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TOPICS IN TIME-DEPENDENT STATISTICAL MECHANICS¹ 2537

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INTRODUCTION

Six years have passed since the appearance in this series of Zwanzig's (1) excellent, didactic review article on time correlation functions and their relationship to transport coefficients. Time correlation functions continue to play an important role in our understanding of the structure and dynamics of gases, liquids, and solids, and since Zwanzig's article appeared, many interesting and important experimental and theoretical studies have been performed on diverse systems. We think it is appropriate at this time to review selected topics in this area of time-dependent statistical mechanics, especially since the subject is finding diverse applications in chemistry, physics, and biology.

According to linear response theory, transport coefficients and spectral lineshapes are directly determined by time correlation functions which represent the way spontaneous fluctuations arise and regress in equilibrium systems. Several books (2-7) and review articles (8-18) have appeared on this subject.

Experimental methods for studying fluctuations can essentially be divided into two categories: those which probe single-molecule dynamics and those which probe collective motion. This provides a natural division in our study of time correlation functions, and our review article will be organized in such a way that we shall discuss single-particle and collective properties independently. Because of limitations of time and space this is not meant to be an exhaustive review of what has now become a popular field. Instead, it will focus on selected topics and include only representative literature. The topics considered include: molecular dynamics, studies of collective modes, generalized hydrodynamics, molecular translations and rotations, computer experiments, and kinetic theories.

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MOLECULAR DYNAMICS

Electronic computers have advanced to such a degree that Newton's equations of motion can now be integrated for a fairly large assembly of interacting particles. This method, now commonly called molecular dynamics, is particularly useful for study of condensed phases of matter. Features common to all molecular dynamics experiments to date are the following: (a) The systems are finite $N \leq 1000$; (b) The interaction potential is pairwise additive

$$V(1, \dots, N) = \sum_{i>j=1}^N \phi(r_{ij})$$

where the pair potential $\phi(r)$ has a finite range r_0 such that for $r > r_0$, $\phi(r) = 0$; (c) Newton's equations of motion

$$m \frac{d\mathbf{V}_i}{dt} = - \sum_{j \neq i} \frac{\partial}{\partial \mathbf{r}_i} \phi(r_{ij}); \quad \mathbf{V}_i = \frac{d\mathbf{r}_i}{dt}$$

are solved by finite difference techniques with time steps Δt between 10^{-14} and 10^{-15} sec; and (d) The positions, velocities, and accelerations are stored on magnetic tape.

Computer experiments on equilibrium liquids all have, in addition, the following features in common: (a) The N particles are contained in a cubic box of edge $L > r_0$; (b) The initial state (initial positions and momenta) are sampled such that the momenta are distributed according to the Maxwell distribution at a given temperature and the positions are sampled such that the initial configuration corresponds to a quite large value of the Boltzmann factor $\exp - \{\beta V(1, \dots, N)\}$; i.e. the system is in a probable state for a member of an equilibrium ensemble; and (c) The equations of motion are solved subject to periodic boundary conditions.

A number of comments are in order. N and $V (= L^3)$ are chosen to give the number density N/V of the physical system under study. Sampling of the configuration is quite complicated and we refer the reader to the literature for a more detailed discussion of this subject.

The equations of motion are solved subject to the initial state together with periodic boundary conditions: the latter means that if (x_i, y_i, z_i) is the position of particle i in the box, there are 26 periodic images at $(x_i \pm L, 0, y_i \pm L, 0, z_i \pm L, 0)$. The particles in the box interact with the periodic images within their range. Consequently when a particle leaves the box through one side, its image enters through the opposite side, which thus preserves the number of particles in the box. These conditions eliminate strong surface effects and essentially simulate an infinite system. Nevertheless, periodic boundary conditions have the following limitations:

1. Because the number of particles in the box is constant, it is impossible to study thermodynamic states in which thermal fluctuations have

correlation lengths of the order of the box size as they do in the critical region.

2. The time scale is limited to times shorter than L/C , where C is the velocity of sound. For times longer than this a disturbance which arises in one region of the box can traverse the box and enter through the opposite side, which thus leads to spurious recurrences.
3. The collective properties that can be studied are limited to discrete wavevectors

$$\mathbf{q} = \frac{2\pi}{L} \mathbf{n}$$

with minimum wavenumber

$$q = \frac{2\pi}{L}$$

This limits the kinds of questions that can be investigated by molecular dynamics.

The computer output is then the sequence of states

$$\Gamma_0, \dots, \Gamma_j, \dots, \Gamma_M$$

through which the system passes in the course of time. Here Γ_j is the state of the system (all positions and momenta) after the j th time step; i.e. at time $t = j\Delta t$. The output is consequently a set of discrete points in phase space and M is the total number of iterations done in the computations.

The computer output may be regarded as a dynamical movie of the many-body system and can be converted into a movie via computer animation techniques. This has been done by several investigators (Harp, Berne, Paskin, Rahman, and Fehder). Such sources are a particularly convenient way to present the enormous data so that the viewer can get some insight into the dynamical behavior of molecules in condensed media. For example, as the strength of the noncentral potential is increased in polyatomic liquids, the movie shows how the rotational motion of molecules becomes more hindered. Such movies give the viewer an opportunity for discoveries by serendipity that exist in connection with laboratory experiments.

These solutions are checked for consistency in the following way:

1. At intermediate times, say j , the velocities of the particles are reversed and the calculation proceeds j steps. The final state should rigorously coincide with the initial state (microscopic reversibility) and any deviation reflects round-off error.
2. The total energy and momentum is computed. Since these are constants of the motion any variation in the total energy and momentum reflects inaccuracies in the solution.
3. The mean kinetic energy per particle is computed and its variation in time is monitored. This should fluctuate about the average desired

“temperature.” Any systematic drift in this quantity reflects the fact that the system is not at equilibrium.

4. An order parameter

$$\zeta_k(t) = \frac{1}{N} \sum_{i \neq j=1}^N \cos Kx_{ij}$$

is monitored, where K is a vector in the reciprocal lattice of the corresponding solid. If the system is ordered $\zeta_k(t)$ should fluctuate around $N - 1$, whereas if it is a liquid $\zeta_k(t)$ should fluctuate around zero.

Note that if 1. checks out it does not by itself imply that the solution is accurate. The numerical algorithm may itself be reversible in time. All 1. does is check round-off error. We regard 1. as an important check on the accuracy of the solution. Many of the studies reported here do not report the degree to which the constants of the motion are conserved, so that we cannot always assess their trustworthiness. In every case, the temperature fluctuates around its equilibrium values, likewise for the order parameter. All these systems are in equilibrium.

The computer generates the state $(\Gamma_0, \dots, \Gamma_j, \dots, \Gamma_M)$ through which the system passes in the course of time so that any property $A(\Gamma_t)$ can be determined at each of these states $(A_0, \dots, A_j, \dots, A_M)$ where $A_j \equiv A(\Gamma_j)$.

In classical statistical mechanics bulk properties of an isolated system are given by infinite time averages

$$\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\Gamma_t)$$

where Γ_t is the state of the mechanical system at time t . In addition, the linear response of a system to “weak probes” is given in terms of the time correlation function

$$\langle A(0)A(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\Gamma_t)A(\Gamma_{t+\tau})$$

The computer unfortunately generates a part of the phase orbit, and only discrete points at that. Thus the infinite time averages must be replaced by the finite sums

$$\langle A \rangle = \frac{1}{M} \sum_{j=0}^M A_j$$

$$\langle A(0)A(t) \rangle = \frac{1}{M-n} \sum_{j=0}^{M-n} A_j A_{j+n} \quad t = n\Delta t$$

Averaging over finite rather than infinite times gives rise to errors in the computed averages. Zwanzig & Ailawadi (19) estimated these errors on the basis of a Gaussian stochastic model of the fluctuations. They found that the errors

grow with the time τ and with a decrease in M . They also find that the single-particle (incoherent) properties can be determined with greater accuracy than the collective (coherent) properties.

In what follows, we present a survey of the results obtained to date by molecular dynamics. Although our review may be incomplete it is hoped that the interested reader will consult the papers cited to find references to the work omitted here.

Computers have come of age in statistical mechanics. Alder & Wainwright (20–24) introduced the method of molecular dynamics. Their pioneering studies of the equilibrium properties, the collision rate, and the velocity autocorrelation function in hard sphere and square well fluids set the stage for what followed. Since their work deals exclusively with discontinuous potentials it forms a self-contained set of studies which can be reviewed separately.

Alder & Wainwright (20) first studied systems containing 100 hard sphere and 100 square well molecules respectively. In this preliminary work they consider the collision rate, pressure equation of state, and velocity correlation function of hard sphere and square well fluids at a sequence of densities. Moreover, they compute the Boltzmann H function and show that it decays monotonically in time even at high densities and that it relaxes to equilibrium in 3 or 4 mean collision times. This preliminary work has two important conclusions: at high densities the velocity autocorrelation function becomes negative due to reflection of the spheres off their nearest neighbors (cage effect), and the results for the collision rate and diffusion coefficients agree with the Enskog equation up to quite high densities. The methods used by Alder & Wainwright are somewhat different than those outlined here because they are dealing with discontinuous potentials. Alder reviews these methods, analyzes their limitations, and gives an excellent summary of the subject in (21).

Alder & Wainwright (22) have investigated how many hard spheres are needed to adequately represent an infinite system of hard spheres. They study the differences in the results of molecular dynamics in systems containing from 4 to 500 hard spheres and also study the effects of the periodic boundary conditions, concluding from this work that periodic boundary conditions cause the least errors of all boundary conditions tried and give the most realistic results. Moreover, they find that as few as 100 particles will accurately describe a hard sphere fluid. They reaffirm their preliminary finding that the Enskog equation is quite adequate for the description of the collision rate up to high densities.

The same authors (23) studied a two-dimensional system containing 870 hard discs. This study is perhaps one of the most important in molecular dynamics because it shows that there is a fluid-solid region with a van der Waals loop. The density change across the transition is 4% and the corresponding entropy change is small. This first order phase transition is studied in some detail by Hoover & Alder (25). They discuss the results in terms of communal entropy and give the number dependence of the pressure.

Alder (24) studied an equimolar mixture of 500 hard spheres, with a radius ratio of 3 to 1. Two important conclusions of this work are: 1. the Percus-Yevick equation, as generalized by Lebowitz to mixtures, agrees well with dynamics; and 2. changes in the thermodynamic functions on mixing at constant pressure are quite small in spite of the large radius ratio. This latter observation leads Alder to conjecture that excess thermodynamic properties are much more sensitive to the attractive forces than to differences in the sizes of molecules. Much of the preceding work is reviewed by Alder in (26, 27).

Dymond & Alder (29) have tested a simple theory of transport in dense gases which they call a van der Waals theory of transport. Their basic assumption is that the transport coefficients of real fluids can be determined from the Enskog equation. For this purpose it is necessary to know the pair correlation function at contact, i.e. at the hard core diameter. The authors determine this from molecular dynamics. The hard core diameter σ is determined for the inert gases, from the actual equation of state data, by fitting this data to the van der Waals equation. This yields a temperature-dependent diameter. The transport coefficients so obtained agree with experiment to within 10% in both absolute value and temperature dependence.

In addition, Dymond & Alder (29) have determined the self-diffusion coefficient for a hard core fluid from molecular dynamics as a function of the hard core diameter. This data was inverted to give the diffusion coefficient as a function of temperature by using the temperature dependence of the hard core diameter determined above. This procedure bypasses the Enskog equation with its concomitant assumptions of molecular chaos and gives diffusion coefficients in qualitative agreement with experimental measurements on liquid methane from the critical point down to near the normal boiling point along the liquid branch of the liquid-vapor coexistence curve.

Alder & Wainwright (28, 30, 31) have made a detailed study of the time dependence of the velocity autocorrelation function over a very long time in two-dimensional hard sphere fluids. The number dependence of the self-diffusion coefficient is

$$D_N = D[1 - 2/N]$$

and the velocity autocorrelation function shows a small positive deviation from exponential behavior at low density, but the diffusion coefficient, when corrected for the N dependence, is in excellent agreement with the prediction of the Boltzmann equation. Also in this study (28) they detected velocity correlations at surprisingly long times. Although they could not explain this long time persistence, they noted that such effects could lead to as much as a 20% enhancement of the diffusion coefficient. The authors then showed (30) that the long time tail in the velocity correlation function (vcf) extends out to more than 20 to 30 mean collision times (mct) whereas there is a fast initial decay of the vcf of the order 1.5 mct. This effect is number dependent $O(1/N)$, and D increases by nearly 10% in going from 108 to 500 hard cores in the high density region. They conjecture that the long time persistence in the

vcf is due to cooperative motions and test this hypothesis by studying the flow pattern around a moving hard disc. They find that a diffusing particle experiences a positive pressure in front and a negative pressure behind with a concomitant double-vortex flow of neighboring particles. This vortex motion brings particles into the region behind the diffusing particle, which thereby prevents its return and leads to an enhancement of the diffusion coefficient.

Alder & Wainwright (31) present an elementary hydrodynamic theory for the long time dependence of the vcf which predicts that the long time tail goes as

$$\psi(t) \propto (\eta_s t / m\rho)^{-d/2}$$

where η_s , $m\rho$, d are the shear viscosity, mass density, and dimension of the system respectively. This conclusion is borne out by the hard disc calculation where $d = 2$. From the Kubo relation [$D \propto \int_0^\infty dt \psi(t)$] it follows that the diffusion coefficient in two dimensions should diverge logarithmically. Dymond & Alder (32, 33) explore these effects in mixtures of hard spheres and find quite comparable results in connection with the mutual diffusion coefficient. Moreover, they explore the mass dependence of the long time tail and find that the tail increases with mass. Alder, Gass & Wainwright (34) find similar long time tails in the kinetic part of the stress tensor and heat flux time correlation functions with corresponding enhancements of the kinetic viscosity and thermal conductivity coefficients. They analyze these in terms of memory effects in hydrodynamics.

Wainwright, Alder & Gass (35) use the Einstein relations (see Helfand 36) instead of the Kubo relations to determine the transport coefficients D , η_s , η_v , λ and compare these results with the Enskog theory. The largest deviations from Enskog occur for η_s and η_v near solid densities where these properties are nearly twice the results predicted by Enskog theory. An interesting result of this calculation is that $\eta_s D$ is a constant over the whole density region and, moreover, is in quantitative agreement with hydrodynamic theory for slip boundary conditions.

Alder, Hoover & Young (34a) have investigated the pressure equation of state for periodic arrays of hard discs and hard spheres. They determined the coefficients of the expansion of PV/NKT in powers of $(V - V_0)/V$ where V_0 is the closest packed volume. This expansion is discussed in connection with various models and it is concluded that those models which include correlations between nearest neighbors work best.

Alder & Hecht (34b) determined pair correlation functions of hard spheres at several densities and compared their results with several integral equations. They used perturbation theory to add various attractive potentials to the hard core and found that the van der Waals energy density parameter a was nearly constant as a function of density. They then used the augmented van der Waals theory to study dependence of the critical properties of a fluid on the shape of the attractive potential and found that these critical properties sensitively depend on the depth and range of the potential.

Einwohner & Alder (34c) made a detailed study of free path distributions and collision rates on square well and hard sphere fluids.

Rahman (37) did a molecular dynamics study of a system of 864 particles interacting with a Lennard-Jones (LJ 6-12) potential with the parameters of argon and in the thermodynamic state (94.4°K, 1.374 g cm⁻³). Not only was this the first molecular dynamics study with a "realistic" potential, it was also the first such study of the Van-Hove self $G_s(r, t)$ and distinct $G_d(r, t)$ space-time correlation function. Rahman determined the pair correlation function, the vcf and its power spectrum, and the self-diffusion coefficient. The vcf has a negative region and the power spectrum has a peak ($\omega = 0.25 kt/\hbar$). $G_s(r, t)$ attains a maximum departure from a Gaussian function of r at $t = 10^{-11}$ sec. $G_d(r, t)$ is compared with the Vineyard convolution approximation which is shown to give too rapid a decay with time. A retarded convolution approximation is suggested for $G_d(r, t)$.

Rahman (37b) studied the triplet correlation function $g^{(3)}(r, r, s)$ in liquid argon. According to the superposition approximation (SA) this function should be the product $g^{(2)}(r)g^{(2)}(r)g^{(2)}(s)$. For $s < a$, where a is the position of the first peak in $g^{(2)}(r)$, the SA exaggerates the triplet correlations and this exaggeration is larger when r is also $< a$. If SA was exact, then the function $R_r(s) \equiv g^{(3)}(r, r, s)/[g^{(2)}(r)]^2$ would be identical to $g^{(2)}(s)$. Rahman's computed $R_r(s)$ displays secondary maxima. In addition Rahman finds that the Born-Green equation, together with the SA, gives poor agreement with his $g^{(2)}(r)$.

In a subsequent paper the same author (38) studied argon with an exponential - 6 potential, at (85.5°K, 1.407 g cm⁻³). The particles around a diffusing particle are separated into shells of primary, secondary, etc neighbors. Each such shell generates a closed polyhedron surrounding the polyhedron of the previous shell. The shapes of these polyhedra are related to the direction of displacement in time of the central particle. The vcf $\psi(t)$ and its power spectrum are related to these fluctuations. Rahman finds that

$$\psi(t) = R_r(t) + S_r(t)$$

where $R_r(t)$ and $S_r(t)$ are respectively the time correlation functions of the velocity perpendicular and parallel to the direction of displacement of the particle in the time τ . $S_r(t)$ can further be separated into two parts $S_r^+(t)$ and $S_r^-(t)$ which correspond to motion of particles that initially have parallel velocity components pointing in the direction of displacement (+) and opposite to that direction (-). $R_r(t) + S_r^-(t)$ shows a rattling motion, whereas $S_r^+(t)$ shows a slipping motion. The power spectrum of these two parts look solidlike and diffusionlike respectively. This study indicates that volume fluctuations are not large enough to justify a jump diffusion model.

Paskin & Rahman (39) have studied a model system of 688 particles with a long range oscillating potential (LRO). They determined the pair correlation function and the self-diffusion coefficient and showed that when the Born-Green (BG) and Percus-Yevick (PY) equations are inverted with their com-

puted pair correlation function, they do not recover their pair potential. They conclude that neither equation is sufficiently accurate to recover the pair potential.

Rahman (40) determined the longitudinal and transverse current correlation function and their corresponding spectra for 500 particles of liquid argon at (76°K, 1.407 g/cc) interacting with a LJ (12-6) potential over a range of wavevectors from $q = 0.77$ to $q = 2.10 \text{ \AA}^{-1}$. The longitudinal currents show damped oscillatory behavior whereas the transverse currents show damped behavior for these values of the wavevector. The isothermal compressibility $\chi_T = +1.6 \times 10^{-10} \text{ cm}^2/\text{dyne}$ determined from molecular dynamics is in better agreement with experiment (2.0×10^{-10}) than would be expected, which indicates that systems as small as 500 particles already give useful information about such collective properties.

Rahman (41), in an excellent unpublished article on a comparative study of atomic motions in liquids and solids, discusses a molecular dynamics study of solid argon in which the particles interact with the LJ (12-6) potential. He discusses lattice dynamics, melting, local order, and diffusion in liquids and points out that waves of wavelengths $\lambda < 30 \text{ \AA}$ do not persist in liquids and have decay characteristics which in the case of longitudinal waves depend on the equilibrium structure through the structure factor (see also 40).

A detailed discussion of the current correlation functions is given by Ailawadi et al (42), where, in addition, detailed plots of the transverse current correlations are presented.

Allen et al (43) have studied the dynamical surface properties of noble gas crystals by molecular dynamics. They find that the mean square displacement of particles from lattice sites near the surface increases faster with temperature than in the bulk crystal. Of course, this crystal contains all anharmonicities.

De Wette et al (44) studied the crystallization of a two-dimensional system of 400 particles interacting through a LJ (12-6) potential. They solved the equations without periodic boundary conditions since such conditions would destroy crystallization. They include a damping term ($-\gamma \dot{S}^i$) in the equations of motion so that the atoms can lose kinetic energy and cool off.

Rahman has reviewed some of the above studies in (45), discussing his own work, preliminary work that he and Levesque have done on a gas of electrons, and work done by Verlet and his group at Orsay.

Verlet (46) did a large scale molecular dynamics study of liquid argon containing 864 particles interacting with a LJ (12-6) potential. He developed a bookkeeping technique (clearly explained in this reference), which enabled him to study argon in several thermodynamic states (ρ, T). The computed pressures, internal energies, high frequency elastic moduli, and isotope separation factors are in excellent agreement with experiments over this wide range of states. As shown by Lebowitz, Percus & Verlet (47) C_v can be determined from the mean square fluctuation in the temperature. In addition, the isothermal compressibility can be determined from an extrapolation of $S(k)$ to $k = 0$. Verlet determined both of these quantities. What is surprising about Verlet's

study is that the LJ (12-6) seems to give excellent agreement in liquids despite the fact that it is inadequate in gases.

In this connection Levesque & Vieillard-Baron (48) have investigated the pressure, internal energy, and critical constants for "liquid argon" over a large range of thermodynamic states with the following pair potentials: Kihara-Rowlinson, Munn and Smith, Kihara, exp -6, LJ (12-6), and LJ (9-6). The LJ (12-6) is the best potential for the description of liquid argon.

Verlet (48a) has also made a detailed study of the pair correlation function, the direct correlation function, and the structure factor.

Schiff (49) has determined the structure factor and velocity correlation functions in liquid metals. He shows that the vcf has long time oscillations in such systems with LRO potentials whereas it does not in systems with LJ potentials, but that these oscillations arise from the short range rather than the long range part of the potential.

Verlet (50) also made an extensive study of the velocity correlation function and its corresponding memory function in argon over a wide range of densities and temperatures.

Perhaps the most monumental calculation using molecular dynamics was done by Kurkijarvi, Levesque & Verlet of $S(q, \omega)$, the spectrum of density fluctuations in argon. As is known from Brillouin scattering, this function consists of three lines: the Rayleigh line and the Brillouin doublets for $q \sim 10^{-3} \text{ \AA}^{-1}$. The first is at $\omega = 0$ and the other two are at $\omega = \pm cq$ where c is the velocity of sound propagation. As q increases from 10^{-3} to 1 \AA^{-1} these three lines increase in width, and finally overlap and become one band which is a monotonic decreasing function of the frequency. Verlet et al computed $S(q, \omega)$ and showed that its triplet structure is still present at such high wavenumbers as $q = 0.2 \text{ \AA}^{-1}$. In addition, the splitting is correctly given by the macroscopic sound velocity. Above $q = 0.5 \text{ \AA}^{-1}$ they claim that it is invalid to describe the collective density fluctuations in terms of phonons. This work is still unpublished. The only place where a graph appears is in Rahman's review (45).

Harp & Berne (16, 17, 51-53) did a series of molecular dynamics studies of fluids containing diatomic molecules, whose purpose was to investigate the dependence of structure and dynamics of polyatomic fluids on the geometry of the constituent molecules and on the form of the noncentral potentials. These studies are useful for determining how energy is exchanged between rotational and translational degrees of freedom. Three potentials were used: the Stockmayer potential, a modified Stockmayer potential containing dipole-quadrupole and quadrupole-quadrupole terms, and a four-center LJ potential. The properties determined were the pressure, internal energy, velocity correlation function and its memory function, the angular momentum correlation function and its memory function, the dipolar correlation functions and their memory function, the Van-Hove self-intermediate scattering function and its memory, the two time joint probability distribution functions of the velocity

and angular momentum, and the center of mass pair correlation function and atomic pair correlation functions. The conclusions of these studies are:

1. The linear and angular momentum of a molecule in a dense fluid are to a good approximation Gaussian random variables but not Markov processes.
2. The velocity correlation function is largely determined by changes in the direction of motion of the molecule and is practically unaffected by changes in the molecular speed.
3. The angular momentum correlation function is largely determined by changes in the direction of the axis of rotation and is practically unaffected by changes in the angular speed.
4. For intermolecular potentials with a strong noncentral component there is a region of time during which the angular momentum time correlation function goes negative, whereas for a weak noncentral component this correlation function stays positive.
5. For intermolecular potentials with a strong noncentral component, the memory function corresponding to the dipolar autocorrelation function is to a very good approximation just the angular momentum autocorrelation function.
6. The atomic pair correlation functions which depend on the intermolecular distance and the relative orientations are very sensitive to the form and strength of the noncentral component of the intermolecular potential.
7. To a very good approximation the Gaussian memory functions corresponding to single-particle properties give good approximations to time correlation functions.

Bishop & Berne (54, 55) have studied one-dimensional systems containing, on the one hand, 100 hard rods and, on the other hand, 1000 particles interacting with a (LJ 12-6) potential. The hard rod system was compared with the exact solution of the one-dimensional hard rod problem given by Jepsen (56) and Lebowitz, Percus & Sykes (57) to ascertain the errors involved in molecular dynamics that stem from the system being finite and from computer round-off error. Agreement is quite good. The hard rod and LJ systems differ in several respects:

1. The vcf is invariant to time in the hard rod system but rapidly relaxes in the LJ system.
2. The vcf of the high density system is quite different in each case. For hard rods it goes negative and stays negative, whereas for the LJ system it oscillates.
3. The structure factors look quite similar.
4. The pair correlation functions for the two systems are very long range and have an upper envelope which looks quite exponential.

Anderson & Percus (55a), prior to this, studied the equilibrium properties of a one-dimensional system of rods interacting with a discontinuous triangular potential.

Bishop & Berne (54) have studied the onset of Brownian (B) motion in a one-dimensional system by investigating the vcf and its memory function for a B particle of mass M in a solvent of mass m for $M/m = 1, 10, 25, 40, 50, 75,$ and 100 . Brownian motion sets in at a mass ratio of 40 and, surprisingly, the self-diffusion coefficient is mass independent over the whole range of mass ratios. They suggest an explanation of this latter result.

Kohler & Bellemans (58) have investigated the approach to equilibrium of a weakly interacting system of 400 electric dipoles which are free to rotate on a rigid lattice.

In addition Fehder (59, 60) has studied a two-dimensional system of particles interacting through a LJ (12-6) potential at several temperatures and densities. These studies essentially repeat Rahman's three-dimensional studies on two-dimensional systems. Fehder & Futrell (61) have studied diffusion in pair space. This is an important process for chemists in that recombination kinetics depends on it.

Having discussed past molecular dynamics studies we would like to mention some studies that are currently in progress or that may be anticipated: (a) dynamics in the presence of many-body forces, (b) collective modes in polyatomic liquids, (c) liquid crystal structure and dynamics, (d) structure and dynamics of water, and (e) polymer dynamics.

In fact (b) and (c) are presently being carried out by Kushick & Berne and (d) is almost completed by Rahman & Stillinger.

Molecular dynamics deals with a completely well-defined mathematical model. The properties of a system can be studied as function of the intermolecular potential and of whatever external perturbations one would like to impose. These studies can be used to develop intuition and to provide a test for theory.

PROJECTION OPERATOR TECHNIQUES

The introduction by Zwanzig (10) and Mori (62) of projection operator techniques into statistical mechanics is a major development. In this section we summarize some of the main features of this technique. We restrict our discussion to classical systems for convenience. All of our conclusions apply, with minor change, to quantum systems.

The inner product of two properties $A(\mathbf{T})$ and $B(\mathbf{T})$ is defined as

$$\langle A|B \rangle \equiv \langle A^*B \rangle$$

where $\langle \dots \rangle$ denotes any of the equilibrium ensemble averages or the infinite time average of the previous section. From this definition of the scalar product it follows that: (a) $\langle A|B \rangle^* = \langle B|A \rangle$; (b) $\langle A|A \rangle \geq 0$; (c) $\langle A|B \rangle$ is a linear functional of B and an antilinear functional of A . The norm $\langle A|A \rangle^{1/2}$ is simply the rms value of $A(\mathbf{T})$. Any property A can therefore be regarded as a

vector (ket, $|A\rangle$) in an inner product space which we call "property space" or "Liouville space." In a classical system any property A obeys the equation of motion $\dot{A} = \{A, H\} \equiv iLA$ so that $A(\Gamma_t) \equiv \exp [iL t] A(\Gamma_0)$ where Γ_0, Γ_t are the states of the system at the times 0 and t and e^{iLt} is the propagator. In Liouville space the time variation of the ket $|A\rangle$ can be represented by the equation

$$|A(t)\rangle = e^{iLt}|A(0)\rangle$$

The propagator is a unitary operator, and the time evolution of $|A(t)\rangle$ can be regarded as a "rotation" of $|A(t)\rangle$ in Liouville space.

The time correlation function $\langle A^*(0)A(t)\rangle$ can thus be regarded as the expectation value of the propagator in the "state" $|A\rangle$. Zwanzig (10) showed that the normalized correlation function $C(t)$

$$C(t) \equiv \langle A|e^{iLt}|A\rangle\langle A|A\rangle^{-1}$$

evolves in time according to the equation

$$\frac{\partial C(t)}{\partial t} = i\Omega C(t) - \int_0^t d\tau K(\tau)C(t - \tau)$$

which he calls the memory function equation. Berne, Boon & Rice (63) derived this equation in a different way. Mori (62) showed that the ket evolves in time according to what he calls the generalized Langevin equation because of its similar form to the Langevin equation of Brownian motion theory

$$\frac{\partial}{\partial t} |A(t)\rangle = i\Omega |A(t)\rangle - \int_0^t d\tau K(\tau)|A(t - \tau)\rangle + |F(t)\rangle$$

In these equations, $K(t)$ is the memory function, Ω is the resonance frequency, and $|F(t)\rangle$ is the "random force" conjugate to $|A\rangle$.

Kubo (64) showed that $K(t)$ is proportional to the time correlation function of the random force

$$K(t) = \langle F(0)|F(t)\rangle\langle A|A\rangle^{-1}$$

Kubo calls this the second fluctuation dissipation theorem.

The explicit forms of the quantities that appear in these equations are given in terms of the projection operators

$$P \equiv |A\rangle\langle A|A\rangle^{-1}\langle A|$$

$$Q \equiv (1 - P)$$

where P and Q respectively project onto the vector $|A\rangle$ and its orthogonal subspace. Then

$$i\Omega \equiv \langle A|iL|A\rangle\langle A|A\rangle^{-1}$$

$$|F(t)\rangle \equiv \exp [iQLt]Q|A\rangle$$

$$K(t) \equiv \langle A|e^{iQLt}Q|A\rangle\langle A|A\rangle^{-1}$$

Moreover, because $Q|A\rangle = 0$ it follows that $\langle A|F(t)\rangle = 0$.

The memory function $K(t)$ is a time correlation function with a "strange" propagator e^{iQLt} in place of e^{iLt} . Berne et al (65) have shown that the Laplace transform of $K(t)$ is related to the Laplace transform of the correlation function

$$\Phi(t) \equiv \langle A | e^{iLt} | A \rangle \langle A | A \rangle^{-1}$$

through the equation

$$\tilde{K}(s) = [1 - 1/s \tilde{\Phi}(s)]^{-1} \tilde{\Phi}(s)$$

This relationship was derived for the special case when the property is such that $i\Omega = 0$ but it is easily generalized.

Mori (66) has expressed the time correlation functions in the form of an infinite continued fraction

$$\tilde{C}(s) = \frac{1}{s + i\Omega_1 + \frac{\Delta_1^2}{s + i\Omega_2 + \frac{\Delta_2^2}{s + i\Omega_3 + \frac{\Delta_3^2}{s + \dots}}}}$$

where the coefficients Δ_j^2 and the frequencies $i\Omega_j$ are related to well-defined equilibrium moments.

Spectral lineshapes, according to linear response theory (9), are given by time Fourier transforms $S(\omega)$ of appropriate time correlation functions, e.g. $C(t)$. A number of investigators have Fourier inverted experimental lineshapes to obtain time correlation functions. This work has been reviewed by Gordon (12) and is discussed by several authors (6, 13, 15-17). These lineshapes can be related to the memory function

$$\pi S(\omega) = K'(\omega) / \{[\omega - \Omega + K''(\omega)]^2 + [K'(\omega)]^2\}$$

where

$$K(\omega) \equiv K'(\omega) - iK''(\omega) \equiv \int_0^\infty dt e^{-i\omega t} K(t)$$

Thus, the memory function provides information about the width and shift of the spectral line. Moreover, $K'(\omega)$ and $K''(\omega)$ are related by Kramers-Kronig relations (see 11, 16, 17). A theory of pressure broadening has been developed along these lines by Fano (67), Ben-Reuven (68), and Greer & Rice (69).

Thermal transport coefficients are related to time correlation functions through the Kubo relations (see Zwanzig 1). From the memory function equation it follows that the inverse of the transport coefficient is related to the time integral of the memory function. This integral can consequently be regarded as a generalized friction coefficient.

The spectra $P_c(\omega)$ and $P_k(\omega)$ of the time correlation function $C(t)$ and the memory function $K(t)$ have the sum rules

$$\int_{-\infty}^{\infty} d\omega P_c(\omega) \omega^{2n} = \langle A^{(n)} | A^{(n)} \rangle \langle A | A \rangle^{-1}$$

$$\int_{-\infty}^{\infty} d\omega P_k(\omega) \omega^{2n} = \langle B^{(n)} | B^{(n)} \rangle \langle A^{(1)} | A^{(1)} \rangle^{-1}$$

where

$$|A^{(n)}\rangle \equiv [iL]^n |A\rangle$$

$$|B^{(n)}\rangle = [iQL]^n |A^{(1)}\rangle$$

$$P_c(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t)$$

$$P_k(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} K(t) / K(0)$$

Thus, the sum rules relate frequency moments of the power spectra $P_c(\omega)$ and $P_k(\omega)$ to equilibrium averages of appropriate dynamical variables.

These equations together with the sum rules have been used in many applications (see later sections). An alternative formulation of spectra was developed by Kadanoff & Martin (70) (see also Martin 11, 71). Although these authors never explicitly mention projection operators, this approach (see 16, 17) is completely equivalent to the memory function formulation. Because of confusion on this score there has been some duplication by different groups using these two different formalisms (e.g. cf 63 and 72).

The memory function formalism provides an excellent vehicle for the analysis and for plausible derivations of phenomenological equations and for the extensions of these equations to microscopic times and distances. This kind of analysis has been applied to the derivation and extension of linear hydrodynamics (11, 17, 71, 73-78a); linear hydrodynamics with molecular relaxation (79-85) and diffusion (16, 17, 86-89); Bloch equations of magnetic relaxation (90); Brownian motion theory (16, 17, 81, 86, 91, 92); linear hydrodynamics in liquid crystals (90, 93, 94); and dynamic scaling (95).

Memory functions are also useful for the discussion of time correlation functions of single-particle properties. Properties that have been treated in this manner are those of linear momentum (63, 72, 96, 97); angular momentum (16, 17, 51-53, 98); and orientational relaxation (16, 17, 51-53, 99).

There have been several attempts to calculate transport coefficients using the sum rules on the memory functions (16, 17, 100, 100a).

In the following we give a brief illustration of how the memory function formalism can be used to derive phenomenological equations. A simple demonstration of this procedure has to do with self diffusion. The function

$$F_s(\mathbf{q}, t) \equiv \langle e^{i\mathbf{q} \cdot \mathbf{r}^{(0)}} e^{i\mathbf{q} \cdot \mathbf{r}^{(t)}} \rangle$$

is the spatial Fourier transform of the Van-Hove space-time self-correlation function $G_s(\mathbf{r}, t)$, which is the probability distribution that the displacement of a specified particle at time t will be \mathbf{r} . Phenomenologically, this would be treated using the diffusion equation

$$\partial_t F_s(q, t) = -q^2 D F_s(q, t)$$

where D is the coefficient of self diffusion. On the other hand we know that $F_s(q, t)$ rigorously satisfies the memory function equation

$$\partial_t F_s(q, t) = -q^2 \int_0^t d\tau \psi_q(\tau) F_s(q, t - \tau)$$

We take q along the z direction

$$\psi_q(\tau) \equiv \langle v_z(q) | e^{iQz} | v_z(q) \rangle$$

where $v_z(q) \equiv v_z \exp [iqz]$. Of course there is the projector Q in the propagator; nevertheless, in the limit $q \rightarrow 0$ for an isotropic system $\psi_q(\tau)$ reduces to

$$\psi_q(\tau) \xrightarrow{q \rightarrow 0} \frac{1}{3} \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle$$

Consequently, for small q the memory function $\psi_q(\tau)$ reduces to the velocity autocorrelation function which in a liquid decays on a time scale ($\sim 10^{-12}$ sec), which is rapid compared with the decay of $F_s(q, t)$ even for relatively large q (see for example 53). The memory function equation then reduces to the diffusion equation with

$$D \equiv \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$$

This procedure can be made systematic (see Zwanzig 86 and Berne 17).

The lesson to be learned from this discussion is that if P projects onto a subspace of Liouville space containing all the "slowly" decaying properties of the system, the projector Q projects onto the orthogonal complement of this slow subspace, which, by definition, must contain all of the rapidly decaying properties. Then the memory functions will decay rapidly compared with the time correlation functions; there will be a separation in time scales, and for long times phenomenological equations will result. It is necessary that one know the set of all slowly decaying properties—such a set is called a "complete" set. If the set is incomplete, then Q will project onto some slow variables and there will not be a separation in times, so that the phenomenological equations will not result. Unfortunately, there is no general procedure for choosing this complete set.

If we consider properties like

$$A(q, t) \equiv \frac{1}{\sqrt{V}} \sum_{j=1}^N A_j(t) e^{iq \cdot \mathbf{r}_j(t)}$$

where $A(q = 0)$ is a constant of the motion, then for small q we expect $A(q, t)$ to vary slowly with time. Thus in the limit $q \rightarrow 0$ we expect that the "densities" of all the conserved properties (in an isotropic system: mass, momentum, and energy) will form a complete set. In this case the memory function equations will reduce to the equations of linear hydrodynamics and the transport coefficients will be given by the Kubo relations (see later sections).

Another application involves Brownian motion. The memory function equation for the velocity correlation function $\psi(t)$ is

$$\partial_t \psi(t) = -\frac{1}{M} \int_0^t d\tau K(\tau) \psi(t - \tau)$$

where

$$K(\tau) \equiv \langle F | e^{iQL\tau} | F \rangle (3kT)^{-1}$$

We investigate a model in which the particle (B particle) whose velocity we are investigating is identical in all respects to the remaining particles (solvent particles) except one: its mass M is much larger than their masses m . Since the forces are the same the only mass dependence of the memory function comes from the propagator $e^{iQL\tau}$. Now the Liouville operator can be separated into two parts

$$iL = iL_f + i\gamma L_B$$

where L_f and L_B are respectively the Liouville operators that generate the solvent motion in the force field of the B particle and the B-particle motion in the force field of the solvent, and the mass ratio $\gamma \equiv \sqrt{m/M}$ is small when $M \gg m$. The γ gives the ratio of the rms velocity of the B particle to the rms velocity of a solvent particle. Thus we see that in the Brownian limit

$$\begin{aligned} \lim_{\lambda \rightarrow 0} \langle F | e^{iQL\tau} | F \rangle &= \langle F | e^{iQL_f\tau} | F \rangle \\ &= \langle F | e^{iL_f\tau} | F \rangle \end{aligned}$$

so that the memory function is just the autocorrelation function of the force on the B particle in a system in which the B particle is stationary and the solvent molecules move under their own interaction and under their interaction with the stationary B particle. Because the fluid particles are light, they move rapidly on the average, and this force autocorrelation should decay rapidly on the time scale during which the massive B particle suffers a very small change in its momentum. Then to a very good approximation, the memory function equation reduces to

$$\begin{aligned} \partial_t \psi(t) &= (-\zeta/M) \psi(t) \\ \psi(t) &= e^{(-\zeta/M)t} \end{aligned}$$

where the friction coefficient is

$$\zeta = (1/3kT) \int_0^\infty dt \langle F(0) \cdot e^{iL_f t} F(0) \rangle$$

This treatment not only gives the same results as the classical Langevin theory of Brownian motion, it also gives a formula for the friction constant. This formula was first derived by Kirkwood (101) by quite different methods. Our treatment has been made systematic (see 17).

The procedure outlined above appears in a recent reference (17); earlier, the Brownian motion problem was studied in different ways by several authors. Rubin (102) has written a series of beautiful papers on the dynamics of a heavy particle in a lattice of light particles in one, two, and three dimensions. He shows how the exact equations of Brownian motion can be extracted from the equations of motion in one and three dimensions. In two dimensions he shows that Brownian motion does not result. Lebowitz & Rubin (103) show how the Fokker-Planck equation for B motion can be extracted from mechanics by using a novel perturbation theory. The same problem was worked out by Resibois & Davis (104) using the diagrammatic techniques of Brout & Prigogine (105). Later Lebowitz & Resibois (91) used projection operators to derive the Fokker-Planck equation in the presence of an alternating electric field in the limit $\gamma \rightarrow 0$. More recently Mazo (106) and Oppenheim et al (92) have studied the motion of two Brownian particles in a solvent. Here there are interactions between the Brownian particles due to Oseen forces.

Let us recall that the generalized Langevin equation will reduce to the Langevin equation if

$$K(\tau) = \langle F | e^{iQL\tau} | F \rangle (3kT)^{-1}$$

decays very rapidly compared with $\psi(t)$. As the mass M increases we have already surmised that

$$e^{iQL\tau} \rightarrow e^{iL_f\tau}$$

so that $K(\tau)$ should decay on the time scale of the solvent (light, rapidly moving particles), whereas $\psi(\tau)$ should decay the more slowly, the heavier the B particle. This follows from the fact that the more massive the B particle the larger its rms momentum and the more ineffective will be the forces in reversing this momentum.

Bishop & Berne (54) studied the mass dependence of $K(\tau)$ and $\psi(\tau)$ in a one-dimensional molecular dynamics study. Interestingly, there is an apparent mass independence of the translational self-diffusion coefficient $D(M)$. So much so, in fact, that the diffusion coefficient is the same for particles of mass m and mass $100m$.

There exists no theory for this. In fact, it has been experimentally observed (107) in three dimensions that Ag and Au both have the same diffusion coefficients in Hg despite the fact that Au is roughly twice as massive as Ag. Rahman (108) has made a preliminary study of this phenomenon in three dimensions and observes the same effect.

Silbey & Deutch (109) recently showed that

$$\langle F | e^{iQLt} | F \rangle = \langle F | e^{iL_f t} | F \rangle$$

holds rigorously for all lattices with harmonic forces. This is the first demonstration that a memory function is identical to autocorrelation function in a Hamiltonian system. Of course, in most systems this will not be the case.

We now turn to velocity correlations in pure liquids. In an ordinary fluid the masses of the particles are equal and the above considerations do not apply. Nevertheless, the generalized Langevin theory is useful here. Essentially, we can regard it as a generalization of the phenomenological theory to small times. We have noted that the memory function is the time correlation function of the random force. In Brownian motion theory it has a white spectrum. Berne, Boon & Rice (63) assumed that in a liquid this fluctuating force is a Gaussian Markov process so that it has a simple exponential decay

$$K(t) = \frac{\langle F^2 \rangle}{3KT} e^{-t/\tau}$$

with a relaxation time τ . $\langle F^2 \rangle$ is the mean square force on the particle which in some cases can be obtained from isotope separation data (Boato et al 110). The velocity correlation function $\psi(t)$ can then be obtained from the memory function equation with an as yet free parameter. The Kubo relation for the self-diffusion coefficient is

$$D = \frac{kT}{M} \int_0^\infty dt \psi(t)$$

When $\psi(t)$ is substituted here a relation between D and τ is found which enables one to evaluate τ from the self-diffusion coefficient. Then $\psi(t)$ is determined and compared with Rahman's computer experiment. The results are in good qualitative agreement. This represented a first attempt at a "Brownian-type" theory for diffusion in pure liquids. Of course in this approximation the spectrum of the velocity does not have frequency moments higher than $\langle \omega^2 \rangle_c$, a fact that is well known in connection with Lorentzian lineshapes.

This calculation was followed by the choice of a Gaussian memory

$$K(t) = \frac{\langle F^2 \rangle}{3KT} e^{-t^2/\tau^2}$$

by Singwi & Tosi (96) who otherwise repeated the same procedure of Berne et al (63). This memory has the advantage of having all frequency moments. It does not, however, give substantially better agreement with Rahman's (37) molecular dynamics study of argon. Another procedure that has been adopted is to calculate τ from the frequency sum rules instead of from the diffusion coefficient. The frequency moments can be obtained from molecular dynamics or can be calculated theoretically. Berne & Harp (16, 17, 32) have carried out this latter procedure for CO and N₂ in a molecular dynamics study. In fact they also determine $K(t)$ from molecular dynamics and find that a Gaussian memory is in excellent agreement with the computer experiment for a substantial period of time, departing only for long times.

Zwanzig & Bixon (97) have presented a hydrodynamic calculation of the vcf based on a generalization of the Stokes theory of the friction coefficient. Among other things this model gives a vcf with a long time tail that behaves as $t^{-3/2}$.

COLLECTIVE FLUCTUATIONS IN LIQUIDS

Many scattering experiments determine dynamical properties to which the particles of a liquid contribute collectively. Light or thermal neutrons, for example, are scattered by collective fluctuations of the particle density; the relevant spectrum is that of the dynamical structure factor

$$S(k, \omega) = \frac{1}{V} \int_{-\infty}^{\infty} dt e^{i\omega t} \left\langle \sum_{\alpha=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}^{\alpha}(0)} \sum_{\beta=1}^N e^{i\mathbf{k}\cdot\mathbf{r}^{\beta}(t)} \right\rangle$$

which represents one of the most fundamental dynamical properties of a many-particle system. The calculation of $S(k, \omega)$ from first principle is of course still a formidable problem. However, in the past few years a variety of methods have been developed to study such correlation functions in a semi-quantitative manner, and considerable progress has been achieved. To describe some of these methods we will, by way of example, consider the fluctuations of the transverse momentum density which are somewhat simpler than those of the particle density, and we will restrict ourselves to simple classical liquids. One is then concerned with the collective variable

$$\mathbf{g}(k, t) = \sum_{\alpha=1}^N \mathbf{p}^{\alpha}(t) e^{i\mathbf{k}\cdot\mathbf{r}^{\alpha}(t)}$$

$\mathbf{r}^{\alpha}(t)$ and $\mathbf{p}^{\alpha}(t)$ are the position and momentum of the α th particle at time t and V is the volume. The wavevector \mathbf{k} is chosen in the z direction so that $g_x(k, t)$ is the k th Fourier component of the transverse local momentum density. The quantities of interest are then the time correlation function $C_i(k, t)$ and its Fourier transform $C_i(k, \omega)$

$$\begin{aligned} C_i(k, t) &= V^{-1} \langle g_x^*(k, 0) g_x(k, t) \rangle \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega t} C_i(k, \omega) \end{aligned}$$

Hydrodynamic flow experiments determine $C_i(k, \omega)$ in the most easily accessible region of long wavelength k^{-1} and small frequency ω . However, computer experiments have now provided us with data in other regions of k and ω , and they have stimulated a great deal of theoretical research.

HYDRODYNAMIC FLUCTUATIONS

By far the most successful theory of collective motion in liquids is the phenomenological continuum theory of fluid dynamics, i.e. the (linearized) Navier-Stokes equations. The solution of these equations in terms of correla-

tion functions is described in several excellent papers (Kadanoff & Martin 70, Felderhof & Oppenheim 73, and Mountain 111).

$C_i(k, \omega)$ is obtained in the form

$$C_i(k, \omega) = \frac{(k\eta^2)2(k_B T)}{\omega^2 + (k^2\eta/\rho)^2}$$

where k is Boltzmann's constant, T is the temperature, and ρ is the average mass density $\rho = mN/V$. The η is a transport coefficient, namely the shear viscosity. Of course the hydrodynamic expression for $C_i(k, \omega)$ is only valid in the region of small k and ω . It is presumably rigorous in the limit $k\lambda_f \ll 1$ and $\omega\tau_c \ll 1$ where λ_f is a mean free path and τ_c a microscopic collision time. The collective aspect of many-particle dynamics is most pronounced in this region. Just as $C_i(k, \omega)$ contains a diffusive peak characteristic of momentum transport, there are corresponding, somewhat more complicated, hydrodynamic expressions for $S(k, \omega)$ which describe the coupled transport processes of sound propagation and heat diffusion (70). In light scattering, these processes are responsible for the Brillouin doublet and the central Rayleigh line. They all describe collective excitations of extremely small energy (compared to $k_B T$) which involve coherent motion of extremely large numbers of particles. The lifetime $\tau(k)$ of these excitations becomes infinite as $k \rightarrow 0$; the width of the peak in $C_i(k, \omega)$ is $\sim k^2$. This property, characteristic of hydrodynamic modes, is ultimately due to momentum conservation which forbids the decay of $C_i(k, t)$ in the limit as $k \rightarrow 0$. The reason why the expressions for $S(k, \omega)$ are more complicated is that the longitudinal conserved densities of number, longitudinal momentum, and energy are dynamically coupled.

The transport coefficient η remains an undetermined parameter within the hydrodynamic theory. It summarizes the influence of fast processes which decay over short times of order τ_c , on the long-lived collective mode. Nevertheless, from $C_i(k, \omega)$ we obtain directly the rigorous expression

$$\eta = (2k_B T)^{-1} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} C_i(k, \omega)$$

which is useful since it relates η to a microscopically well-defined time correlation function which can, at least in principle and in fact approximately, be calculated. This expression, generally known as a Kubo relation, is perhaps more familiar in the form

$$\eta = (k_B T \cdot V)^{-1} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \int_0^\infty dt \langle \tau_{xz}^*(k, 0) \tau_{xz}(k, t) \rangle e^{-\epsilon t}$$

which Zwanzig (1) has discussed in his review article. Here $\tau_{xz}(k, t)$ is the microscopic stress tensor, defined by $\dot{g}_x(k, t) = ik\tau_{xz}(k, t)$.

MEMORY FUNCTIONS

The hydrodynamic result for $C_i(k, \omega)$ has been known for at least a decade. An important goal of more recent theoretical work has been to calculate transport coefficients like η for dense liquids and to extend the description to

values of k and ω for which conventional hydrodynamics no longer holds. Much of this work has been based, in one way or another, on the concept of memory functions and dispersion relation representations. It is convenient to describe this concept in terms of one-sided Fourier transforms defined by

$$C_i(k, z) = \int_0^\infty dt e^{izt} C_i(k, t) = \int_{-\infty}^\infty \frac{d\omega}{2\pi i} \frac{C_i(k, \omega)}{\omega - z}$$

where z is a complex frequency. If z is in the upper half of the complex plane, $C_i(k, z)$ is analytic in z . It can, in complete generality, be represented in the form

$$C_i(k, z) = \frac{i}{z + ik^2\eta(k, z)/\rho} \rho k_B T$$

in terms of a memory function $\hat{\eta}(kz)$ which can be regarded as a complex, wavenumber- and frequency-dependent shear viscosity. The projector formalism described earlier gives an "explicit" expression for $\hat{\eta}(kz)$ in the form

$$\hat{\eta}(k, z) = \int_0^\infty dt e^{izt} \eta(k, t)$$

$$\eta(k, t) = (k_B T V)^{-1} \langle \tau_{xz}^*(k) | e^{-iQLt} | \tau_{xz}(k) \rangle$$

where L is the Liouville operator and Q a projector which projects out fluctuations of the transverse momentum density $g_x(k)$ itself. Clearly $\hat{\eta}(k, z)$, like $\hat{C}_i(k, z)$, is analytic in z for $\text{Im } z > 0$. Both functions can be continued into the lower half of the complex frequency plane, but they will in general have poles there and possibly other singularities.

Of course this representation for $C_i(kz)$ is, while completely general, only useful if $\hat{\eta}(k, z)$ is a simpler object than $\hat{C}_i(k, z)$ itself. This is presumably the case, at least for moderately small k and z . Indeed, its value as $k \rightarrow 0$ and $z \rightarrow 0$ must be real and positive, since it is just given by the transport coefficient $\eta = \hat{\eta}(0, 0)$. [In this limit, the projector Q in $\hat{\eta}(k, z)$ can be omitted.] Notice, by contrast, the complicated and highly singular behavior of $\hat{C}_i(k, z)$ in this limit, a behavior caused by the momentum conservation law. It is intuitively reasonable (though difficult to prove) that $\hat{\eta}(k, z)$ should be simpler. As our "explicit" expression indicates, $\hat{\eta}(k, z)$ can itself be understood as a "correlation function," but with a changed dynamics determined by QL rather than L . Since it thus no longer involves the conservation law, there is no apparent reason why $\hat{\eta}(k, z)$ should be singular near $k = 0$ and $z = 0$.

The only processes remaining in $\hat{\eta}(k, t)$, then, are fast microscopic processes which decay over presumably short times of order τ_c . Most approximations result from the assumption that these numerous processes can be lumped into one, or a few at most. Such approximations have been developed in great variety; they are usually known under the key word of "generalized hydrodynamics." Conventional hydrodynamics results, of course, if the "memory" is infinitely short (compared to the times in which one is interested) so that

$\eta(k, t) = \eta\delta(t)$ as $k \rightarrow 0$, or $\hat{\eta}(k, z) = \eta$. A somewhat less drastic assumption is that of "exponential" memory

$$\eta(k, t) = \frac{\eta}{\tau} e^{-t/\tau} \quad \text{or} \quad \hat{\eta}(k, z) = \eta(1 - iz\tau)^{-1}$$

which has been described earlier. As is seen here, this ansatz replaces the detailed dynamics by a simple pole in the lower half z plane, at $z = -i\tau^{-1}$. The correlation function $C_i(k, \omega) = \frac{1}{2} \text{Re } \hat{C}_i(k, z)$ as $z \rightarrow \omega + i0$ is then given by

$$C_i(k, \omega) = \frac{k^2 \eta (2k_B T)}{\omega^2 + [k^2 \eta / \rho - \omega^2 \tau]^2}$$

which extends the hydrodynamic theory to higher frequencies by introducing an additional parameter τ which can be fitted to computer dynamics data.

This may be an appropriate point to mention the exciting possibility of long time tails in functions like $\eta_i(k, t)$ which has come under study recently. The function $\eta_i(t) = \lim_{k \rightarrow 0} \eta_i(k, t)$ must approach zero as $t \rightarrow \infty$. (If it approaches a constant $\mu \neq 0$ instead, the system will be a solid, not a liquid, and μ is its elasticity coefficient). However, we cannot rule out, on rigorous grounds, the possibility of long time tails $\eta(t) \sim 1/t^{d/2}$ where d is the dimensionality as $t \rightarrow \infty$. If so, the shear viscosity $\eta = \int_0^\infty dt \eta(t)$ does not exist, in two dimensions, and the system will have no hydrodynamics. The computer studies of Alder & Wainwright (31) mentioned earlier suggest that this might indeed be the case in two-dimensional hard disc fluids. While a rigorous explanation of this effect is not available at present, several recent papers (112–112b) have given very strong arguments which relate the existence of long time tails to the internal consistency of two-dimensional linearized hydrodynamics itself. In particular, the beautiful paper by Zwanzig (112b) shows that nonlinear streaming terms lead to a renormalization of the transport coefficients of the linear theory and points out that in two dimensions the renormalized coefficients diverge at least in the perturbation approximation considered.

SUM RULES

Important microscopic information about the dynamical structure of liquids can be obtained from frequency sum rules. These are expressions of the form

$$(\rho k_B T)^{-1} \int \frac{d\omega}{2\pi} \omega^n C_i(k, \omega) = \langle \omega_i^{(n)}(k) \rangle$$

so that

$$\begin{aligned} \langle \omega_i^{(n)}(k) \rangle &= (\rho k_B T)^{-1} (i\partial_t)^n C_i(k, t)|_{t=0} \\ &= (\rho k_B T V)^{-1} i^n \langle g_x^{(n)*}(k, 0) g_x^{(n)}(k, 0) \rangle \end{aligned}$$

where $g_x^{(n)}(k, 0)$ is the n th time derivative of the momentum density, taken at time $t = 0$. The calculation of the $\langle \omega_i^{(n)}(k) \rangle$ thus reduces to the problem of calculating time-independent static equilibrium averages. Since $C_i(k, \omega)$ is an

even function of ω , all odd moments vanish. Of course, the dynamical problem would be essentially solved if all moments could be computed. Unfortunately, only the first few of them can in fact be evaluated. For example, the second moment is of the form, for a classical fluid

$$\langle \omega_i^{(2)}(k) \rangle = \frac{k_B T}{m} [k^2 + n^2 \int d^3 r g(r) [1 - \cos kz] \nabla_x^2 V(r)]$$

involving the interparticle potential $V(r)$ and the pair correlation $g(r)$ which is numerically available from computer data, at least for some simple liquids. Higher order sum rules involve higher order equilibrium correlations, and the numerical evaluation becomes rapidly prohibitive. Nevertheless, numerical data for the first two moments, $\langle \omega_i^{(2)}(k) \rangle$ and $\langle \omega_i^{(4)}(k) \rangle$, are available (100a) at least for small values of k . Also available are several sum rules for longitudinal correlation functions, in particular $S(k, \omega)$.

Sum rules function prominently in almost all theories of collective correlations outside the purely hydrodynamic regime. The hydrodynamic results, which we have given for transverse current fluctuations, give the form which $C_t(k, t)$ must approach in the limit of long times (and small k). On the other hand, as their derivation indicates, sum rules are (in principle rigorous) results which pertain to very short times. Most recent theories of collective modes represent schemes designed to interpolate between these two limits in a plausible, but ultimately ad hoc, fashion. The importance of memory functions like $\eta(k, t)$ is that they appear to be a particularly suitable vehicle for such interpolation schemes. We will briefly describe several calculations of this type, and indicate others.

CALCULATION OF TRANSPORT COEFFICIENTS

The viscosity η summarizes, as we said, the influence of short-lived processes upon the dynamics at long, hydrodynamic times. In principle, the short time information is fully contained in the memory function $\eta(k, t)$ or its two-sided Fourier transform

$$\eta(k, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \eta(k, t)$$

The function $\eta(k, \omega)$ must be real and, even in ω , a consequence of time reversal symmetry. It also must die off at large ω sufficiently rapidly since all of its sum rules exist. Indeed, one shows easily that

$$\int \frac{d\omega}{2\pi} \eta(k, \omega) = \rho k^{-2} \langle \omega_i^{(2)}(k) \rangle \equiv \rho C_t^2 \omega(k)$$

$$\int \frac{d\omega}{2\pi} \omega^2 \eta(k, \omega) = \rho k^{-2} \{ \langle \omega_i^{(4)}(k) \rangle - \langle \omega_i^{(2)}(k) \rangle^2 \}$$

and so forth.

A plausible ansatz compatible with these general properties is, for example, a Gaussian

$$1/(2\rho)\eta(k, \omega) = C_{i\infty}{}^2(k)\tau(k)e^{-[\omega\tau(k)]^2/\pi}$$

which fulfils the first sum rule, and the second if $\tau(k)$ is chosen to be

$$\tau^2(k) = (\pi/2\rho)k^2[\langle\omega_i^{(4)}(k)\rangle - \langle\omega_i^{(2)}(k)\rangle^2]^{-1}$$

which is finite as $k \rightarrow 0$, as it must be. The shear viscosity η is then given by

$$\eta = \frac{1}{2}\eta(0, 0) = \rho \lim_{k \rightarrow 0} C_{i\infty}{}^2(k)\tau(k)$$

and can be numerically obtained from the known values of the sum rules (100a). The agreement with experiment in liquid argon is remarkably good, giving about 20% accuracy over a fairly large range of temperature and density. This is all the more remarkable as this simple theory involves an intuitive ansatz for the frequency dependence of the memory, but determines all parameters from first principle. Similar calculations can be made for the other transport coefficients.

GENERALIZED HYDRODYNAMICS

The hydrodynamic theory described above is appropriate and indeed extremely accurate in the region of small k and ω where flow and light scattering experiments are performed. [Light and neutron scattering measure $S(k, \omega)$, of course, not $C_i(k, \omega)$ which we consider here for simplicity.] Neutron scattering and computer experiments involve typically wavenumbers $k \sim 10^8 \text{ cm}^{-1}$ and frequencies $\omega \sim 10^{12} \text{ sec}^{-1}$ which are intermediate between hydrodynamics and essentially free particle behavior (large k). No theory of comparable rigor and success exists in this intermediate region. However, considerable progress has nevertheless been achieved towards understanding the dynamical structure in a semiquantitative fashion. We shall call these theories by the only vaguely appropriate name "generalized hydrodynamics," and we will briefly describe three of them which appear to us to be representative. It is an important and common feature of such theories to represent $\hat{C}_i(k, z)$ by its memory function $\hat{\eta}(k, z)$ or similarly defined functions. On the basis of more or less plausible arguments a parameterized ansatz for these is then inserted and the parameters (generally functions of k) determined from the sum rules and a few related considerations.

The paper by Chung & Yip (76) directly uses the memory function introduced here. Instead of a Gaussian ansatz which is computationally somewhat difficult to handle, they use an exponential (in time) memory or equivalently

$$\hat{\eta}(k, z) = \rho \frac{C_{i\infty}{}^2(k)\tau(k)}{1 - iz\tau(k)}$$

which fulfils the first nontrivial sum rule above. The second sum rule, involving $\langle \omega_l^{(4)}(k) \rangle$, cannot be fulfilled with this ansatz. However, $\tau(k)$ can be estimated from the experimental value of the shear viscosity η by noting that

$$\eta/\rho = \lim_{k \rightarrow 0} C_{t\infty}^2(k)\tau(k)$$

Since $\tau(k) \rightarrow 0$ as $k \rightarrow \infty$ to reproduce free particle behavior in this limit, several simple interpolation schemes are tested which allow $\tau(k)$ to decrease by about a factor of 2 in the region $k = 0$ to $k = 1 \text{ \AA}^{-1}$. The results are in good agreement with computer experiments for $k \sim 1 \text{ \AA}^{-1}$. Similar analyses have been performed by many authors, among them Ailawadi (42), Akcasu & Daniels (77), and others.

In the intermediate region of k on the order of 1 \AA^{-1} , not only $S(k, \omega)$ but also $C_t(k, \omega)$ develop phononlike maxima for $\omega \neq 0$, $\sim 10^{13} \text{ sec}^{-1}$. Qualitatively, these peaks can be understood by noticing that at sufficiently large frequency $|z|$ or short times

$$\hat{\eta}(k, z) = \frac{i}{z} \rho C_{t\infty}^2(k)$$

leading to peaks at $\omega = \pm k C_{t\infty}(k)$. These peaks, which in liquids are of course smeared out into fairly broad bumps, are thus a consequence of the general property of many-body systems to behave in a reactive fashion at sufficiently high frequency, a property familiar in the dielectric response of many-body systems. Clearly, to reasonably reproduce this property, correlation functions must be represented in some fashion similar to the memory function representation, i.e. "the dynamics must be put into the denominator."

These broad bumps can of course be understood as vestiges of the narrow phonon peaks in solids. This is the viewpoint taken in the paper by Hubbard & Beeby (113) who have discussed the dynamical structure factor $S(k, \omega)$ in liquids. The formal framework of their theory is identical to the memory function representation discussed above. This paper is particularly interesting because of a very illuminating discussion of the "solidlike" aspects of liquids for sufficiently large k . Of course, since a single memory function for $S(k, \omega)$ is not simple in the limit of small k due to the coupling of heat and sound, this theory does not properly reproduce the hydrodynamic limit. This is also true for the papers by Singwi and co-workers (114-114b) who have proposed a somewhat different (though closely related) scheme. This scheme is formulated in terms of a "screened response function" which carries the frequency dependence and a "polarization potential" fitted to reproduce the static structure factor $S(k)$ [the frequency integral of $S(k, \omega)$] exactly. The screened response function is modeled by a Gaussian frequency dependence, whose width is determined from the first nontrivial sum rule. The scheme is thus free of parameters "to be fitted," as is the case for most of the theories described here; of course, computer results for $S(k)$ are used. The resulting $S(k, \omega)$ is in impressive agreement with computer dynamics and neutron scattering data, for k up to a very large $k \sim 4.5 \text{ \AA}^{-1}$. An interesting application (114b) of this

procedure to neutron scattering from superfluid helium results in a best fit if the fractional condensate density n^0/n is 6% at $T = 0$.

The representation of time correlation functions by memory kernels, while formally exact, is still hardly a solution of the fundamental dynamical problem. For actual microscopic calculations, the projected propagator $\exp [iQLt]$ is difficult to handle. That memory functions are nonetheless useful to derive hydrodynamic theories and to motivate approximation schemes should be apparent from the examples discussed. Let us finally mention a particularly interesting recent application which goes somewhat beyond the ansatz procedure of generalized hydrodynamics, namely the mode-mode coupling theories of dynamical scaling near the critical point. The propagator $\exp [iQLt]$ no longer contains the simple hydrodynamic modes, the single phonon states as it were; but it still does contain processes in which these are self-coupled, i.e. two- and multiple-phonon states. In the critical region where hydrodynamic fluctuations are strongly enhanced, such multiple transport processes must be singularly important. In the papers by Kawasaki (95) and Kadanoff & Swift (95a), these processes are separated out to obtain the behavior of hydrodynamic memory functions, and therefore time correlation functions, in the critical region.

Nonetheless, for more detailed microscopic calculations one must go on at least to the next level, one step closer to a full microscopic description, namely to the level of kinetic theory.

KINETIC THEORY

Kinetic theory is a particularly old and important part of nonequilibrium statistical mechanics. The kinetic description of the many-particle dynamics occupies a logical level halfway between the full, 10^{23} -dimensional, Liouville equation, and that stressed in this article which concentrates on the time correlation functions of a few variables in which we happen to be interested (because we can measure them). We cannot begin to describe the many important advances which have been achieved in recent years in the kinetic theory proper [see, for example, (2, 105, 115) and the excellent little book by Uhlenbeck & Ford (116)]. Rather, we will comment on a few papers whose aim is to derive and use kinetic equations specifically to calculate time correlation functions of gross variables such as the density.

In traditional kinetic theory, the dynamics is summarized in the singlet [or, as in the Rice-Allnatt (2) theory, doublet] distribution function $f(rpt)$ for which one writes down an equation of motion. The best-known example is Boltzmann's equation. Close to equilibrium this equation can be linearized, and it then takes the form

$$\left(\frac{\partial}{\partial t} + \frac{p\nabla}{m} \right) \delta f(rpt) = \int d\bar{p} \Gamma(p, \bar{p}) \delta f(r\bar{p}t)$$

where $\Gamma(p, p')$, the linearized collision operator, is determined from molecular scattering cross sections. Clearly, the integral over the momentum variable

$\delta n(rt) = \int dp \delta f(rpt)$ describes the propagation of small density fluctuations in the system. It must therefore be essentially identical to $S(rt)$, the dynamical structure or Van Hove density-density correlation function.

There is, however, one difficulty in making this connection complete. The kinetic equation poses an initial value problem, which is complete only if $\delta f(rp, t = 0)$ is specified. Which initial condition will give the correct, or even the best, $S(rt)$? Note that $S(rt)$, being an equilibrium-averaged time correlation function, is a mathematically fully specified object. Its initial value, in particular, is given by a well-defined static correlation function, namely $S(r0) = \langle n(r)n(0) \rangle - n^2$.

For dilute gases, this problem is not severe. Nelkin and co-workers (117, 117a) suggested and van Leeuwen & Yip (117b) have shown by a cluster expansion method that the proper initial condition for the linearized Boltzmann equation is the one which omits static correlations so that $\delta f(rp, t = 0) = \delta(r)\phi(p)$ where $\phi(p)$ is a Maxwellian momentum distribution. Ranganathan & Yip (117c) have calculated $S(rt)$ and a few other correlation functions of interest from Boltzmann's equation for a dilute Maxwell gas and compared the results to those obtained from a variety of kinetic models of the Fokker-Planck and BGK (117d) type.

For dense fluids, the problem of the proper initial conditions is more severe. It is rather closely connected to the question of whether there is really a kinetic stage in the dynamics of liquids. Markovian, Boltzmannlike kinetic equations were expected to remain valid for times far shorter than hydrodynamic times, but larger than some initial chaoticization period of a few collision times (116). The proper initial condition would then have to reflect the partial loss of correlations during the initial period.

In recent years it has become increasingly doubtful whether for dense fluids such a kinetic region does in fact exist. Indeed, the experience from molecular dynamics speaks rather eloquently against it, as do theoretical considerations, at least for simple systems such as weakly coupled particles (78). What is therefore needed is a kinetic equation with a memory-retaining and spatially nonlocal collision term, i.e. an equation of the form

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p} \cdot \nabla}{m} \right) \delta f(rpt) = \int_0^t d\bar{t} \int d\bar{r} d\bar{p} \Gamma(r - \bar{r}, t - \bar{t}; p\bar{p}) \delta f(\bar{r}\bar{p}\bar{t})$$

Such an equation has been derived by Severne (118) and others using the involved diagrammatic methods of the Prigogine school (105, 115). The approximation consists in omitting the "destruction fragment" which contains the initial state correlations. At least in the hydrodynamic region, this omission appears to be justified. In a very interesting paper, Resibois (78a) has shown that this kinetic equation leads to the proper hydrodynamic behavior, with transport coefficients which, in addition to the "kinetic" contributions (those usually obtained from Boltzmann's equation), include all potential contributions. Of course, because initial correlations are omitted, even this memory-

retaining kinetic equation cannot be used to extend calculations much beyond the hydrodynamic regime.

This problem is solved, at least formally, in a novel approach to linearized kinetic theory which connects directly to the ideas presented earlier. Consider the dynamical variable

$$D(rpt) = \sum_{\alpha} \delta(\mathbf{r} - \mathbf{r}^{\alpha}(t)) \delta(\mathbf{p} - \mathbf{p}^{\alpha}(t))$$

Clearly, its average, taken in a nonequilibrium ensemble, closely resembles the distribution function $f(rpt)$ and indeed obeys a hierarchy of equations formally (though not logically) identical to the famed BBGKY hierarchy (116, 119). What is of interest here is the correlation function

$$S_{pp'}(rt) = \langle D(rpt) D(0p'0) \rangle - \langle D(rpt) \rangle \langle D(0p'0) \rangle$$

where the average is again taken in an equilibrium, say grand canonical, ensemble. Obviously, from $S_{pp'}(rt)$ we can obtain the dynamical structure factor $S(r,t)$, as well as most other functions of experimental interest, by appropriate integration over the momentum variables. Moreover, since $S_{pp'}(rt)$ is a correlation function, the projector techniques discussed earlier apply immediately, and they lead to a "kinetic equation" of the form

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p} \cdot \nabla}{m} \right) S_{pp'}(rt) = i\Omega_p(\mathbf{r} - \bar{\mathbf{r}}) S_{\bar{p}\bar{p}'}(\bar{r}t) - \int_0^t d\tau K_{p\bar{p}}(\mathbf{r} - \bar{\mathbf{r}}, t - \tau) S_{\bar{p}\bar{p}'}(\bar{r}\tau)$$

where integrals over the barred variables are understood. This equation is exact and valid for all times, with the initial condition determined by the definition of S . It contains a "resonance frequency" term separated for convenience into $p\nabla/m$ and Ω , and the usual memory kernel K . If the latter is omitted, one is left with the well-known collisionless Vlasov equation which Ranganathan & Nelkin (120) have used to explain neutron scattering data in liquid lead, with only qualitative success. Akcasu & Duderstadt (121) have derived the full equation using Zwanzig-Mori techniques, and Lebowitz, Percus & Sykes (122) obtained it using methods more akin to those of traditional kinetic theory. Both authors have then proposed, and to some extent solved, approximations obtained by modeling the time dependence of K in an ad hoc fashion, but so as to retain the correct initial value of $K_{p\bar{p}}(r, 0)$ (i.e. its first sum rule). The procedure of Ortoleva & Nelkin (123) leads to essentially similar results; using ideas due to Zwanzig (124) they approximate K by incorporating correctly a few of the variational eigenfunctions of the Liouville operator. All of these approximations are short time approximations. Sum rules and some other general properties of K have been discussed by Forster & Martin (78). For weakly coupled particles they have then replaced Ω and K by the lowest nontrivial order in perturbation theory and shown that the

resulting equation leads to a consistent description even in the hydrodynamic regime, which traditional weak-coupling theory does not. Forster (125) has discussed the general requirements which the exact or modeled collision kernel $K_{pp'}(r)$ must satisfy if it is to correctly render both hydrodynamic and short time behavior.

Time correlation functions are what we measure. They offer a convenient and rational vehicle for the study of many-body dynamics. Their direct use on a kinetic level, which we have just sketched, clearly needs and merits further study. One of the obvious advantages of the correlation function method is that it allows one to introduce approximations in a clear, operational, and controllable fashion. In the light of such disappointments as that over the (probable) nonexistence of a "kinetic stage," and such puzzling phenomena as the "long time tails," this advantage is not a minor one.

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