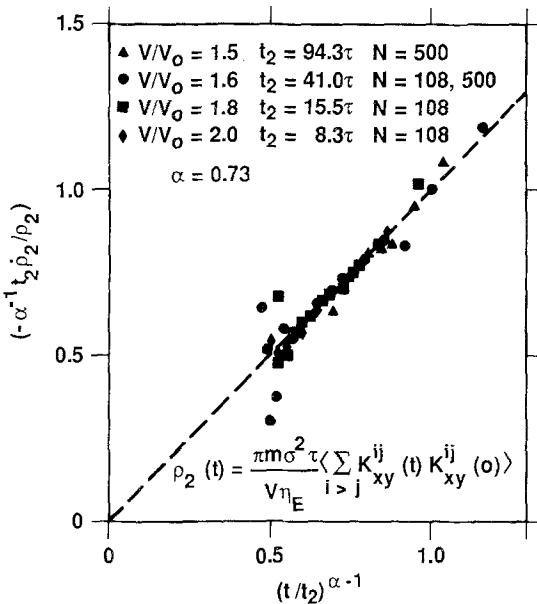


Fig. 4. Pair orientation autocorrelation function at high densities. The decay rate $(-\dot{\rho}_2/\alpha\rho_2)$ is normalized by the density-dependent pair relaxation time t_2 instead of by t . The time is measured in units of the pair relaxation time also. The "stretched" exponent α was assigned the value of 0.73 at all densities. The relaxation time t_2 used at each density is shown.

cancellation also means that the self-correlation function decays much faster than the pair, as indicated by the relaxation times shown in Figs. 4 and 5. In fact, the relaxation of self-correlations is comparable to, though not as fast as, the relaxation of the total.

Although the universality hypothesis is consistent with the decay of all the correlation functions at high density, it cannot be checked at lower densities, because the correlations decay too rapidly. This is shown in Fig. 6, where even the pair correlation at $V/V_0=5$ is consistent with a purely exponential decay. One might surmise that at lower densities a different mechanism decorrelates the orientation of the "bonds" connecting colliding pairs of particles, namely, they might just diffuse apart. Such a mechanism would start to become important at $V/V_0=3$, where the mean distance between particles is comparable to the diameter of the spheres. Such a pair diffusion mechanism would be expected to lead to a power-law decay of the correlations when analyzed by a hydrodynamic (diffusion) model. A preliminary run at $V/V_0=3$ could possibly be interpreted as going from "stretched" exponential at intermediate times to a power-law decay at long times. However, at this stage the statistical errors are too

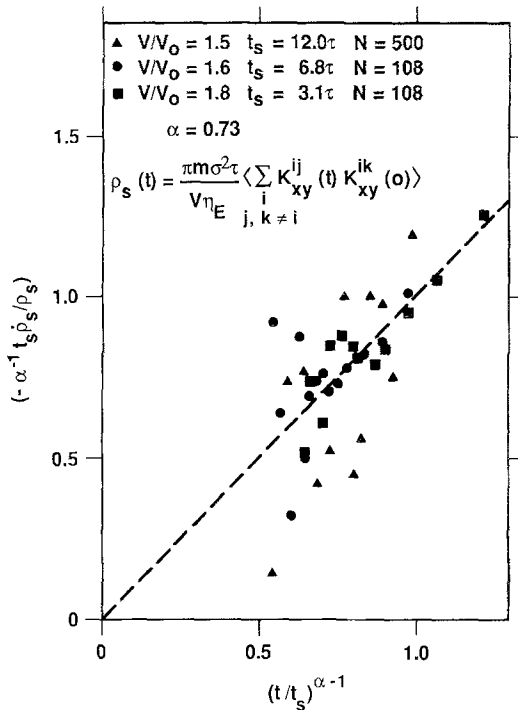


Fig. 5. Self-orientation autocorrelation function at high densities. The decay rate $(-\dot{\rho}_s/\alpha\rho_s)$ is normalized by the density-dependent self-relaxation time t_s instead of by t . The time is measured in units of the self-relaxation time also. The “stretched” exponent α was assigned the value of 0.73, as for the pair orientation correlation functions. The relaxation time t_s used at each density is shown.

large to allow any meaningful conclusions. At $V/V_0 = 5$ such a power-law decay is lost in the noise.

Any possible universality of the “stretched” exponent is not derived from a hydrodynamic mechanism. This is indicated in Fig. 7, where it is shown that in two dimensions, the decay of pair correlations is qualitatively different from that in three dimensions. The pair correlations are observed to be purely exponential at a high density near solidification and not just a “stretched” exponential with a different exponent, unless $\alpha = 1$ is considered to be a special case of a “stretched” exponential. Rather, the results are consistent with the experimental observation that glass formation has not been observed in two dimensions, presumably because the grid-lock mechanism is not operative.

These computer experiments have suggested that the “stretched” exponent characterizing high-density orientational relaxation is universal.

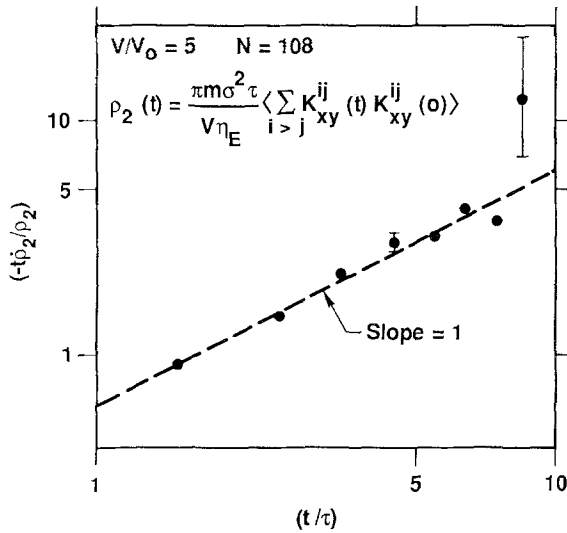


Fig. 6. Pair orientation autocorrelation function at $V/V_0=5$. The logarithm of the normalized decay rate $(-t\dot{\rho}_2/\rho_2)$ is plotted against the logarithm of the time for 108 hard spheres.

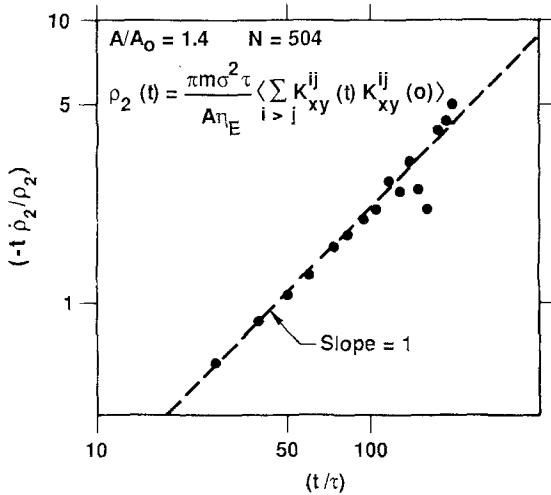


Fig. 7. Two-dimensional pair orientation autocorrelation function at $A/A_0=1.4$. The logarithm of the normalized decay rate $(-t\dot{\rho}_2/\rho_2)$ is plotted against the logarithm of the time for 504 hard disks.

To confirm this hypothesis more extensive runs are required. These runs should reduce the uncertainty in the "stretched" exponent to about 0.01 and thus determine whether or not the exponent is (weakly) density-dependent. Furthermore, it might be possible to establish the existence of a hydrodynamic tail near $V/V_0=3$. To establish the successive unlocking mechanism, we intend to resolve the total correlation function as a function of the distance between the centers of mass of the colliding pairs at time t and at time 0. This will not only determine the spatial range of the angular correlations, but also whether the closer-in pairs have longer relaxation times. Finally, we want to return to the depolarized light scattering problem, to study the decay of these orientational correlation functions in more detail, and see whether they, too, have a "stretched" exponential decay, possibly with the same "stretched" exponent as the "molasses" tails. Once these facts are well established for this very simple system, it is hoped that a theory can be developed to predict analytically the "stretched" exponent, by incorporating the physical mechanism for the slow structural relaxation.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy and Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

REFERENCES

1. B. J. Alder and T. E. Wainwright, *Phys. Rev. A* **1**:18 (1970).
2. A. J. C. Ladd, W. E. Alley, and B. J. Alder, *Z. Phys. Chem.*, to be published.
3. B. J. Alder, in *Molecular-Dynamics Simulation of Statistical-Mechanical Systems* (North-Holland, Amsterdam, 1987).
4. P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. Lett.* **47**:1297 (1981).
5. J. G. Amar and R. D. Mountain, *J. Chem. Phys.* **86**:2236 (1987).
6. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
7. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **24**:455 (1981).
8. R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, *Phys. Rev. Lett.* **53**:958 (1984).
9. G. Williams and D. C. Watts, *Trans. Farad. Soc.* **66**:80 (1970).
10. W. Götze, *Z. Phys. Chem.*, to be published.
11. T. R. Kirkpatrick and J. C. Nieuwoudt, *Phys. Rev. A* **33**:2651 (1986).
12. I. M. de Schepper, A. F. E. M. Haffmans, and H. van Beijeren, *Phys. Rev. Lett.* **57**:1715 (1986).
13. B. J. Alder, J. J. Weis, and H. L. Strauss, *Phys. Rev. A* **7**:281 (1973).
14. A. J. C. Ladd, T. A. Litovitz, and C. J. Montrose, *J. Chem. Phys.* **71**:4242 (1979).
15. H. Janeschitz-Kriegl and J. L. S. Wales, in *The Photoelastic Effect and Its Applications*, J. Kestens, ed. (Springer-Verlag, New York, 1975).
16. D. M. Heyes, J. J. Kim, C. J. Montrose, and T. A. Litovitz, *J. Chem. Phys.* **73**:3987 (1980).