

1. Ultrasonic Studies of Binary Liquid Structure in the Critical Region. Theory and Experiment for the 2,6-Lutidine/ Water System.
2. Hartree-Fock Calculations of Electric Polarizabilities of Some Simple Atoms and Molecules, and Their Practicality.
3. Calculation of Vibrational Transition Probabilities in Collinear Atom-Diatom and Diatom-Diatom Collisions with Lennard-Jones Interaction.

Thesis by
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In partial fulfillment of the requirements
for the degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1972

(submitted August xx, 1971)

Dedication

This thesis is dedicated to the people who contributed to my present predicament...to my parents in Chicago, for every manner of help--and my sisters and their families...to my cousin Mae in Huntington Beach, for much hospitality...to my advisors Neil Pings and Vincent McKoy, for a free hand in research, the tools of the trade, the cross-fertile research interests in their groups, and help with employment--and to G. Wilse Robinson, W. A. Goddard, III, Harry Gray, and Angelo Lamola (Bell Labs) for the latter...to the two research groups I was in, for a general, mutual increase in scientific knowledge, for a social life, and for moral support in the face of shared frustrations with computers, experimental apparatus, and other perverse items...to Profs. Robinson and Kuppermann, for stimulating my interest in other directions through their courses on photosynthesis and scattering, respectively...to Dennis Diestler, for some direction in scattering theory research and much entertainment...to the NSF, for financial support past and future, with no strings attached...to the Morrisons Paul and Sandy and the Wagners Al and Arlene, my best friends...with some notable and mostly very visible exceptions, to the people of California, for entry into the promised land after living in Chicago...to past teachers, formal and informal: Drs. Hofman, Freeman, and Klawiter at Notre Dame; Tollestrup, Feynman (damn the hacks, full speed

ahead), and Peck here; and Robinson and Holzer of my high school days...to the buggers who thought up candidacy exams and propositions--traumatic but useful...to departmental staffs, who usually provided dependable and unbureaucratic help...not to University Microfilms, for their damn thesis margins...to boring seminar givers, authors, and assorted bigwigs, for steering me away from science as cult or even tool, to science as culture and simple world-enjoyment; on the positive side of same, to R. P. Feynman, Stalkie, and even the authors of Time-Life and Scientific American...to IBM, for not changing computers every year, bless their souls...to the keepers of mountains, desert, and sea, for recreation...to the city of Pasadena and its neighbors, for shutting down at 10 P.M. and trying to keep me out of trouble...to my draft board, for a II-S, but not for participating in the loss of my Miller Fellowship...but I wouldn't do it over again; there must be an easier, mellower way to live.

Abstract

Part 1. Many interesting visual and mechanical phenomena occur in the critical region of fluids, both for the gas-liquid and liquid-liquid transitions. The precise thermodynamic and transport behavior here has some broad consequences for the molecular theory of liquids. Previous studies in this laboratory on a liquid-liquid critical mixture via ultrasonics supported a basically classical analysis of fluid behavior by M. Fixman (e. g., the free energy is assumed analytic in intensive variables in the thermodynamics)--at least when the fluid is not too close to critical. A breakdown in classical concepts is evidenced close to critical, in some well-defined ways. We have studied herein a liquid-liquid critical system of complementary nature (possessing a lower critical mixing or consolute temperature) to all previous mixtures, to look for new qualitative critical behavior. We did not find such new behavior in the ultrasonic absorption ascribable to the critical fluctuations, but we did find extra absorption due to chemical processes (yet these are related to the mixing behavior generating the lower consolute point). We rederived, corrected, and extended Fixman's analysis to interpret our experimental results in these more complex circumstances. The entire account of theory and experiment is prefaced by an extensive introduction recounting the general status of liquid state theory. The introduction provides a

context for our present work, and also points out problems deserving attention. Interest in these problems was stimulated by this work but also by work in Part 3.

Part 2. Among variational theories of electronic structure, the Hartree-Fock theory has proved particularly valuable for a practical understanding of such properties as chemical binding, electric multipole moments, and X-ray scattering intensity. It also provides the most tractable method of calculating first-order properties under external or internal one-electron perturbations, either developed explicitly in orders of perturbation theory or in the fully self-consistent method. The accuracy and consistency of first-order properties are poorer than those of zero-order properties, but this is most often due to the use of explicit approximations in solving the perturbed equations, or to inadequacy of the variational basis in size or composition. We have calculated the electric polarizabilities of H_2 , He, Li, Be, LiH, and N_2 by Hartree-Fock theory, using exact perturbation theory or the fully self-consistent method, as dictated by convenience. By careful studies on total basis set composition, we obtained good approximations to limiting Hartree-Fock values of polarizabilities with bases of reasonable size. The values for all species, and for each direction in the molecular cases, are within 8% of experiment, or of best theoretical values in the absence of the former. Our results support the use of unadorned Hartree-

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I. Introduction

We have recently completed an experimental study of the velocity and linear attenuation or absorption coefficient of ultrasonic waves in 2,6-lutidine: water mixtures. We concentrated on the behavior near the lower consolute or critical mixing point of temperature and composition. Our intent was learning more of the statics and dynamics of the large, correlated fluctuations in order parameter--here, the local composition--occurring at critical points. Among probes of such phenomena, ultrasonics is convenient for its simplicity and for the directness of its relation to the dynamics. The raw ultrasonic data were carefully corrected for systematic experimental errors and statistically analyzed. Results were reduced to molecular parameters (persistence length, friction constant) using Fixman's¹ theory for the critical fluctuations and their coupling to the sound waves. We selected this theory over rival theories^{2,3} principally for its good balance of tractability and rigor. The formalism was rederived with some correction and reinterpretation, in order to extend it to the mixed behavior of our system.

The present studies cover but one aspect of liquid state theory, and employ but one experimental probe of structure and dynamics. We review below the present status of theories for fluids of complexity ranging from simple

monatomic fluids through pure and mixed systems possessing rotational, vibrational, and chemical degrees of freedom. The context of our research, which is summarized in the two journal preprints following, should become clear in the process.

Various levels of microscopic structure and dynamics develop through the progression of fluid types under study: simple fluids and their mixtures, fluids with well-defined internal degrees of freedom as rotation or vibration, fluids where the molecules self-associate in large aggregates, and mixtures of an associated liquid with a species it solvates chemically. These four classes are not inclusive: for example, we have excluded dilute solutions of reactive species, electrolytes, or polymers. In such solutions the fluid acts as a carrier phase, a dielectric or solvating medium, or a large reservoir of one reactive species, rather than being of central interest.

Simple fluids are under the most intensive study. Their thermodynamic and transport properties have been correlated with model solid- and gas-like structures by approximate theories. More rigorously, one can correlate their properties with the basic molecular parameters, the mass m and the intermolecular potential $V(r)$. One does not assume a small set of basic structures; rather, one employs full statistical mechanical theory and describes the fluid with very general distributions containing complete infor-

mation. Critical phenomena are still beyond fully successful quantitative description by rigorous or even approximate theories, as the critical region's thermodynamic instability is reflected strongly in its microscopic structure. In the second class of fluids, the members are necessarily polyatomic and nonspherical. Equilibrium properties are modified either by the strong coupling of rotation and translation, or (in the dimerization case) by the strong coupling of all internal degrees of freedom in two molecules.

Repartitioning of phase space allows adequate treatment by rigorous statistical mechanics or thermodynamics. Transport in dilute fluids of this type involves more complex (angle-dependent) distributions and some new mechanisms, and is difficult to describe. Dense phases pose a virtually insoluble problem to date. The associated liquids forming the third class possess extensive spatial and motional structure, built from a great modification of the degrees of freedom of the isolated molecules through an n -body interaction potential deviating strongly from pairwise additivity. So much of the framework of rigorous molecular statistical mechanics on the few-body level is inapplicable, that only phenomenological descriptions are possible, based on a few large and fixed structures or on a set of linked chemical reactions. The behavior of a mixture of another liquid with an associated one is even more difficult to explain with molecular or other microscopic units of structure. More

narrow empirical relations of bulk properties are required, except for critical mixing phenomena, which are qualitatively similar to all other critical systems.

A. Simple Dense Fluids

These fluids show no evidence of internal structure, meaning they are generally monatomic. We exclude from consideration the liquid metals, whose cohesive forces are qualitatively different from those of insulating liquids; a recent conference⁴ has summarized what is known of liquid metal structure and dynamics. We also exclude quantum effects^{5a,6a} as manifested by the light atoms He and Ne even to "high" temperatures. The properties typically of interest are, for equilibrium, the PVT data or equation of state, the heat capacity C_p or C_v , the chemical potential μ , and the surface tension σ ; and for transport, the shear and bulk viscosities η_s and η_v , the thermal conductivity λ , and the diffusion coefficient D , as they depend on the equilibrium state and possibly on the transport process angular frequency ω . The dynamic responses of the fluid to nonthermal, mechanical perturbations or probes such as elastic and inelastic light and neutron scattering are also of interest, on independent grounds as well as for further confirmation of our understanding of related bulk transport coefficients.

Experimental techniques for equilibrium and transport properties are many and varied. PVT data have been compiled extensively by straightforward pressure bomb measurements⁷ on confined samples. Ultrasonic studies yield the velocity β , which provides a simple and accurate additional determination of the adiabatic compressibility $K_s = (\rho \beta^2)^{-1}$,

which otherwise requires extensive numerical analysis of the straight PVT data. The critical region equation of state is also probed on special cuts in the thermodynamic plane by such unseemly means as NMR⁸. Heat capacities \underline{C}_v or \underline{C}_p are taken by direct calorimetry,⁷ by and large. The ultrasonic value for \underline{K}_s is also used to check the critical region divergence of $\underline{C}_v = \underline{C}_p \underline{K}_s / \underline{K}_T$ from the better-known behavior of \underline{C}_p and \underline{K}_T ⁹. Surface tension σ is primarily measured by capillary rise¹⁰. Among transport coefficients, the best-studied are η_s and λ , the former by capillary flow or rotating disk viscometers^{11,12a} and the latter by heat flux measurements across parallel plates or concentric cylinders^{11,12a}. The self-diffusion constant \underline{D} requires some ingenuity (though for mixed fluids mutual diffusion also exists and is straightforward to determine). Radioisotope diffusion¹³, NMR spin echoes^{12b}, and light scattering^{14,15} are in use, the latter two particularly near criticality. Ultrasonics provides the only measure of the bulk viscosity η_v ¹⁶⁻²⁰ through its proportionality to the absorption coefficient $\alpha = \omega^2 \eta_v / 2\rho\beta^3$. Additional fluid properties which touch more or less directly on the microscopic structure we seek to understand include pair distribution functions $\underline{g}(r)$ from x-ray^{21a,22} or neutron scattering^{23a}. The validity of the $\underline{g}(r)$ concept and calculations as well as the form of the intermolecular potential is investigated. The long-range structure of $\underline{g}(r)$ near the critical point is probed by

light scattering^{7,12c}. Other light-scattering information includes the velocity and attenuation of hypersonic thermal waves (Rayleigh and Brillouin scattering¹⁵), also investigated ultrasonically^{18a,19a}, depolarization spectra²⁴, and induced Raman²⁵. Further afield are such properties as second-order transport coefficients, of which thermal diffusivity^{5b} is an example.

The bulk properties of the liquid phase pose the greatest theoretical problems. They reflect the properties of the solid and of the gas to which the liquid is related by the first-order transitions of melting and evaporation; in addition there is the dramatic connection to the gas through or above the second-order critical transition. Similarly to the gas, the liquid has high fluidity η_s^{-1} ; an entropy S much higher than the solid; diffusion constant D and dilational viscosity η_v of similar magnitude to those of the gas; and modes of bulk motion described by the Navier-Stokes equations^{18b}. In common with the solid, the liquid has a heat capacity C_v , internal energy E , and enthalpy H reflecting strong molecular interactions; a compressibility K and a molar volume \bar{V} showing similar packing and mean forces; and a heat conductivity λ indicating similar mechanisms of energy transport^{23b}. Of course, the similarities or differences are often more quantitative than qualitative and depend upon which thermodynamic cut one chooses. There is also the more microscopic structure such as equilibrium

pair distribution functions $g(r)$ to compare among phases. We wish to explain the properties above, in their dependence on the thermodynamic state within the liquid or dense gas phases as well as across the transitions. Correlations with the solid or gaseous phases are useful, but a more basic explanation should derive primarily from the molecular parameters of mass m and potential $V(r)$, which also ground the properties of the other two phases. The critical region connection of gas and liquid poses a special challenge by its anomalous rate of change of properties (C_v, η_s , light scattering power = opalescence, e.g.^{12,26}) and its violation of classical thermodynamics based on the analytic nature^{27a} of the free energy G . The cooperative phenomena here are apparently in basic analogy^{27b,28} to many other thermal many-body phenomena in highly dissimilar systems such as ferromagnets and superfluids, or in the more closely related consolute binary liquids.

B. Equilibrium Theory

The earliest success in explaining dense gas non-ideality and in correlating the same to the existence of a gas-liquid phase transition was achieved by van der Waals in the equation²⁹ bearing his name. He postulated an excluded volume b in the total volume due to finite molecular size, as well as a pressure term a/V^2 proportional to the inverse square volume due to the attractive portion of the pair potentials. The parameters can be set from the critical parameters of the fluid to yield a reasonably good gas description. There arises a principle of corresponding states^{5,29} among all gases when \underline{P} , \underline{V} , and \underline{T} are all reduced to their ratio with the corresponding critical values \underline{P}_c , \underline{V}_c , and \underline{T}_c . Experiments bear out the principle rather well. In the true liquid region the van der Waals equation describes fictitious states, but the ad hoc Maxwell construction^{29a} locates the liquid-gas phase boundary. The shape of the coexistence curve in the critical region is now known to be qualitatively incorrect³⁰, but this defect is shared with every theory based on classical thermodynamics assuming the analyticity of the free energy in the intensive variables. Basically, we assess that the van der Waals theory takes a gas to be structureless: within the excluded volume the molecules are entirely random in time-average placement. However, both the repulsive core and the attractive tails in the pair potential induce structure^{5c,31a} in the pair

distribution, directly between two bodies and indirectly through third bodies. Statistical mechanics notes that the momentum-averaged probability of occurrence of a spatial configuration $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ of N molecules is proportional to $\exp(-U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N))$, where U is the total potential energy.

The search for a better equation of state, particularly for the liquid state and preferably a less empirical one based more on the intimate molecular mechanics, yielded no essential advance until the 1930's. At this time, the x-ray diffraction patterns of liquids were measured³² and found to show remarkable short-range order reminiscent of the solid state. Quasi-crystalline models of liquids sprung up in number, all partitioning the configuration of the liquid into effective single-particle distributions for one particle moving in the averaged field from a lattice of the other particles. Originally, these cell theories^{5,6b,33} postulated a complete lattice structure and uncorrelated one particle motions under hard-sphere or Lennard-Jones potentials. They considerably underestimated the entropy by overestimating the structure, particularly by not allowing the interchange of particles among cells, much less multiple cell occupancy. The equation of state is quite poor, while the internal energy is quite acceptable. Lennard-Jones and Devonshire accounted for the extra potential from two further 'coordination shells' in the lattice in establishing both free volume and total lattice energy. They also corrected

the 'communal entropy' from particle exchange fully toward the gas value. Double occupancy of lattice sites was proposed later, introducing the communal entropy more gradually through the liquid range and giving better critical constants and overall liquid properties. Allowance for vacant sites in the lattice, to an extent dependent on temperature, marks the hole theories, with the best accounting for the entropy. The net equation of state is little better than the three-shell straightforward cell theory. A tunnel theory proposed by Barker incorporated effective linear channels in the lattice for freer motion but only partially corrected the entropy errors. Eyring and coworkers³³ ad-

mechanical partition function or, equivalently, the configuration integral. They start from hole theory and reject all but the 'significant structures' in the N -particle distribution, meeting with modest success.

These solid-like models can give reasonable properties in limited ranges. They fail near the gas region, of course, and will ever be insensitive to the features of the intermolecular potential. They still provide empirical correlations for engineering usage, particularly for mixtures, and do incorporate enough of the proper energetics to ground reasonable transport theory. The first steps toward an a priori equilibrium theory were taken in the same era by Ursell³⁴ and especially by Mayer and coworkers³⁵, work-

ing from the definition of the configuration integral and expanding it in orders of the density--the so-called virial or cluster expansions. One chooses a parameterized pair potential and then carries out successively higher-order integrations of $\exp -U_N/kT$ involving larger and larger clusters of n molecules. The required time and effort limit the approach to the lowest orders of virial coefficients (of P/kT), less than six for the Lennard-Jones potential³⁶. Convergence difficulties appear^{36a,37} to defeat any application to real liquids in any case. The chief use of virial theory now is production of exact virial coefficients for a given potential, to compare to the effective coefficients from equations of state yielded by promising approximate theories.

Yvon³⁸ and Born and Green³⁹ in the late '30's and '40's proposed a description of fluids by n -particle distribution functions $g^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$, which are integrals over $(N-n)$ other particles of the configuration probability $\exp -U_N/kT$, times a combinatorial factor for the ways n particles can be chosen among N . The pair function $g^{(2)}(\vec{r}_1, \vec{r}_2) = g(r_{12})$ is central for all properties (but total entropy^{21b}) of our type of fluids. One may derive a coupled set of inhomogeneous integro-differential equations for the hierarchy of the $g^{(n)}$ from the Liouville equation in total phase space or its equivalents. The resulting Born-Green-Yvon (BGY) equations are unclosed, in that the $g^{(n)}$ equation in-

volves an integral with $\underline{g}^{(n+1)}$. Closure can be obtained by approximating $\underline{g}^{(3)}$ as a product of $\underline{g}^{(2)}$'s--the superposition approximation of Kirkwood⁴⁰--or a little more flexibly as in Cole's⁴¹ or Fisher's⁴² approximations. Bogolyubov⁴³ also postulated similar equations without practical extensions. Kirkwood⁴⁰ proposed an alternate set of equations to go with the closure scheme, using a coupling parameter for a test particle and obtaining slightly different results in the superposition approximation.

The pair distribution approach is desirable for several reasons. Its prime quantity $\underline{g}^{(2)}(\underline{r})$ has a direct integral relation to the macroscopic equilibrium properties^{21c} and to the Fourier components (in the space of $\underline{s} = 4\pi \sin\theta/\lambda$) of the x-ray scattering intensity. By reason of this second relation (an analogous one exists for neutron scattering), the theory's output $\underline{g}(\underline{r})$ can be checked in point-by-point detail, over and above as a weighted average with potential operators for bulk properties. X-ray experiments are not currently accurate enough to be a prime source for $\underline{g}(\underline{r})$, since the computed properties, especially the pressure⁴⁴, are rather sensitive to errors in $\underline{g}(\underline{r})$. A third 'advantage' of the distribution theory is that the equations are readily truncated by an approximation (superposition) with some intuitive physical interpretation. Unfortunately, alternate approximations more appropriate for true liquids are not possible and the theory is presently

bogged down. Critical phenomena remain outside the competence of the theory by any foreseeable extension, as they are true many-body instabilities.

The superposition technique has been tested extensively^{36a} up through liquid densities and temperatures, where it fails badly in predicting the equation of state. Rushbrooke and Scoins⁴⁵ looked at the effective 'direct' correlation function $c(r)$ which determines $g(r)$ by the Ornstein-Zernicke integral equation⁴⁶ and advanced a simplification called the netted-chain (NC) equation. This was quickly replaced by the better hypernetted chain (HNC) which gave encouraging results in dense systems. Near this time, Percus and Yevick⁴⁷ derived a related approximation (PY) and justified it on the basis of arguments in many-body theory for collective motion of the Fourier density components. PY theory is the most successful distribution approach, as it even shows a phase transition in appropriate conditions. It has been improved (the PY2 form⁴⁸) and also adapted for nonspherical systems⁴⁹ and for the presence of three-body potentials⁵⁰. Further advances are still needed for the densest liquids near the melting transition and for the critical region, but they are not foreseen as extensions of present forms. There exists the direct expansion of $g(r)$ in cluster integrals⁵¹ that can be systematically extended to any order in density, amounting to stopping at the next-to-last stage in virial theory. However, the theory is at

least as difficult as the latter and has mostly formal utility in searching for new approximate theories.

Several groups, beginning with Zwanzig⁵², have developed theories for the equation of state starting from the free energy, and perturbing it from the hard-core reference result to change the configuration integral and the pair distribution function. A limited class of systems are treated successfully by this approach in a straightforward application.

Two 'brute force' approaches to fluids are applicable with all pair potentials and all thermodynamic states. They provide reference values for other theories to measure up to, essentially giving the experimental behavior of ideal fluids uncomplicated by any trace of triplet potentials or experimental errors. The Monte Carlo theory^{21,53a} generates the configuration integral by assembling random points or N -particle configurations for the integrand. The latest practical versions select configurations with a probability proportional to $\exp(-U_N/kT)$ to gather the largest contributions with the least work. Properties are excellent when referred to real substances such as argon. They are accurate enough to relate deviations from experiment to triplet potentials and other complications. The limited size of systems of N particles that can be handled leaves a little doubt on some properties, certainly near criticality where the long-range correlations cannot be represented. The

second approach, molecular dynamics^{53b}, consists in numerically integrating the equations of motion for N particles over a representative time span, in two or three dimensions. This technique is also very accurate and is packed with information including transport coefficients (autocorrelation function theory⁵⁴ relates macroscopic gradient dissipation to that of spontaneous microscopic gradients). It is restricted to even smaller systems than MC for the same effort or computing time. Neither theory can be considered an everyday working theory for investigating liquids, particularly as the quantitative results are not readily broken down into a limited number of qualitative concepts for a physical understanding.

Critical phenomena are in a territory of true many-body instabilities untouched by all the microscopic theories. The vanishing of the derivative $(\partial P / \partial V)_T$ and of the gas-liquid density difference (and hence, the meniscus) makes for dramatic mechanical and visual effects²⁶. Several cuts in the PVT plane are of interest--the isotherms, the isochores, and particularly the coexistence curve. Anomalous--even diverging--specific heats are present^{12d}. The microscopic parameters of correlation, as the total correlation length K^{-1} in the asymptotic part of $g(r) \sim e^{-K r}/r$, become macroscopic and show up in strong light scattering or opalescence^{7,26}. Transport also shows significant anomalies, though we are presently considering only equilibrium aspects.

The original phenomenological theory of van der Waals did touch on critical phenomena. Its principal predictions^{7,55,56} are a parabolic shape for the coexistence curve in $(T-T_c)$ versus $(p-p_c)$, a simple discontinuity in specific heat across the critical point on the isochore, and an inverse linear divergence of the isothermal compressibility K_T with $(T-T_c)$. We may use the shorthand of Fisher's^{27c} critical exponents to express these results. The exponents are power laws relating two intensive variables' differences from their critical values. The van der Waals' exponents corresponding to the three predictions above are $\beta = \frac{1}{2}$, $\alpha = \alpha' = 0$, and $\gamma = 1$, the same for all fluids. The critical point in van der Waals theory appears to originate in cooperative motion from long-range forces^{12e}, while the quantum theory of intermolecular forces⁵⁷ by London and others showed the forces to be of short range, varying as r^{-6} asymptotically. Ornstein and Zernicke⁴⁶ proposed an alternate microscopic theory to calculate the long-range total correlation function $g(r)$ from a short-range direct correlation function $c(r)$. They focused on the critical opalescence intensity and on the related divergence of K_T , both tied to the behavior of the correlation length ξ^{-1} . Their results for K_T agree with van der Waals theory, despite the assumed different nature of the forces. A more detailed microscopic theory originally applied to ferromagnetic systems, Landau theory⁵⁸, clarified the connection. All the theories to

that time were mean field theories, in which the order parameter for the transition ($\rho - \rho_c$ for fluids) is not allowed to fluctuate spatially while computing the free energy, but the form of the free energy allows the spectrum of fluctuations to diverge at the same time. Any assumption of the analyticity of the free energy in T and V brings these conclusions.

Experimentally, the coexistence curve was shown³⁰ in time to be flatter than parabolic, consistent with a β closer to $1/3$ than $\frac{1}{2}$ and contrary to classical theories. The Ising model^{58,59} for the analogous ferromagnetic transition predicts a β of nearly $5/16$, however, and this is encouraging. The Ising model can be converted⁶⁰ to a model of the gas-liquid critical point called the lattice gas by redefining variables and interactions. The fluid molecules are restricted to lattice sites which may be singly occupied or unoccupied. Nearest neighbors interact with a single fixed strength. It is essentially a hole or free volume description with exact correlation of the particles and holes, though the Hamiltonian is oversimple. The other critical exponents it predicts are quite good. An important result is $\alpha = 0$, in the sense that the isochoric specific heat C_V diverges logarithmically. This definitely quashes hopes for applying classical thermodynamics to the model. Experimental verification of the C_V anomaly was slower in coming, due to the difficulty of doing calorimetry in the critical

region. The ultrasonic value for K_s was and is used to confirm the anomaly through the known divergences of \underline{C}_p and K_T and the relation $\underline{C}_v/K_s = \underline{C}_p/K_T$ ⁹.

A total of nine critical exponents are now defined and more or less accurately known²⁷ from classic PVT data as well as from more exotic and direct probes such as refractive index differences⁶¹ and NMR line splittings⁸. Their universal disagreement with classical predictions has stimulated the development of a nonclassical thermodynamic scheme known as the static scaling laws^{58b,62}, which relate the exponents to each other. The basis is a universal equation of state in the reduced intensive variables, in turn based on the analyticity of the chemical potential through the critical transition. It is by no means a complete explanation, for it does not yield enough relations to predict all the exponents; it does not give the coefficients in the power law relations; and it cannot locate the critical parameters \underline{P}_c , \underline{V}_c , and \underline{T}_c on any basis, much less a molecular one. It is useful in displaying the essential analogy^{28,60} among all fluid transitions and even among all critical transitions. (We exploit this analogy in our work here, as we study the experimentally convenient binary liquid-liquid transition in lieu of the harder gas-liquid one.) More microscopic theoretical leads have come from Fixman and from Kawasaki and several others for the behavior of K^{-1} , under investigation by light scattering^{63,64} and also ultrasonic absorption^{1,2}, although the latter has a

strong connection to the dynamics to cloud the issue. Other problems faced by critical thermodynamic theory include slight variations^{58c} of exponents among systems, possibly from quantum corrections or residual sensitivity of exponents to the exact form of the intermolecular potential.

Many investigators continue to look at the critical region with greater precision and more sophisticated techniques. It is important to qualitatively and quantitatively refine our understanding of this gas-liquid connection, for its basic many-body character reflects on our general ability to describe fluids. The dynamic aspects are similarly important and will be discussed under transport theory.

C. Transport Theory

A fluid subjected to external stresses (such as shear or dilational forces from forced flow or sound wave passage, or heat stress from a temperature gradient on its boundaries) reacts against the stresses to dissipate them. Outside the Knudsen regime^{5d, 64X} of extremely low density, and excluding gradients over distances comparable to molecular separations, the bulk fluid may be treated as a continuum described^{5e} by local mass density ρ , temperature T , and velocity \vec{v} for these nonequilibrium conditions. Gradients in these quantities are dissipated by corresponding fluxes of mass, energy, and momentum. The empirical equations of motion for these five local variables have been formulated thoroughly as continuum mechanics or hydrodynamics, beginning with the work of Newton, of Euler, and others^{65, 66}. The equations express the conservation^{67a} of mass, momentum, and energy (the respective densities of which are ρ , $\rho \vec{v}$, and $\frac{1}{2} \rho v^2 + \rho \epsilon(T, \rho)$, where ϵ = internal energy per unit mass for the same T and ρ at equilibrium) and introduce the phenomenological coefficients of transport η_s, η_v , and λ :

$$\text{Mass flux} \quad \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad \text{continuity} \quad (1)$$

$$\text{Momentum flux} \quad \frac{\partial (\rho \vec{v})}{\partial t} + \nabla \cdot \underline{\Pi} = 0 ,$$

$$\pi_{ij} = \begin{cases} \underbrace{\rho v_i v_j}_{\text{circulation}} + \underbrace{p \delta_{ij}}_{\text{source}} & \text{Euler,} \end{cases} \quad (2a)$$

$$\text{OR} \quad \begin{cases} \rho v_i v_j + p \delta_{ij} + \sigma'_{ij} & \text{Navier-Stokes,}^{68} \\ & \text{for viscous} \\ & \text{fluids,} \end{cases} \quad (2b)$$

$$\sigma'_{ij} = \eta_s \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot \vec{v} \right) + \eta_v \delta_{ij} \nabla \cdot \vec{v}. \quad (2c)$$

$$\text{Energy flux} \quad \frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 + \rho e \right) + \nabla \cdot \left[\vec{v} \left(\frac{1}{2} \rho v^2 + \rho h \right) \right] = 0, \quad (3a)$$

$h = h(T, \rho) = \text{enthalpy per unit mass,}$

OR

$$\rho T \left(\frac{\partial s}{\partial t} + \vec{v} \cdot \nabla s \right) = 0 \quad \begin{array}{l} \text{linearized} \\ \text{adiabatic equation.} \end{array} \quad (3b)$$

For viscous, heat-conducting fluids,
add to (3a) the extra terms (ref. 67b):

$$-\nabla \cdot [\vec{v} \cdot \underline{\underline{\sigma}}' - \lambda \nabla T].$$

(Pure heat conduction follows the
empirical law:

$$\vec{q} = \text{heat flux} = -\lambda \nabla T \quad (\vec{v} = 0),$$

or equivalently,

$$\frac{\partial T}{\partial t} + \frac{\lambda}{c_p} \nabla^2 T = 0, \quad \text{Fourier's law.})$$

These equations describe an enormous range of possible bulk flow patterns, depending upon the boundary conditions and the magnitudes of the transport coefficients. The whole of hydrodynamics is not of immediate interest to us in this review (but see ref. 66). We are concerned with the eventual explanation of the transport coefficients in terms of molecular parameters---and also with the bulk

response to special boundary conditions such as the time-dependent periodic motion in sound waves, that allows us to measure the coefficients. To develop this last point: it suffices here to linearize^{18c,69} all the equations, i.e., to retain terms only of first order in the small fluctuations $\delta\rho$, δP , δT , and \vec{v} . In this event, the energy equation (3) to first order expresses the adiabatic equation of state $dS = 0$. Internal dissipative processes give second-order perturbations, and thus an entropy production or energy loss restricted to quadratic or higher order in the gradients^{19b,67c}, as required for stable equilibrium and a propagative mode. Heat conduction and shear viscosity are two dissipative processes that have a reasonably direct intuitive picture. Bulk viscosity is more of a catch-all for all other dynamic additions to the equation of state, from the finite-time relaxation of internal degrees of freedom (relative concentration in a mixture, chemical equilibria in an associated liquid, e.g.). We must find additional empirical rate laws for these degrees of freedom, or relaxation equations^{19c}. In conclusion, the energy loss from the combined effects of η_s , η_v , and λ manifests itself as a linear attenuation^{18d,19d} $\left(\frac{d\delta P}{\delta P} = \alpha dx\right)$ of the travelling sound wave,

$$\alpha = \frac{\omega^2}{2\rho\beta^3} \left[\underbrace{\frac{4}{3}\eta_s + \lambda\left(\frac{1}{c_v} - \frac{1}{c_p}\right)}_{\text{'classical'}} + \underbrace{\eta_v}_{\text{'excess'}} \right].$$

We may identify η_s with momentum transport, λ with energy transport, and η_v with a mixture. The self-diffusion

constant \underline{D} clearly concerns mass transport, but in a special sense, as ρ is unchanged by self-diffusion unless the experimental probe can distinguish molecular labels such as spin (NMR)^{12b} or isotopic mass differences¹³. The empirical equation in which \underline{D} appears relates the labelled mass flux \vec{j} and the gradient in concentration \underline{c} ^{67d},

$$\vec{j} = - \rho \underline{D} \nabla \underline{c} - \beta \nabla T$$

or $\nabla \underline{c} \rightarrow (\partial \mu / \partial \underline{c})^{-1} \nabla \mu$ in complex cases;

$$\Rightarrow \frac{\partial \underline{c}}{\partial t} = \underline{D} \nabla^2 \underline{c} \quad \text{isothermally; Fick's law.}$$

The molecular-mechanical explanation of these transport coefficients lies ultimately in the parameters \underline{m} and $\underline{V}(\underline{r})$ and in the classical mechanical equations of motion for the \underline{N} identical particles. (Quantum equations of motion for transport make only small corrections for simple liquids and have been put together very piecemeal, in any event,^{5f, 6c, 70, 71a, 72a} after von Neumann⁷³ laid the basics.) For \underline{N} particles, the Hamiltonian equations of motion are most compactly expressed as the single Liouville equation^{5, 74a, 75a} for a trajectory of the system (or flow, for a statistical average or distribution^{5, 36b, 74a, 75a, 76} of initial conditions) in the $6\underline{N}$ -dimensional space of positions and momenta. On an ensemble average for \underline{N} very large, the system exhibits (irreversible) continuum hydrodynamic behavior at times much longer than individual collision times. Before we can solve for the motion and numerically evaluate the transport coef-

ficients, we face the great conceptual and practical problems of (a) reducing the Liouville equation and N -particle distribution functions to the level of few-body collisions and distributions, rigorously or approximately, and (b) resolving the dilemma posed by the time-reversibility^{11a, 36b, 74b, 75b, 77} of the Liouville equation in contrast to the irreversibility of the long-time phenomena it describes. Rice, et al.^{11b} break down the molecular theory of transport into three major areas: (1) analysis of the essential mechanical nature of irreversibility, (2) derivation of a suitable kinetic equation for the long-time evolution (much beyond individual collision transients) of some few-body distribution, and (3) solution of the equation for the transport coefficients in terms of the molecular parameters plus ρ and T . The first two problems are not simply annoying obstacles to the final numerical calculations; rather, they lead to rich and useful concepts in statistical condensation of the intricate molecular motions down to the level of observation in real systems, all of which are extremely complex many-body systems.

On the first level, important work was furthered by Kirkwood^{11c, 36c, 71b, 77a} on coarse-graining the detailed molecular distributions down to the level of crudity of real observations, and by Prigogine and coworkers^{11d, 36d, 74b, 78a} on the destruction of motional invariants (=mechanical order) by the collisions. It is now understood that for

systems of macroscopic size reversibility manifests itself only at times so long as to be cosmologically meaningless^{36e}. In autocorrelation function theory^{54a,71c,77b,78b}, the practical irreversibility of the bulk equations of motion and of the low-order molecular distributions is postulated, and then used to declare the identity of the regression laws for fluctuations in both cases. Generally, the formal studies on the first problem of irreversible behavior have been peripheral to the more intensive work on the second problem of constructing actual few-body kinetic equations. The third step, numerical testing of the equations, follows the second quite rapidly and establishes the limits of applicability. We'll recount below the general history of kinetic equations as a way of summing up transport theory.

The first kinetic equations were limited to dilute gases, where the collision phenomena are easiest to sort out. The N -body motion can be reduced to considering only binary collisions occurring in a completely random fashion. Early free-path models for hard-sphere gases were proposed by Maxwell and others^{72b,79,80a,78c} in the nineteenth century and made almost fully quantitative by the time of Jeans⁸⁰. While providing adequate fits to data and a very good intuitive picture of transport, the free-path models depend upon some undetermined coefficients which must be estimated, and they also apply only to hard spheres^{71d}. Boltzmann's⁸¹ work culminating in his famous equation solved

these problems, but some work did continue on these lines: Eucken^{5g,72} developed corrections for nonspherical molecules which can carry extra momentum and energy in rotation; and Bhatrager, Gross, and Krook⁷⁵ constructed a complementary approach based on the distribution of collision times rather than free paths, leaning on some of Boltzmann's formalism.

In 1872 Boltzmann postulated a fully determinate equation for the time-dependence of the singlet distribution function, which is the time-dependent generalization of the $\underline{f}^{(1)}$ of equilibrium theory, and the carrier of the hydrodynamic information. (1) $\underline{f}^{(1)}$ is presumed to be a functional of the initial gradients which relaxes by isolated binary collisions occurring under the influence of arbitrary but short-ranged intermolecular potentials. Ternary and higher collisions are taken as negligible. (2) The equation for $\underline{f}^{(1)}$, $\dot{\underline{f}}^{(1)}$ is made closed by factoring the pair distribution occurring in the collisional driving term into a product of singlet distributions. This is the same as assuming that pair and higher correlations do not build up for successive collisions. (3) The gradients and time-dependence of the distribution functions on the molecular collision time and distance scales are assumed negligible. All these conditions hold for dilute gases^{36f,71e}, with (2) being most difficult to justify. Condition (2), called the molecular chaos assumption, short-circuits the infinite hierarchy of time-dependent BGY equations in the exact but impossible \underline{N} -body

treatment, and it introduces the irreversibility. Its analysis as a coarse-graining of the distribution functions remained the primary, if not fully satisfactory, explanation of irreversibility until the time of Prigogine and his school.

Jeans⁸⁰ and others used the Boltzmann theory for qualitative and formal studies. Enskog, with others^{5h,82}, gave the explicit solution for the transport coefficients in terms of collision integrals, starting in 1922. Final numerical solutions⁵ⁱ for a series of model potentials, including the Lennard-Jones, came in the 1940's. The results were good enough for a quantitative understanding of transport in dilute gases. The analogous equation for truly quantum-mechanical systems like the lighter atoms and plasma electrons was shown in 1928 by Pauli⁸³. Grad⁸⁴ extended the Boltzmann approach to very low densities and other conditions where the continuum nature of the fluid begins to disappear. Grad also notes⁸⁵ that the Boltzmann equation is even more important for strong-gradient phenomena (shock waves, ultrahigh frequency sound) than for standard stationary transport. An extension to polyatomic systems in a realistic description of internal motion has been made by Wang-Chang, Uhlenbeck, and deBoer⁸⁶.

The initial work for the dense gas region was done by Enskog⁸⁷, who accounted for finite molecular separation during collision (hard-sphere) in calculating the collision

integrals. The Boltzmann theory thus corrected works down to liquid densities and explains^{5j,71f} qualitatively the observed minimum in viscosity as a function of density. However, a hard-sphere model with fixed parameter σ is inadequate through the liquid range, as new mean forces and structure develop; Enskog's theory cannot be made quantitative over any extended density range. Bogolyubov⁸⁸ proposed a hierarchy of Boltzmann-like equations as an expansion in powers of density, to be used with realistic non-impulsive intermolecular forces, hopefully for all densities. While the numerical results are good for moderately dense gases, the series does not converge. It has been discovered in consequence that the density expansion of transport coefficients is non-analytic⁸⁹, due to the subtle growth of high-order correlations among collisions. The formal, exact theories that can handle this problem have come only recently and suffer from great complexity and other inadequacies; they will be discussed shortly.

More phenomenological approaches gloss over the details of the individual binary collisions, all coupled strongly to one another in dense gases and liquids. At the same time, they make more tenuous the connection of molecular parameters with numerical values for transport coefficients. The principle of corresponding states^{5k} for non-equilibrium states was developed early, and continuously, on dimensional analyses of model kinetic equations. The

principle as applied far into the liquid region seems to work well for the rare gases. However, some discrepancies occur with polyatomics, even those so nearly spherical as CH_4 . The simple two-parameter models for the intermolecular potentials smooth over small features that differ between rare gases and polyatomics, while transport seems to be much more sensitive to such features than equilibrium properties.

A second approach is that of Eyring's⁹⁰ rate process theory, first advanced in 1936. Here it is presumed that every transport process has some rate-limiting step, of the character of a unimolecular passage over a barrier in an appropriate space. Quasi-molecular parameters for a relaxation time and an energy of activation are needed. Reasonably consistent connections can be made to simple equilibrium properties for all kinds of molecules, if one avoids the dilute gas region. The shear viscosity is well accounted for in its P - and T -dependence; D is poorly given: and λ is given well, except in its P -dependence.

Kirkwood^{40b,71g} started a third approach, using a Brownian motion model for the evolution of singlet and pair distributions. The Markovian nature of the time-evolution (a generalization of Fokker-Planck form⁹¹) ensures irreversibility. The pair function $f^{(2)}$ or g is required, since liquids with nonimpulsive interactions have special^{71h} potential contributions to transport, in addition to the

kinetic or 'piggyback' part considered in Boltzmann-like theories. The new phenomenological parameter is the molecular friction constant ζ , of uncertain relation^{36g,71i} to the molecular parameters and equilibrium distribution functions; this is the method's weakness. Kirkwood's theories give us fair numerical results, but quite sensitive to the friction constant value and not mutually consistent even with ζ adjusted^{71j}. Insofar as the theory is correct quantitatively, it gives us some insight into the nature of collisional correlations and new mean forces in liquids. However, molecular dynamics data on model systems have recently provided⁹² evidence against Kirkwood's picture of velocity autocorrelation decays. The principal defect is the lack of validity of Markovian equations for the strong collisions^{71k} which are responsible for much of the transport, in contrast to their validity for the more common weak collisions in the 'cage' of neighbor molecules. Rice and Allnatt⁹³ attempted to correct this defect in large part by introducing 'hard' and 'soft' friction constants at the expense of greater empiricism. Their results for realistic systems, especially for pressure and temperature dependence, are encouraging but may never be adequate--even if only due to the need for gross approximations in equilibrium $g(r)$ and other input data^{11f}. As a final note, many workers⁹⁴ have extended Brownian theories for mixtures, principally to provide good engineering correlations of data.

Cell models are a fourth empirical approach. Cohen and Turnbull⁹⁵ proposed a dynamic version of the hole or free volume theory. A molecule may move only if a void of some critical size opens next to it, by the random coalescence of the free volume. It requires the hard-sphere diameter σ as an additional empirical parameter and can fit transport data quite well in temperature, except for D^{11g} . It fails to represent the intermolecular potential flexibly enough, apparently.

Of recent origin are the rigorous formal theories of transport which provide an analysis of the fluid response to a perturbation of any nature or frequency. They begin with an operator resolution of the Liouville equation or of the quantum density matrix and delve into the many-body phenomena to define the most meaningful collision events. Particularly, they show how correlations are destroyed to generate irreversibility; they further provide, as by the partial summation techniques of many-body theory, approximate kinetic equations on the few-body level. Their value lies in their facility with all kinds of transport for any state of the system (in principle only, at present), their utility in developing concepts about the collisional nature of irreversible processes, and their position to start and to assess different model kinetic equations. Really adequate theories for liquids may derive from these soon.

The early BGY or BBGKY hierarchy^{38,39,40,43} of

equations for the time-dependent reduced distribution functions is rigorous in principle but shows no systematic way to analyze irreversibility and then to generate new kinetic equations. (Born and Green³⁹ did use a superposition approximation in transport to get fair results for dense gases.) Kirkwood^{40b} suggested a many-body operator technique be used before reducing the Liouville equation to the few-body level. vanHove⁹⁶ later succeeded in treating weakly-coupled (weak potentials) systems, stirring much enthusiasm. Essentially, he obtains a master equation for the time-dependent populations of the unperturbed N -body states, by disregarding phase-coherence and interference of the successive sets of collisions, in quantum terms. Brout and Prigogine⁹⁷ derived a similar classical master equation on rather intuitive grounds (classically, one works with similar N -body eigenstates of the Liouville equation, defined in phase space). Finally, Prigogine⁷⁴ developed an operator resolution of the classical Liouville equation (looking very much like quantum mechanics in form) and showed how a simple master equation resulted from summing certain classes of the perturbation expressions to infinite order. The formalism displayed an explanation of irreversibility without extra, ad hoc statistical postulates: the collisions destroy motional or mechanical invariants of the system on the hydrodynamic time scale to give increasing disorder; correlations built up by success-

-ive binary collisions flow^{77c} into higher-order correlation functions whose detailed structure is unimportant for observed properties. It also shows, in the structure of the master equation, that the short-time evolution of the system is non-Markovian^{11h,74c}, degenerating to Markovian (random, Brownian) only for longer times. Transport and relaxation in weakly-coupled gases and weakly-anharmonic solids were understood quantitatively⁷⁴ with Prigogine's theory, but strongly-coupled systems like real liquids are still too complicated to treat. A more approximate form suitable for liquids on the pair distribution level was derived⁹⁸ and tested^{11f} recently, but found lacking.

The other principal formal theory concerns itself with autocorrelation functions.^{54a,71c,77b,78b} These are time correlation functions for simple dynamic variables such as ρ or \vec{v} , e.g.,

$$C_{vv}(t) = \langle \vec{v}(t) \vec{v}(0) \rangle.$$

The brackets indicate that an equilibrium ensemble average is to be taken, and imply that the autocorrelation functions are implicitly dependent on the equilibrium intensive variables ρ, T , etc. The ACF's or their Fourier transforms contain all the basic dynamic data. This remarkable discovery of transport information in equilibrium fluctuations has been known quite a while in diverse systems such as electrical resistors⁹⁹. The application to transport in dense neutral (molecular) systems is more recent¹⁰⁰.

The usual transport coefficients are just zero-frequency components^{54a} of a few autocorrelation functions times definite numerical factors.

The ACF's can be represented as the linear or first-order response of the system to the appropriate adiabatically-applied perturbation, either mechanical---electromagnetic radiation, a moving boundary, e.g., or thermal--temperature gradient, pressure gradient, etc. However, explicit solution for the perturbed (N-body) phase-space distribution involves solution of the complete N-body problem. We must depend upon further leads within or outside the theory to compute ACF's using only few-body dynamics. Some approximate kinetic equations for the ACF itself directly are being tested^{54a}. Also, the numerical results of molecular dynamics calculations can be reduced to numerical values for transport coefficients, using the basic discovery noted initially¹⁰⁰.

The ACF approach is extremely difficult in principle and in practice now, but it holds much promise. Certainly, it has the advantage of using the entire frequency spectrum of transport to understand and check the model kinetic equations. It also interrelates data from ordinary transport and relaxation (such as the dielectric relaxation spectrum derived from the ACF for one molecule's electric dipole $\langle \vec{u}(0) \cdot \vec{u}(t) \rangle$) with data from special probes from more complex perturbations (such as fluorescence

depolarization: $\langle \frac{3}{2} [\vec{u}(0) \cdot \vec{u}(t)]^2 - 1 \rangle$).

Critical region anomalies in transport were slow to be recognized and studied experimentally^{12g}, so the corresponding theory is relatively new and undeveloped. The earliest, and qualitative, theories were directed toward the excess ultrasonic attenuation^{101,102} in critical liquid mixtures. These theories claimed that other wave propagation phenomena (shear viscosity in special flow patterns around fluctuations¹⁰¹, or Rayleigh scattering by same¹⁰²) were masquerading as anomalous changes in the bulk viscosity. They ignored the possibility that near the critical point there were changes in the nature of mutual diffusion, which is the principal mode of relaxation of the fluctuations in concentration. These theories were wrong, for diffusion is altered from its standard form^{19e}; Fixman's ideas on this line¹ gave the first quantitative success for the anomaly in bulk viscosity. His related theories for shear viscosity¹⁰³ and for static heat capacity¹⁰⁴ also worked fairly well. Kawasaki² advanced another microscopic approach to critical sound absorption. It was based on ACF theory and is much less transparent, but only slightly different--in fact, he uses Fixman's modification¹⁰³ of the diffusion law, though in a more rigorous way (as we do, in paper I). Kadanoff and Swift³ have recently presented very general theories for all transport coefficients in both gas-liquid and liquid-liquid (mixture) critical regions. The K & S

perturbation approach to the master equation is very complex. However, it is of the same strain as Fixman's and Kawasaki's, in that it describes dissipative processes as the breakdown of one transport mode into several others. As such, it is called 'mode-mode coupling'. Unfortunately, it is less successful¹⁰⁵ with experimental data than the other two theories.

The final generalization for critical region transport is a type of corresponding states theory, called the dynamic scaling laws^{3,106}, very similar in form to the static scaling laws of Widom and others for equilibrium. Kadanoff¹⁰⁷ reviews their experimental support, which is incomplete in itself, and not very encouraging.

(paper I gives detailed comparisons of sound absorption data with the various theories.)

D. Fluids with Well-Defined Internal Degrees of Freedom

The first level of complication above simple fluids is represented by non-associated polyatomic molecules, which possess permanent multipole interactions (esp. dipoles) and the new internal motions of rotation, vibration, internal rotation (rotational isomerism, when rotation is restricted), or simple dimerization equilibrium. These extra internal motions and the multipole interactions coupling them allow the molecules to structurally store and to transport additional energy and momentum. The coupling of these motions, particularly to the external translational motion---sometimes so strongly as to merge identity with the latter, alters the nature of collisions and of static structural correlations. Quantitative changes from simple fluid behavior are found in the equation of state (particularly in the location of phase boundaries), heat capacities, and transport coefficients; qualitative trends with pressure, temperature (and frequency, for transport) are sometimes altered, especially in polar fluids. Rotational reorientation or rotational diffusion¹⁰⁸ arises in dense fluids as a new transport process. In consequence, the electromechanical response becomes interesting: dielectric relaxation¹⁰⁹ in (di)polar fluids, or in nonpolar fluids the lineshapes for microwave,^{110d} IR, Raman^{110b}, visible, UV^{110a}, and NMR¹¹¹. Static dielectric constant and strength and

materialism^{111a} are equilibrium aspects. Rotational relaxation^{16-20,112,113} (as well as vibration, internal rotation, and dimerization) also makes a dominating contribution to the old transport coefficient, the bulk viscosity.

We exclude from consideration very large polymers or macromolecules, with yet more drastically different properties. For example, their transport even at modest frequencies is governed by viscoelastic equations^{114,115} rather than Navier-Stokes equations. We leave untouched the large field of rheology.

To be sure, much of the interest in properties of such polyatomic fluids as we consider is still outside our scope: color, reflectivity, and other electromagnetic properties which are more utilitarian; chemical stability and kinetics of degradation or reaction; and all manner of chemical and physical behavior in complex, possibly multiphase, mixtures. Still other interesting aspects are only in part related to the simple equilibrium and transport behavior we'll study, and may be touched on briefly, e.g., relaxation of artificially inverted vibrational populations in chemical lasers¹¹⁶. We justify our artificial limitations of interest on pure convenience, as well as on the opinion that qualitative and quantitative understanding of these simple properties is the major work in understanding all the properties of these fluids---and by extension those of the associated liquids, in particular the compound of

greatest chemical and biological interest, water.

We have previously mentioned some new transport behavior. We should now like to elaborate on some more qualitative effects in properties, beginning with equilibrium. Dipolar forces and orientation in the fluids, especially dense fluids, cause imperfectly understood but significant additions⁵¹ to heat capacities and to the equation of state. The melting and boiling transitions are raised in temperature, and the critical constants' interrelations are changed^{5m}. Empirical equations of state like van der Waals or approximate virial still apply with more error; more parameters are now desirable. In the corresponding states treatment^{5m}, the reduced dipole moment is a necessary new parameter. Even in polyatomics which are not dipolar, there are new small terms in the heat capacity¹¹⁷ and the virial coefficients⁵ⁿ or other representation of the equation of state. The well in the spherical-average pair potential is also generally deeper in polyatomics¹¹⁸, from stronger dispersion forces, more densely-packed excited electronic states. The liquid ranges are also higher in temperature and the specific heats higher in value¹¹⁹ than those of simple fluids, in consequence. The exact treatment of the equilibrium properties must include the new mutual-orientation dependence in the fluid structure. For example, in the distribution function approach one uses a host of coupled pair distribution functions⁴⁹. These are a type of

harmonic expansion of the pair function as used for simple fluids, and are quite difficult to use. (This is a proper description of combined translation and rotation. Vibration remains essentially separable even in dense fluids; some subtle changes show up spectroscopically¹²⁰ to give evidence of the fluid structure and interactions.) The dimerization equilibrium causes the grossest changes in equilibrium properties. Its sensitivity to temperature increases the heat capacity, to 4-5 times the expected value^{121a} in the case of NO_2 . The volume change in forming the dimer modifies the PVT behavior as well. The energy storage in the internal motion, especially vibration, manifests itself in yet more ways, even for gases. The restriction to quantized levels may become evident at low temperatures. For example, the molar vibrational heat capacity begins to 'freeze out'^{122a},
 50 from its high-temperature value of \underline{R} per vibration mode as the temperature is lowered, but still well above room temperature. Rotation freezes out well below room temperature. Quantum symmetry^{122b} restricts the pairing of vibrational with rotation levels in cases as H_2 , causing further divergences in heat capacities. Free internal rotation¹²³ partially freezes to become few-state hindered rotation or (for asymmetrical barrier) rotational isomerism^{19f,124} before it disappears.

The nature of molecular collisions is also new. Momentum and energy are transported internally by the

molecules--quite dramatically in the case of dimerizing species; NO_2 has 4-5 times the thermal conductivity^{121b} expected. Collision dynamics are quite definitely quantum mechanical, particularly for vibrational excitation, as shown by interpretation of ultrasonic data. The nature of trajectories is also affected by the initial orientation correlations imposed by the static structure. In dense gases, rotational relaxation or reorientation degenerates to small, diffusive steps described by a new transport coefficient, the rotational diffusion constant $\underline{D}_{\text{rot}}$ ¹⁰⁸. Dipolar molecules show strongest correlation and are probed easily by dielectric relaxation¹⁰⁹. This rotational diffusion persists even in solids¹²⁵. Ordinary transport--viscosity, conductivity, diffusion--is also presumably affected by the new orientation-dependent packing and the anisotropy of the interactions. "Piggyback" and potential contributions are both altered. The changes in magnitudes of the transport coefficients η , λ , and \underline{D} from simple fluid values are not large^{119b,121,126} and the theory⁸⁶ is difficult, so this aspect has not seen much work. On the other hand, the bulk viscosity is greatly increased and otherwise affected by the new internal relaxations possible. The extra energy in the internal motions is traded around or exchanged with translational energy at finite rates^{18e,19g}. Time lags in energy adjustment in response to temperature (or sometimes pressure) fluctuations cause dissipation of the energy in

passing sound waves^{18f,19h}. The study of this relaxation-- vibrational, rotational, rotational isomeric, and chemical-- is a well-developed and dominant part of ultrasonics. Time-dependent order parameters (say, effective temperatures^{18e, 19g} of internal motions) are needed to formulate the relaxation laws in the new 'dynamic' equation of state. Each kind of relaxation has its characteristic dependence upon ω , P , and T , which is helpful in qualitative identification. Detailed molecular models using quantum scattering theory are needed to explain the parameters of the empirical relaxation equations (or η_v directly). Among the first successes of molecular collision theory^{18g,127} and the first uses of ultrasonics were studies of relaxation in gases.

Chemical reaction, specifically the dimerization we consider here, is an extreme limit of the interaction of the degrees of freedom of two (or more) molecules. The statistical mechanical description of structure in a reactive fluid merits some discussion. A pair interaction defined in a relative coordinate is an insufficient description of binding. The rotations, the vibrations, and even the relative translation are totally recast with new energy levels. The new quantization and new phase space alters the partition function¹²⁸ and hence the thermodynamic properties rather intricately compared to the simply interacting molecules. The interaction of the dimerized pair with a third molecule is now given by a second effective pair potential.

Overall, reaction is too complex to be described in detailed phase- space distributions as were simple fluids. More phenomenological groupings into all the monomer states and all the dimer states are used, with thermodynamic parameters and gross rate constants^{18h,19i,129}.

The overall magnitudes of transport coefficients for non-simple fluids are not greatly different from those of simple fluids in analogous states of packing and temperature,^{119b,121,126} but for the bulk viscosity and the new \underline{D}_{rot} and in isolated cases of other transport (λ for NO_2). Both the equation of state and transport properties can often be 'explained' in the framework of simple fluid theories by using effective spherical pair potentials. However, the resultant state-dependence of the effective simple fluid parameters, especially trying to reproduce contrary trends with \underline{P} , \underline{T} , or ω , is unsatisfactory. More elaborate theoretical frameworks are then justifiable. Certainly we will need them on the way to understanding associated liquids like water.

New probes are available for the new features of non-simple fluids. All the common gases have been studied by ultrasonics^{16-20,112,113} for their rotational and vibrational relaxation (actually coupled into one vibrational-rotational-translational --VRT--relaxation set). Initially the studies were prompted by shock and combustion phenomena, since bulk viscosity is unimportant in ordinary conditions.

After initial triumphs of crude quantum explanations^{18g,127}, ultrasonics and VRT relaxation were kept as a proving ground for scattering theory, including classical and semi-classical modifications¹³⁰, and as an adjunct to molecular beam and other experiments for determining intermolecular potentials¹¹³. At low temperatures the relaxation times between distinct quantum levels have been pinned down^{18i, 19j,132; 18j,19k,133a}, though in general multiple relaxation^{18k,19l,134} occurs and complicates analysis--even worse in liquids. The dimerization kinetics of NO₂ were also studied early^{133b} and adequate interpretation of other properties was made. Dimerization by H-bonding in acetic and propionic acids has been studied in liquids^{19m}. Similarly, liquids have been probed for vibrational relaxation, as in CS₂^{18l}--though the new nature of collisions makes definition of basic collision rates ambiguous^{18m,19n}. Pure rotational isomeric transitions^{18n,19o,135} are studied primarily by ultrasonics, though the presence of isomerism was first demonstrated¹³⁶ by spectroscopy, electron diffraction, calorimetry, and dielectric behavior. Liquids are, in fact, classified^{18o} as simple (no relaxation or excess sound absorption from η_v), Kneser (distinct thermal relaxation from a well-defined internal degree of freedom), and associated (modest excess absorption, nearly T -independent, etc.). The characteristic ω , P , and T -dependence of different relaxation processes makes ultrasonics a good tool, rich in

information. Dramatic cross-relaxation^{19p} of one species by another in mixtures has seen some work. Equilibrium properties, especially in mixtures, are often taken¹³⁷ from ultrasonic measurements.

NMR¹¹¹ is another probe for rotational relaxation or diffusion, at the Larmor frequency ω_L . IR, UV, and Raman lineshapes¹¹⁰ inform us of vibrational or rotational relaxation at the vibrational relaxation itself. Dielectric relaxation¹⁰⁹ lineshapes probe rotational relaxation. X-ray scattering¹³⁸ may conceivably be developed for studying orientational effects in liquid structure. Relaxation of nonthermal vibrational populations inverted by light absorption¹³⁹, laser scattering¹⁴⁰, or chemical laser action¹¹⁶ is more precise for level-by-level studies.

E. Equilibrium Theory

Our coverage of theory for non-simple fluids will be more sketchy than for simple fluids. Some general observations have been included in the previous section. Many of the theories of §B can be simply extended. van der Waals theory and other few-parameter empirical equations give about as good agreement with small non-polar non-simple fluids as for simple fluids. Larger molecules such as hydrocarbons require a greater number of parameters¹⁴¹, as do polar species. Corresponding states treatments^{5m} are good for small molecules and can be explicitly adjusted to three-parameter form for dipole forces. Cell theories are similarly used for polyatomic species with somewhat less success^{5p} than for simple fluids.

Virial cluster theories and distribution function theories, including PY and HNC approximate forms, are less often used for polyatomics, for they do more in the role of exhaustive testing as quite accurate, rigorous equilibrium theory. The proper extension is to include multipole forces and harmonically expand the pair function in orientation angles. Pople and Buckingham¹⁴² have used cluster theory with dipole and quadrupole forces added. Levine and McQuarrie¹⁴³ and Stogryn¹⁴⁴ have included higher multipoles and proceeded to the third virial, for both ordinary and dielectric coefficients in the first case. Frisch and Lebowitz¹⁴⁵ have done a scaled particle theory extension.

Gibbons and Steele¹⁴⁶ and also Buckingham¹⁴⁷ have done some less quantitative work at liquid densities. Steele and Chen⁴⁹ have used angle-dependent PY theory through liquid densities with encouraging results. Perturbation theories^{52,117} based on the free energy function with a hard-sphere zero-order model are by and large inapplicable, as the angle dependent forces so complicate the perturbation expansion as to eliminate the advantage over more direct approaches. Molecular dynamics⁵⁴ and Monte Carlo¹⁴⁸ calculations have been done for a few moderately nonspherical potentials including dipoles.

Dimerization, and solvation in mixtures, are too complex for present a' priori theories. Phenomenological theories are in use^{149a}, at least for the deviations from additivity of thermodynamic functions for mixtures in which one component either self-associates or solvates the other. Pure species' gas imperfection from dimerization is calculable^{149b}, but there is no treatment for dense gas or liquid.

In all, much more work has been done on empirical representation of data on real systems than on a' priori approaches. The latter must be greatly improved within the simple fluid domain before moving up to more complex fluids.

Critical phenomena occur at higher temperatures and pressures than in simple species, reflecting stronger pair potentials. The critical compressibility factor $\frac{P_c V_c}{R_c T_c}$ is altered from the general simple fluid value of 0.292

by polar forces in particular.^{5m} The critical exponents are not detectably altered for the moderately nonspherical molecules⁷ commonly studied. This indicates once more that the critical region equation of state is not sensitive to the exact nature of the intermolecular potential. Critical exponents for dipolar gases, on the other hand, could be very interesting. The generally stronger molecular interactions, within or between species, can lead to strongly nonadditive thermodynamic behavior in mixtures. Regions of liquid^{149,150a} (or even gaseous^{150b}) immiscibility and new liquid-liquid critical mixing points occur. Here we have a whole new field for critical investigations, often at more convenient conditions of temperature and pressure. These systems seem to behave analogously to gas-liquid critical systems, with the appropriate transcription of intensive variables^{12h,105a}. The few equilibrium exponents known appear to be the same^{7,12h} as for gas-liquid transitions. Liquid-liquid critical mixtures are more commonly used for transport studies than for equilibrium.

F. Transport Theory

As for equilibrium, transport in non-simple fluids is often handled by simple extension of simple fluid theories. Now, it is often easiest to use effective spherical models, except for η_v and D_{rot} . In light of the unspectacular differences among all manner of fluids in ordinary transport, this is justifiable in large part. It is also necessary in generating semi-empirical forms for transport in mixtures^{5i,11i,94}, quite a large field. When one does explicitly consider the internal motions, there are more or less evident corrections or generalizations of simple fluid theory. The Eucken correction^{5g,72} for rotation can be appended to the early free-path models for gases with some success, especially at elevated temperatures^{5g}. It may also be used with the Boltzmann equation solution^{5q} of Chapman and Enskog. A more rigorous treatment is given by Wang-Chang, Uhlenbeck, and deBoer⁸⁶ for all separable degrees of freedom as we are considering. There are also many models of loaded spheres and other rigid bodies¹⁵¹ for which the Boltzmann equation has been solved, in an attempt to include nonspherical interactions in the repulsive core. The dense gas and liquid are less amenable to such models, as the necessary Enskog correction⁸⁷ involves a difficult pair distribution; molecular dynamics calculations are more suitable. More phenomenological models have little difficulty with polyatomics. Corresponding states^{5k}, rate

process⁹⁰, and cell⁹⁵ theories gloss over so much detail and are so heavily empirical that the qualitative subtleties are lost. They give often acceptable fits to data, as discussed in § C, and are useful for semi-empirical calculation of transport in mixtures¹¹¹. Reactions such as dimerization are a complication tending to invalidate all but Eyring's rate process model. Brownian models^{40b,71g,93} are too inaccurate and undeveloped to warrant worries about the anisotropy of interaction, though they are also used semi-empirically for mixtures⁹⁴.

The rigorous formalisms which might incorporate non-spherical molecules are principally Prigogine's⁷⁴ and ACF^{54a,71c,77b,78b} theory. The minor effort³⁹ on the gradient-dependent BGY pair distribution in the superposition approximation has not been continued for either simple or polyatomic fluids. It is inevitably inaccurate at true liquid densities and is not a notable advance over competing dense gas theories. Prigogine's theory has not been explicitly developed for nonspherical molecules, again because simple fluids (with their strong coupling) still are waiting. Internal degrees of freedom are quite a complication for the theory and apparently will make it a complete master equation^{78d} formalism (internal quantum states are resolved), while their inherently weak coupling makes them better suited for study, given quantum scattering calculations for excitation cross sections. The ACF theory, on

the other hand, has been used at least once^{54a}, in conjunction with molecular dynamics, on nonspherical and even dipolar molecules. D_{rot} can be derived from the results, along with more detailed information, principally on the electromechanical response.

The two transport properties which really show the new features of unassociated polyatomic fluids are η_v and D_{rot} , as we have said in the previous section. In consequence, most theoretical effort has been expended on them, including specialized theories outside the realm of the other transport modes. Rotational diffusion is the subject of several phenomenological theories. A mechanism of small diffusive steps was proposed early by Debye¹⁰⁸ and others and seems to be confirmed for larger molecules, while finite random reorientations are proposed for smaller molecules¹⁵². The internal relaxations responsible for the large bulk viscosity η_v are usually approached by calculating the inelastic binary collision cross-sections, which are then plugged into elementary free-path theories. As a result, the relaxation time is the inverse of a simple Boltzmann average^{19q} of probability of excitation per collision. Multi-level relaxation is given inadequately; coupled relaxation equations^{18k,19l,134} for all the levels can be formed, again in the free-path approximation for collisions. While the more detailed relaxation process in dense gases and liquids deserves much attention in statistical mechanics, most of

the recent work in relaxation phenomena tries to improve the realism and scope of binary scattering theory calculations. Much of this effort, in turn, is expended on bimolecular reactive collisions¹⁵³, particularly simple exchange reactions. The advent of better molecular beam¹⁵⁴ and other^{116, 139, 140} techniques for direct observation of partial cross-sections has much to do with the resurgent interest in a priori kinetics.

The anomalous increase of η_v from slowed diffusive decay of increasingly large fluctuations in critical fluids gets the lion's share of the attention, both theoretically and experimentally. This is primarily because it is most straightforward. The experiments for η_v , which are fairly numerous (esp. in liquid-liquid cases) and are reviewed in paper II, are readily done with ultrasonics. Fixman¹, Kawasaki², and Kadanoff and Swift³ give quantitative theoretical explanations, which are discussed at the end of § C. The dynamical scaling theory^{3, 106}, an outgrowth primarily of the last theory, touches upon the other transport coefficients but is not very successful even for η_v .¹⁰⁵ Fixman has adapted his ideas for the shear viscosity¹⁰³. Otherwise, critical transport theory is unexplored. The experiments on η_s , by standard^{11, 12a} or torsional crystal¹⁵⁵ viscometers, on λ again by standard apparatus^{11, 12a}, and on D by NMR^{12b} or light scattering^{14, 15} cover both gas-liquid and liquid-liquid phenomena. In aggregate the work is not definitive^{12a}

in establishing the existence and nature of anomalies in these three transport modes.

G. Associated Liquids

Some polyatomic species can hydrogen-bond into extensive arrays in the liquid (and solid). Water is the most famous example, while others are low-molecular weight alcohols and polyols (e.g., glycerol), HF, and HCN. H-bonding is weak^{156a} by the standards of chemical bonds, but strong compared to the van der Waals forces binding the types of fluids discussed previously. As a result, associated liquids have anomalously high melting and boiling points, heats of transition, and surface tension. Water, which bonds to as many as four neighbors, boils 162 degrees above its congener H_2S . The strongly directional character of chemical H-bonds also shows in bulk properties. The strong molecular alignment causes high dielectric constants in these liquids^{119b}. Water also has to great extent a distinct, extensive three-dimensional network^{156b}. This contributes to its melting and boiling anomalies, high molar volume, and high viscosity. Its thermal breakdown is responsible for a large heat capacity and for its density increase on melting and on slight further warming of the melt. Thermal conductivity is large through the semi-rigid solid-like lattice, and compressibility is low. The lattice structure is also broken down by pressure, leading to an anomalous decrease in viscosity^{156c}. It is labile on a short time scale so that molecules do rotate and flow rather independently. Self-diffusion, most reliably measured by

NMR, is normal^{156,126}.

The other associated fluids usually show less dramatic anomalies. Most alcohols to modest size are somewhat higher-boiling and the polyols in particular are quite viscous. Glycerol is so extensively bonded as to have a huge viscosity which relaxes much like bulk viscosity does at modest frequencies^{19r}; relaxation is so slow at low temperatures that it acts glassy. All associated liquids show a modest bulk viscosity which is in near constant ratio to shear viscosity over the temperature range^{19s,18p}.

In water, HF, and HCN the protons are very mobile, unbonding and rebonding to travel, aided by their lightness. Noticeable electrical conductivity^{156d} is found in the pure liquids, and it is greatly enhanced by solvation ionic compounds normally conductive themselves only as melts. Water in particular shows great solvating power for a wide range of substances. Great chemical and biochemical importance accrues to water for its abilities to solvate so many species and to promote reactions, particularly those with ionic intermediates. Solvation is accompanied by lattice breakdown to smaller units, and by strong electrical forces. Isotopic substitution of deuterium or tritium for normal hydrogen makes noticeable changes in properties¹⁵⁶, principally by altering the H-bond strength. In the vapor phase, association is weakened essentially to dimerization, causing lesser anomalies^{156e} in the gas imperfection.

Associated liquids are certainly very difficult to describe theoretically because they show cooperative motion of very many molecules. The intermolecular potential is well-established^{156f} as non-pairwise-additive, involving three-body and possibly higher distortions. The short range and directional nature of the H-bond aggravates the problem of describing transport a priori. There are some new tools for help in qualitatively understanding the added structural and dynamic features. X-ray^{156b} and neutron scattering give us pictures of inter- and intra-molecular structure. Water shows such definite orientational effects that the lattice-like structure found in the 1930's prompted the cell models of all liquids. The proton magnetic resonance^{156g} is strong and readily resolved into chemical shift and linewidth information on various environments and rates of motion. Vibrational spectroscopy^{156h} is at its most informative for associated liquids. While properties under normal conditions are heavily studied, the critical phenomena of associated fluids remain unknown, partly because of their high critical temperatures and pressures (water: 373 C., 218 atm, methanol: 240 C., 79 atm.).

The rather spotty equilibrium and transport theory will be briefly recounted in this one section. We will concentrate on the story of water, with occasional comments on other species. Most of the equilibrium theories for water are heavily phenomenological and can be classified as

mixture models. A finite set of distinct chemical structures is presumed in equilibrium. Each structure is assigned an enthalpy and specific volume (in interstitial models, the smaller species--monomers--can hide in the free volume of major structures). Eucken¹⁵⁷ and Hall¹⁵⁸ postulated mass-action (straight chemical) models, based primarily on the ultrasonic bulk viscosity. Both temperature and pressure dependence of η_v and K_s are acceptably given in Eucken's form. Application of Hall's theory to alcohols' ultrasonic behavior has been attempted with slight success¹⁵⁹; since there is no density minimum, the thermal driving term neglected by Hall is no longer small compared to the pressure driving term in the dynamic equation of state. A number of other workers¹⁵⁶ⁱ have used similar chemical models for water, obtaining the molecular parameters from molar volumes, compressibilities, or radial distribution functions.

Getting away from mass-action equilibria models, Pauling and others¹⁵⁶ⁱ advanced simpler interstitial forms with one major structure. They have difficulty explaining the high configurational heat capacity of water. Recently, Eyring and others¹⁵⁶ⁱ have given multiple-species models for the partition function directly, sometimes including vacancies, and all using extensive thermodynamic data. The large number of variational parameters tends to make these theories simply empirical fits, hard to test for reasonable-

-ness of the parameter values. The general problem with mixture models is the variability they imply for the environments of individual molecules, contraindicated by the narrow spread of dielectric relaxation times^{156j}. They also fail to explain the strong molecular alignment leading to the high dielectric constant.

Pople^{156k} proposed distortion of a complete network of H-bonds to explain the observed radial distribution functions, assigning a bending force constant for each bond. The dielectric constant and volume decrease on melting seem to come naturally from the model, while the viscosity from such a model would be too high. The very characterization of intact--perhaps bent-- and broken H-bonds is difficult either macroscopically or microscopically^{156l} within any model, however.

There are two recent a' priori approaches employing effective pair potentials. Ben-Naim¹⁶⁰ performed a PY calculation on water, having directly approximated the potential of mean force. His results reproduce features in the pair distribution but he does not compute properties. Barker and Watts¹⁴⁸ did a Monte Carlo study on water, taken to have a spherical potential plus a strong dipole. The vapor has been the subject of virial cluster theory^{156e} in which it is characterized by a pair multipole potential or by a dimerization equilibrium. Neither alternative is consistently good for the temperature dependence, particularly

for the third virial coefficient.

In summary, there is no consistent and successful nonempirical theory through an extended domain in the thermodynamic plane. Eisenberg and Kauzmann¹⁵⁶ have collected a great mass of experimental data and theoretical correlations for water, from which one might make more detailed judgments.

Transport is more fragmented than equilibrium theory, as most transport theories correlate only one such property with some equilibrium or distribution data, and do not cross-correlate transport data. Again, Eisenberg and Kauzmann have assembled the data on water. Dielectric relaxation in water^{156j} is interesting for its very small spread of relaxation times, implying near uniform molecular environments on a quite short time scale (but not so short as a vibration time, where a spread of environments shows up spectroscopically^{156m}). It also possesses a large high-frequency limit ϵ_{∞} , indicating persistent rapid motions, probably rotations. Generally, qualitative models are employed to explain its behavior. Haggis, et al.¹⁶¹ used their complicated mixture model of equilibrium among zero-through four-bonded molecules plus postulates on simple reorientational motions available to these species. This theory also covers equilibrium and other transport, notably, though it is highly parameterized. Rotational diffusion apparently occurs at a slightly faster rate¹⁵⁶ⁿ with a

similarly low spread in ω -dependence of the obviously related relaxation it represents. Eyring's rate process theory is used^{156o} to obtain an energy of activation for dielectric reorientations, which energy happens to match that for self-diffusion and viscosity, tying them to some common mechanism too.

Self-diffusion has been the subject of rate process theory^{156o} only, to date. Neutron-scattering data^{156o} on the ω -dependence of D may soon be helpful in generating better detailed models. Shear viscosity^{156p} is also given only in a rate process analysis. Its decrease with pressure at low temperatures supports the qualitative equilibrium picture of network breakdown, with shear flow sustained primarily in the free (monomer) phase. Rate process theory reflects this feature.

Bulk viscosity is curious in all the associated liquids in that it has a ratio^{19s,18p} to η_s largely independent of T and P . Some underlying identity of mechanism is apparent, while the only theoretical treatments cover only η_v and equilibrium. Eucken's¹⁵⁷ and Hall's¹⁵⁸ models, developed originally for ultrasonics, are rather successful in correlating the bulk viscous behavior with the bulk compressibility and molar volume as functions of pressure and temperature. For the very viscous fluids as glycerol, both shear and bulk viscosity appear to relax together^{19t} in frequency and temperature. Shear and bulk 'fluidities' or

moduli are used in the largely empirical viscoelastic description^{19u,114}, as they are now the additive quantities. A considerable spread in relaxation times is evident^{19u}.

H. Mixtures Containing an Associated Liquid

Fluid mixtures quite commonly show nonadditive thermodynamic and transport properties. Some of the largest of such effects are shown by solutions in associated liquids of unassociated species which are solvated by new H-bonding. Aqueous solutions of organic amines or of higher alcohols are examples. Some important features are large heats and volumes of mixing \underline{E}^e and \underline{V}^e , as well as partial liquid immiscibility^{149c,162a} leading in particular to lower consolute points. The anomalous properties of the associated liquid may be much reduced in mixing, due to the structural breakdown needed to accomplish solvation. The dielectric behavior, thermal expansion¹⁶³, and molar volume become more normal. On the other hand, the heat capacity and bulk viscosity have new contributions from the solvation equilibria, with the latter being greatly increased^{19t,163,164}. The compressibility anomaly is increased¹⁶³, which may be unexpected at first glance; the shear viscosity is likewise increased (see paper II, e.g.). Mutual diffusion is interesting, especially near the critical consolute point where it vanishes.

Many simple fluid equilibrium theories have been generalized to treat the odd forces in polyatomic and even associated fluids, and also to treat mixtures. Cell theories¹⁶⁵ and distribution function theories¹⁶⁶ come to mind,

but in any event these generalizations are largely formal. They are mostly unexplored and very much more difficult than the parent theories. Few, then, are up to the task of handling both association and mixture behavior at the same time. More often the work falls to more empirical theories from physical chemistry, seeking solely to explain nonadditive thermodynamic behavior in terms of the pure component parameters. This separate handling of the association and mixing problems gives a more reasonable return for the effort involved. The physicochemical approaches to nonelectrolyte solubilities also gets much attention because of the direct technological application of solution thermodynamics, solute partition between two solvents, etc. Prausnitz'¹⁴⁹ book on solutions recounts in detail the physical bases for the major theories. Again, few of these theories are adequate for associated liquids, due principally to their assumptions of simple-fluid equations of state for both components. Many of them also require that volume changes or entropy changes \underline{V}^e or \underline{S}^e vanish, making them extremely doubtful for associated solvents. Several of them (Guggenheim's quasi-chemical^{149d,167} method; Flory-Huggins polymer^{149e,162} theory; two-liquid theory^{149f,168}) attempt a crude treatment of the nonrandom mixing of the two components, the preferred molecular aggregations in the process of solvation.

The most satisfying empirical tack begins with the chemical theory of solutions^{149g}. Here explicit association

chains ($A + A_{n-1} \rightleftharpoons A_n$) and solvation ($A_n + B \rightleftharpoons BA_n$) equilibria are proposed, with quite simple progressions of equilibrium constants and of ΔH , ΔV values for each step. The activity coefficients, hence thermodynamics, of solvent A and solute B are calculated from their true mole fractions as free monomers. Many thermal and volumetric properties are given reasonably well. However, the solutions of the postulated species must actually be nonideal from additional 'physical' forces (difficult to divide from stronger 'chemical' forces) to give any immiscibility^{150c}. Renon¹⁶⁹ has given the most comprehensive theory in this regard, one which is fairly heavily empirical. Of course, the usual objections to mixture models for associated liquids do imply the inadequacy of Renon's and other theories for some properties, such as dielectric behavior, especially at low mole fractions of the unassociated component. Andreae, et al.¹⁶³ tested the simpler chemical theories on the thermodynamics and ultrasonic absorption behavior (see next paragraph) of aqueous amine and alcohol solutions, but achieved poor results and extracted only qualitative indications of the real structure and dynamic processes. To close the discussion, we note that Rowlinson^{150d} regards aqueous nonelectrolyte solutions as the hardest, least understood aspect of equilibrium phenomena, though a mass of data and empirical correlations has been obtained, as seen in the book by Hildebrand and Scott¹⁶².

Dynamics are again a great problem. The ultrasonic bulk viscosity is handled in the chemical theory of solutions. Over and above the equilibrium constants and thermodynamic changes for each partial reaction, rate constants^{19t,163,164} are fitted to the absorption and perhaps some equilibrium data. Andreae, et al.¹⁶³ achieved only partial success. Qualitatively it is quite clear that the relaxing solvation equilibria are responsible for the large bulk viscosity; the relaxation times can even be resolved in some cases. However, any adequate treatment should dynamically generalize Renon's theory. To justify the effort in obtaining the latter, one would require very precise ultrasonic and thermodynamic data and would achieve only a rather unwieldy semiempirical correlation. Advances in associated liquid theory are highly desirable beforehand.

For the other transport phenomena, particularly η_s , λ , and \underline{D} (dielectric relaxation and \underline{D}_{rot} are generally ignored), there are again formal generalizations of simple fluid models. The generalizations of corresponding states¹⁷⁰, rate process⁹⁰, and Brownian⁹⁴ theories have been given, at least for mixtures of normal liquids. None is particularly suited to mixtures containing an associated component: pure associated liquids and normal fluids do not have corresponding states; Brownian models have not been used for associated liquids pure or otherwise, with their complex potentials and hard-to-represent structure. Only

rate process is sufficiently empirical, and it does not do well for thermal conductivity¹⁷¹, for example.

The liquid-liquid critical phenomena are qualitatively different in origin from those in simple fluids as discussed in §§ D-F. The immiscibility and critical consolute behavior in the latter arise from largely athermal mixing which is nonetheless non-random (cf. the success of Flory-Huggins polymer theory even for simple molecular mixtures¹⁷² ---this may be fortuitous, however); upper consolute behavior is the rule, with complete miscibility at higher temperatures from the wiping out of the nonrandom structure. On the contrary, the strong H-bonding in solvation by associated liquids most commonly^{149h} leads to lower consolute behavior. In many systems, the phase diagram is quite skewed toward low mole fraction of the unassociated component¹⁷³. The obvious occurrence of solvation equilibria points to a large chemical contribution to the free energy of mixing, hence the phase behavior. However, the analysis of our own experiments on 2,6-lutidine/water in paper II shows that the phase phenomena are hard to explain with chemical theory augmented by any simple physical (nonideality) corrections.

As for the liquid-gas transition, the critical region equation of state in liquid-liquid transitions is not given by classical, analytic thermodynamics. After transcription of the intensive variables, the two kinds of

critical points appear similar, as noted in §§ D-F. For example, the shape of the phase diagram (now in the X - T plane, X = mole fraction) is cubic rather than parabolic. There is less detailed information deep in the critical region than for the gas-liquid transition, however, so very few analyses have been made for critical exponents. Only α for the C_p divergence and β for the coexistence curve shape are reasonably well established^{12h}. In transport, η_v receives the most attention, from the theories of Fixman¹, Kawasaki², and Kadanoff and Swift³. As noted in § F, these gave the first quantitative explanations of the anomalous critical region absorption. The anomaly in the diffusive decay of the fluctuations is now in mutual diffusive decay of relative composition fluctuations at constant density. Some recent work, as that in our following two papers, has attempted to show the identity in nature of liquid-liquid critical phenomena at upper and lower consolute points. Paper II indicates this is not clear, for at the lower consolute point the ultrasonic absorption from the critical processes is partly obscured by non-anomalous but large thermal relaxation (this has not been generally recognized in investigations of other lower consolutes^{102,174} which did not include the composition-dependence of absorption). Furthermore, the separation of the critical and thermal ultrasonic effects once recognized is still difficult, due to the implicitly classical and wrong thermodynamics of

the coexistence curve--hence also of the \underline{X} -dependence of ---in all three absorption theories. In general, we expect that the dynamic critical exponents will be hard to pin down and to compare among systems.

More realistic irreversible thermodynamics should be worked into Fixman's and other theories of transport to analyze critical phenomena, complemented by better equilibrium thermodynamics combining chemical and physical models of the solutions. The pressure dependence of the consolute temperature is also interesting. The excess volume of mixing gives a \underline{P} -sensitivity to \underline{T}_c , through the \underline{X} -dependent free energy of mixing \underline{G}^e acquiring a term $\underline{P}\underline{V}^e$. (See paper II for a treatment of the extra ultrasonic absorption from the harmonic variation of \underline{T}_c with the sound wave's $\delta \underline{P}$.)¹⁴⁹¹ For the air-saturated (hence ternary) solutions commonly used, the nature of the consolute point as a true critical point deserves some attention¹⁷⁵.

I. Concluding Remarks

We have reviewed the status of theory and experiment aimed at understanding basic equilibrium and transport properties of fluids, particularly in terms of the few most basic molecular parameters and the classical equations of motion. We have seen many shortcomings in our understanding, particularly in theory. In this final section, we should like to speculate as to what advances are most needed for describing liquids and dense gases.

In equilibrium theory, a list of 'reasonable' expectations might read as follows: 1) use of a small basic set of 'structures' to compose pair distribution functions, as if in variational theory; or a more direct description of liquid structure in a transformed phase space, not necessarily reduced uniformly to the two-body level--less sensitive to errors in small regions of phase space; 2) better representation of molecular interaction than $V(r)$, one with capabilities for nonadiabatic encounters; complementing an improved choice of zero-order degrees of freedom and (quantum phase space) states; and lending itself to flexible yet simple mixing rules for unlike-molecule interactions; 3) more semiempirical entries into fluid theory; tractable variational approaches to $g(r)-1$, and/or truncation of the infinite hierarchy of BGY equations by use of simple, experimental, directly physical parameters describing the medium

of other particles; 4) overhaul of water structure description--also aqueous nonelectrolytes; involving an overhaul of mass action principles (cf. Renon's¹⁶⁹ work) by an appeal to a simply-parameterized partition function still distinguishing chemical species on some few-body level; also involving a rigorous few-body description of structures, yet with room to describe cooperative effects as in dielectric alignment; 5) a coherent explanation of structural, largely chemical, relaxation in aqueous solutions and of phase behavior (duly noting its nonanalytic nature); 6) in elementary fluid reactions, an overhaul of the net representation of degrees of freedom upon reaction; one which allows chemical species distinction, and also remedies inadequacies of the pair potential description; 7) more detail on critical many-body phenomena--on the location of T_c , on explaining exponent differences among systems; real use of the liquid-gas connection, in a comprehensive theory for the dilute gas through the liquid region; (b) better semiempirical, nonanalytic thermodynamics for critical phase behavior, as for use in Fixman theory; 8) developing spectroscopy in mixed/dense media (with their increased number of degrees of freedom and states) for details of internal motion interactions; including linewidth information for 'state' lifetimes.

In transport: 1) modelling of correlation decays in the few-body space parametrically; alternative perturbation summations from many-body theory, for new quasi-

particle descriptions generalizing Prigogine's⁷⁴ approach; more studies on the functionality of $\underline{f}^{(N)}$ in terms of $\underline{f}^{(1)}$, and of $\underline{f}^{(1)}$ in terms of gradients; formalisms for nonthermal processes; 2) less artificial connection of the various time scales of evolution (collisional, kinetic, hydrodynamic); multiple parametric representation of non-Markovian time evolution; 3) clarification of the problem in density-expanding transport coefficients; rational function representations; 4) developing concepts of the nature of collisions in liquids, especially involving polyatomic species; probing the utility of quasi-particle descriptions or of interrupted binary-collision formalisms; analyzing the boundary conditions and other aspects of getting a general form for two-body motion in a medium; learning to average over neglected degrees of freedom by adiabatic, stochastic, or intermediate postulates--possibly in a uniform semiclassical approximation¹³¹; clarifying piggyback and potential contributions; handling multiple relaxation, local nonequilibrium effects; utilizing the best resolution of elementary flow patterns in phase space, perhaps reducing from autocorrelation theory⁵⁴; 5) handling the nature of collisions and fluxes in water and aqueous solutions in particular; remedying the inadequacies of pair potential descriptions; pinning down the role of physical interactions and of the recasting of degrees of freedom upon association; 6) developing spectroscopy as a tool for details of nonadiabatic

encounters, extending the equilibrium applications; 7) utilization of the ω -dependence in transport (even in \underline{D} , as from neutron scattering¹⁵⁶⁰) for full inversion from thermal and mechanical responses to the complete several-body dynamical features--a reversal of the ordinary procedure of testing theories by predictive numerical calculations of the response from the theory.

Our ultrasonic experiments and their analysis have brought us up against several of the stumbling blocks noted above, especially (4),(5), and (7b) under equilibrium, and less directly (4) and (7) under transport. The following two papers outline our findings in these regards. The appendices after them give the details of the apparatus, operating procedure, calibrations, data reduction, and theoretical fittings. We achieve limited advances in our qualitative understanding of liquid-liquid phase behavior and structural relaxation from these investigations. These are reviewed at the end of paper II. To proceed further requires more comprehensive experiment and theory. Specifically, we recommend more isotherms for absorption and velocity measurements, including at least one quite far removed from critical, and perhaps one in the two-phase region (separate measurements in each phase, of course). Thermodynamic data on the phase diagram and vapor pressure should be obtained, to numerically evaluate the derivatives $\partial^2 \mu_1 / \partial n_2 \partial T$ to plug into Fixman theory in place of ad hoc, classical analytic approximations.

This remedies the defects of classical thermodynamics, particularly for the X -dependence of the absorption. It allows essential testing of Fixman's mode-coupling, and removes one obstacle to separating CR and TR effects in α . To remove the other obstacle, the TR theory should be made quantitatively accurate and consonant with the phase behavior (free energy of mixing) by generalizing Renon's¹⁶⁹ theory of associated solutions to relaxation phenomena. Detailed excess volume and heat of mixing data will be necessary to fix the ΔH and ΔV values for reaction steps in the expanded model. The composition dependence for α in at least one other lower consolute system--say, triethylamine/water--should be observed (only the relatively crude level of the present work is necessary) to see the uniformity in relative magnitudes of CR and TR relaxations in lower consolute systems. All of this extra work is probably within the scope of one more doctoral research effort.

References

1. M. Fixman, J. Chem. Phys. 36,1961(1962).
2. K. Kawasaki: a) Proc. Phys. Soc. 90,791(1967); Phys. Rev. 150,291(1966); b) ibid.,A1,1750(1970).
3. L. P. Kadanoff and J. Swift, ibid., 165,310(1968); 166,89(1968); J. Swift, ibid., 173,257(1968).
4. P. D. Adams, H. A. Davies, and S. G. Epstein, eds., The Properties of Liquid Metals (Taylor and Francis, London, 1967); reprinted from Adv. Phys. 16, parts 62-64(1967).
5. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, N.Y., 1954): a) Chs. 6,10; b) 541 ff., 582 ff.; c) 321 ff.; d) 695; e) 468; also 492; f) Ch. 10; g) 498 ff.; h) §7.3; i) Ch. 8; j) 647 ff.; k) §9.1; l) §§3.10,3.B; m) 248 ff.; n) §§3.8,3.9; o) 114 ff. p) 304 ff.; q) 534.
6. J. deBoer and G. E. Uhlenbeck, eds., Studies in Statistical Mechanics (North-Holland, Amsterdam, 1962): a) Vol. 3; b) Vol. 2; c) Vol. 1.
7. P. Heller, Rep. Prog. Phys. 30,731(1967).
8. L. M. Stacey, B. Pass, and H. Y. Carr, Phys. Rev. Lett. 23,1424(1969).
9. V. F. Nozdrev, Applications of Ultrasonics in Molecular Physics (Gordon and Breach, N.Y., 1963), 265 ff.
10. F. P. Buff and R. A. Lovett, in Simple Dense Fluids, eds. H. L. Frisch and Z. W. Salsburg (Academic, N.Y., 1968), 17ff.
11. S. A. Rice, J. P. Boon, and H. T. Davis, ibid., 252 ff. a) 262 ff.; b) 259; c) 260 ff.; d) 278 ff.; e) 326-328; f) §3.2; g) 329-332; h) 279 ff.; i) §2.5.
12. M. S. Green and J. V. Sengers, eds., Critical Phenomena (N. B. S. Misc. Publ. 273, 1966): a) 165 ff.; b) 178 ff.; c) 116 ff., and 123 ff.; d) 86 ff.; e) 4; f) 110; g) Sec. "Transport and Relaxation Phenomena"; h) 9 ff.

13. R. P. Mills and L. A. Woolf, The Diaphragm Cell (Australian National U. Press, Canberra, 1968).
14. R. D. Mountain and J. M. Deutch, J. Chem. Phys. 50, 1103 (1969).
15. B. Chu, Ann. Rev. Phys. Chem. 21, 145 (1970).
16. T. A. Litovitz and C. M. Davis, in Physical Acoustics, ed. Warren P. Mason (Academic, N. Y., 1965), Vol. IIA, 293.
17. General accounts of ultrasonics as a probe of transport or relaxation are infrequently presented as a formal bulk viscosity; see the remainder of the volume in ref. 16; also all of refs. 18-20.
18. K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic, N. Y., 1959): a) 361 ff.; b) 38 ff.; c) Ch. 1; d) §§7,8; e) §§10,11; f) §31; g) §66; h) §§27-29; i) §§49, 69; j) §§50-51; Ch. 7; k) §§20-25; Chs. 6,11; l) §97; m) §95; n) §98; o) §73; p) Tables 73-2, 73-3.
19. A. B. Bhatia, Ultrasonic Absorption (Oxford, London, 1967): a) 259 ff.; b) Ch. 4; c) Ch. 9; d) §4.6; e) §14.3; f) 205 ff.; g) Ch. 5; h) §9.1; cf. §5.1, thermal response only; i) §§9.4,9.5; j) §§6.5,6.6, 7.8; k) §§6.2-6.4, Ch. 7; l) §§5.9,5.10,5.13, Chs. 6, 10; m) §10.3; n) §10.1; o) §10.2; p) 199 ff.; q) 137 ff., 152; r) §10.6; s) §8.1; t) 232 ff.
20. S. Flügge, ed., Handbuch der Physik (Springer-Verlag, Berlin, 1961), Vol. 11/1.
21. I. Z. Fisher, Statistical Theory of Liquids (U. Chicago Press, 1964): a) 64 ff., plus recent references by many authors too numerous to mention; b) 54 ff.; c) 46 ff.
22. R. W. James, The Optical Principles of the Diffraction of X-Rays (Cornell U. Press, Ithaca, N. Y., 1948), Ch. 9.
23. P. A. Egelstaff, An Introduction to the Liquid State (Academic, London, 1967): a) 66 ff.; b) 4.
24. For chemical reactions: B. J. Berne and R. Pecora, J. Chem. Phys. 50, 783 (1969); for rotational diffusion: H. Z. Cummins, F. D. Carlson, T. J. Herbert, and G. Woods, Biophys. J. 9, 518 (1969).

25. J. P. McTague, P. A. Fleury, and D. B. DuPre, Phys. Rev. 188,303(1968).
26. J. V. Sengers and A. Levelt-Sengers, Chem. Eng. News 46,104(1968).
27. M. E. Fisher, Rep. Prog. Phys. 30,615(1967): a) 659 ff. b) 624 ff; c) 623 ff.
28. R. B. Griffiths, Phys. Rev. 158,176(1967).
29. J. A. Pryde, The Liquid State (Hutchinson U. Library, London, 1966), 15.
30. E. A. Guggenheim, J. Chem. Phys. 13,253(1945).
31. J. S. Rowlinson, Rep. Prog. Phys. 28,169(1965): a) 174 ff.; b) see § 5.3, 185.
32. F. Zernicke and J. Prins, Z. Phys. 41,184(1927); P. Debye and H. Menke, Ergeb. d. Tech. Röntg. 2(1931).
33. H. Eyring and M. S. Jhon, Significant Liquid Structures (Wiley, N. Y., 1940).
34. H. D. Ursell, Proc. Camb. Phil. Soc. 23,685(1927).
35. J. E. Mayer, J. Chem. Phys. 5,67(1937); with M. G. Mayer, Statistical Mechanics (Wiley, N. Y., 1940).
36. S. A. Rice and P. Gray, The Statistical Mechanics of Simple Liquids (Wiley, N. Y., 1965): a) end of Ch. 2; b) Ch. 3; c) § 3.3; d) 486 ff.; e) 200; f) 270; g) 462.
37. J. E. Lebowitz and O. Penrose, J. Math. Phys. 5,84 (1964).
38. J. Yvon, Actualités Scientifiques et Industriel (Herman et Cie, Paris, 1935); La Théorie Statistique des Fluides et l'Equation d'Etat (Herman et Cie, Paris, 1935).
39. M. Born and H. S. Green, Proc. Roy. Soc. (London) A188, 10(1946); A General Kinetic Theory of Liquids (Cambridge U. Press, N. Y., 1949); H. S. Green, Molecular Theory of Fluids (North-Holland, Amsterdam, 1952).
40. J. G. Kirkwood: a) J. Chem. Phys. 3,300(1935); b) 14, 180(1946); c) 15,72(1947).

41. G. H. A. Cole, Adv. Phys. 8,225(1959).
42. I. Z. Fisher, Soviet Phys. Usp. (Engl. transl.) 5, 239 (1962).
43. N. N. Bogolyubov, Problems of Dynamical Theory in Statistical Physics (State Tech. Press, Gostekhizdat, 1946).
44. Rice, Boon, and Davis, op. cit., 336; P. Egelstaff, op. cit., 86.
45. G. S. Rushbrooke and H. I. Scoins, Phil. Mag. 42,582 (1951); Proc. Roy. Soc. A216,203(1953).
46. L. S. Ornstein and F. Zernicke, Proc. Acad. Sci. Amst. 17,793(1914).
47. J. K. Percus, Phys. Rev. Lett. 8,462(1962); with G. J. Yevick, Phys. Rev. 110,1(1958).
48. L. Verlet, Physica 30,95(1964).
49. Yi-Der Chen, thesis, Penn. State. U., March, 1970 (unpubl.); with W. A. Steele, J. Chem. Phys. 52,5284 (1970); 54,703(1971).
50. G. S. Rushbrooke and M. Silbert, Mol. Phys. 12,505(1967) J. S. Rowlinson, ibid., 12,513(1967).
51. J. E. Mayer and E. W. Montroll, J. Chem. Phys. 9,2,626 (1941); J. deBoer, Rep. Prog. Phys. 12,305(1949); with A. Michels, Physica 6,97(1939).
52. R. W. Zwanzig, J. Chem. Phys. 22,1420(1954); J. A. Barker and D. Henderson, ibid., 47,4714(1967); with W. R. Smith, ibid., 53,508(1970); D. Levesque and L. Verlet, Phys. Rev. 182,307(1969).
53. G. A. Neece and B. Widom, Ann. Rev. Phys. Chem. 20,167 (1969): a) refs. 45-52; b) refs. 40-44.
54. a) B. J. Berne and G. D. Harp, Adv. Chem. Phys. 17,63 (1970); b) B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53,3813(1970).
55. M. E. Fisher, J. Math. Phys. 5,944(1964).
56. L. P. Kadanoff, et al., Rev. Mod. Phys. 39,395(1967), 417.
57. F. London, Z. f. Physik 63,245(1930). Modern account:

- J. O. Hirschfelder, ed., Adv. Chem. Phys. 12(1967).
58. H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Oxford, London, 1971): a) part 4; b) Chs. 11,12; c) §3.3.
 59. C. Domb, Phil. Mag. Suppl. 9,151(1960).
 60. T. D. Lee and C. N. Yang, Phys. Rev. 87,410(1952); R. B. Griffiths, ibid., 158,176(1967).
 61. C. J. Pings and R. K. Teague, Phys. Lett. 26A,496(1968); J. Chem. Phys. 48,4973(1968).
 62. B. Widom, ibid., 43,3898(1965).
 63. W. Botch and M. Fixman, ibid., 36,3100(1962); 42,199(1965).
 64. K. Kawasaki, Ann. Phys. (N. Y.), 1970 (in press).
 - 64X. M. H. C. Knudsen, Kinetic Theory of Gases (Methuen, 1946); W. Crookes, Phil. Trans. 172,387(1882).
 65. L. Euler, Principes Généraux du Mouvement des Fluides (Hist. de l'Acad. de Berlin, 1755); D. Bernoulli, Hydrodynamica (Argentorati, 1738); I. Newton, Principia (Le Seur et Jacquier, 1686).
 66. H. Lamb, Hydrodynamics (Dover, N. Y., 1932).
 67. L. D. Landau and E. M. Lifshitz, Fluid Mechanics (Pergamon, London, 1959): a) §§1,2,6,7,15,49; b) §49; c) §§49,77; d) 224.
 68. C. L. M. H. Navier, Mém. de l'Acad. des Sciences 6,389(1822); G. Stokes, Trans. Camb. Phil. Soc. 8,287(1845).
 69. P. M. Morse, in Handbuch der Physik, ed. S. Flügge. (Springer-Verlag, Berlin, 1961), Vol. 11/1.
 70. S. Fujita, Introduction to Non-Equilibrium Quantum Statistical Mechanics (W. B. Saunders, Philadelphia, 1966).
 71. R. M. Mazo, Statistical Mechanical Theories of Transport Processes (Pergamon, Oxford, 1967): a) 28 ff. b) 53 ff.; c) Ch. 10; d) 61, 66-7; e) Ch. 5; f) 66 g) Chs. 7-9; h) Chs. 8,9; i) 119 ff.; j) 118; k) 91
 72. S. Chapman and T. G. Cowling, The Mathematical Theory

- of Non-Uniform Gases (Cambridge U. Press, 1952);
a) Ch. 17; b) Chs. 5, 6.
73. J. von Neumann, Nachr. Ges. Wiss., Göttingen 1,245,273 (1927); Mathematische Grundlagen der Quantenmechanik (Springer-Verlag, Berlin, 1932).
 74. I. Prigogine, Non-Equilibrium Statistical Mechanics (Interscience, N. Y., 1962): a) Ch. 1; b) Chs. 12, 14; c) Ch. 11.
 75. R. L. Liboff, Introduction to the Theory of Kinetic Equations (Wiley, N. Y., 1969): a) Ch. 2; b) 180.
 76. J. W. Gibbs, Elementary Principles of Statistical Mechanics, Vol. 2 of Collected Works... (Yale U. Press, New Haven, Conn., 1948).
 77. S. A. Rice and H. L. Frisch, Ann. Rev. Phys. Chem. 11, 187(1960): a) II.3; b) 215 ff.; c) 203.
 78. G. V. Chester, Rep. Prog. Phys. 26,411(1963): a) 433 ff. b) 445 ff.; c) 415; d) 417.
 79. F. Reif, Fundamentals of Statistical and Thermal Physics (McGraw-Hill, N. Y., 1965), Ch. 12.
 80. J. H. Jeans, The Dynamical Theory of Gases (Dover, N.Y., 1954), Ch. 11.
 81. L. Boltzmann, Vorlesungen über Gastheorie (2 vols; Barth, Leipzig, 1912); Engl. Transl. by S. G. Brush, Lectures in Gas Theory (U. C. Press, Berkeley, 1964); also, S. B. Akad. Wiss. Wien (II) 58, 517(1872).
 82. D. Enskog, Archiv för Matematik, Astronomi, och Fysik 16,§16(1922); in German.
 83. W. Pauli, in Probleme der Moderne Physik, ed. P. Debye (Hirzel, Leipzig, 1928), 30.
 84. H. Grad, Communication in Pure and Applied Mathematics 2,331(1949).
 85. H. Grad, in Handbuch der Physik, ed. S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12.
 86. C. S. Wang-Chang and G. E. Uhlenbeck, Transport Phenomena in Polyatomic Molecules (U. Michigan Publ. CM-681, 1951); with J. deBoer, in Studies in Statistical Mechanics 2,243(1964).

87. D. Enskog, Kgl. Svenska Vetenskap. akad. Handl. 63, no. 4(1922).
88. N.N. Bogolyubov, J. Phys. U. S. S. R. 10,256,265(1946).
89. J. D. Dorfman and E. G. D. Cohen, Phys. Lett. 16,124 (1965); J. V. Sengers, Phys. Rev. Lett. 15,515 (1965); J. Weinstock, ibid., 140,A461(1965); K. Kawasaki and I. Oppenheim, ibid., 139,A1763(1965).
90. H. Eyring, J. Chem. Phys. 4,283(1936); with J. H. Kincaid and A. E. Stearn, Chem. Revs. 28,301(1941); with S. Glasstone and K. J. Laidler, The Theory of Rate Processes (McGraw-Hill, N. Y., 1941).
91. S. Chandrasekhar, Rev. Mod. Phys. 15,1(1943).
92. R. A. Fisher and R. O. Watts, J. Chem. Phys. (subm. for publ., 1971).
93. S. A. Rice and H. R. Allnatt, ibid., 34,2144,2156(1961).
94. refs. 63-74 and 88 of Rice, Boon, and Davis, op. cit.
95. M. H. Cohen and D. Turnbull, ibid., 31,1164(1959).
96. L. van Hove, Physica 21,517(1955); 23,441(1957).
97. R. Brout and I. Prigogine, ibid., 22,621(1956).
98. I. Prigogine, G. Nicolis, and J. Misguich, J. Chem. Phys. 45,4516(1965).
99. H. Nyquist, Phys. Rev. 32,110(1928); H. B. Callen and T. A. Welton, ibid., 83,34(1951).
100. M. S. Green, J. Chem. Phys. 20,1281(1952); 22,398(1954); and others more recent--see refs. 9-12 of Mazo, ref. 71 here.
101. R. Lucas, J. Phys. Rad. 8,41(1937).
102. A. E. Brown and E. G. Richardson, Phil. Mag. 4,705 (1959); A. E. Brown, Acustica 18,169(1967).
103. M. Fixman, J. Chem. Phys. 36,310(1962).
104. M. Fixman, ibid., 36,1957(1962).
105. M. P. Puls, thesis, McMaster U., May, 1970, 126, 137-8; K. Kawasaki, Prog. Theor. Phys. 40,930(1968).

106. R. A. Ferrel, et al., Phys. Rev. Lett. 18,891(1967).
107. L. P. Kadanoff, J. Phys. Soc. Japan, 26,S122(1969).
108. P. Debye, Polare Molekullen (Hirzel, Leipzig, 1929).
109. V. V. Daniel, Dielectric Relaxation (Academic, London, 1967).
110. a) Y. Toyazawa, Prog. Theor. Phys. (Kyoto) 20,53 (1958); b) J. van Kranendonk, thesis, Univ. of Amsterdam, Holland, Dec. 17, 1952; d) G. Birnbaum, Adv. Chem. Phys. 12,487(1967).
111. A. Abragam, The Principles of Magnetic Resonance (Oxford, London, 1961).
- 111a. T. B. Bottomore, Early Writings of Karl Marx (McGraw-Hill, N. Y.).
112. K. Takayanagi, Prog. Theor. Phys. 25,1S(1963).
113. R. Gordon, W. Klemperer, and J. I. Steinfeld, Ann. Rev. Phys. Chem. 19,215(1969).
114. D. Sette, in Handbuch der Physik, ed. S. Flügge (Springer-Verlag, Berlin, 1961), Ch. A.III.
115. F. W. Billmeyer, Jr., Textbook of Polymer Science (Interscience, N. Y., 1962), Ch. 6; P. Meares, Polymers: Structure and Bulk Properties (D. van Nostrand, London, 1968), Chs. 6-9.
116. J. V. V. Kasper and G. C. Pimentel, Phys. Rev. Lett. 14 (1965); Appl. Phys. Lett. 5,231(1964); K. L. Kompa and G. C. Pimentel, J. Chem. Phys. 47,857 (1967); R. E. Honig and J. R. Woolston, Appl. Phys. Lett. 2,138(1963); A. deMaria and C. J. Ultee, ibid., 2,67(1966).
117. J. A. Pople, Disc. Far. Soc. 15,35(1953).
118. See, for example, Table I-A of ref. 5.
119. See tables in the Handbook of Chemistry and Physics (Chem. Rubber Publ. Co., Cleveland, Ohio); note that the organics cluster about the same value of specific heat, implying a heat capacity proportional to mass or size.
120. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water (Oxford, London, 1969), §§3.5,

- 4.4, 4.7; H. L. Strauss, Ann. Rev. Phys. Chem. 19, 419(1968).
121. International Critical Tables (McGraw-Hill, N. Y., 1929), Vol. 5; a) 81; b) 213-4.
 122. D. F. Eggers, Jr., N. W. Gregory, G. D. Halsey, Jr., and B. S. Rabinovitch, Physical Chemistry (Wiley, N. Y., 1964): a) § 6.4; b) 662 ff.
 123. G. N. Lewis and M. Randall (rev. K. S. Pitzer and L. Brewer), Thermodynamics (McGraw-Hill, N. Y., 1961), 438 ff.
 124. J. Lamb, in Physical Acoustics, ed. W. P. Mason (academic, N. Y., 1965), Vol. IIA, 227 ff.
 125. E. R. Andrew, Nuclear Magnetic Resonance (Cambridge U. Press, 1955).
 126. For D in cryogenic liquids: G. T. Preston, T. W. Chapman and J. M. Prausnitz, Cryogenics 7, 274(1967); in normal liquids: P. A. Johnson and A. L. Babb, Chem. Rev. 56, 387(1965); D. W. McCall, D. C. Douglass and E. W. Anderson, J. Chem. Phys. 31, 1555 (1959).
 127. Herzfeld and Litovitz, op. cit., 328.
 128. S. Golden, Quantum Statistical Foundations of Chemical Kinetics (Oxford, London, 1969).
 129. D. Sette, in Handbuch der Physik, ed. S. Flügge (Springer-Verlag, Berlin, 1961), Vol. 11/1, 287 ff.
 130. D. Rapp and T. Kassal, Grumann Res. Dept. Rept. RE-345.
 131. W. H. Miller, J. Chem. Phys. 53, 1949, 3587(1970).
 132. C. Sluitjer, in Dispersion and Absorption of Sound by Molecular Processes, ed. D. Sette (Academic, N. Y., 1963), 338 ff.
 133. H. O. Kneser, in Physical Acoustics, ed. W. P. Mason (Academic, N. Y., 1965), Vol. IIA: a) § II.B; b) 193 ff.
 134. M. Eigen and L. deMayer, in Techniques of Organic Chemistry, ed. Weissberger, et al. (Wiley, N. Y., 1962), Vol. 8, Part 2; see esp. Eq. (II.3.90b).

135. J. Lamb, op. cit., §§3,4.
136. S. Mizushima, Structure of Molecules (Academic, N. Y., 1954).
137. D. Sette, op. cit., 339 ff.
138. W. Steele and R. Pecora, J. Chem. Phys. 42,1863(1965).
139. R. C. Millikan and L. A. Osburg, ibid., 41,2196(1964).
140. F. deMartini and L. Ducuing, Phys. Rev. Lett. 17, 117 (1966).
141. J. J. Martin, Ind. Eng. Chem. 59,34(1967).
142. A. D. Buckingham and J. A. Pople, Trans. Far. Soc. 51, 1173(1955).
143. H. B. Levine and D. R. McQuarrie, Physica 31,749(1965); J. Chem. Phys. 44,3500(1966).
144. D. E. Stogryn, ibid., 50,4967(1969).
145. H. Reiss, H. L. Frisch, and J. L. Lebowitz, ibid., 31, 3699(1959).
146. R. M. Gibbons, J. Mol. Phys. 17,81(1968); with W. A. Steele, ibid., 15,567(1968).
147. A. D. Buckingham, Disc. Far. Soc. 43,205(1967).
148. J. A. Barker and R. O. Watts, Chem. Phys. Lett. 3,144 (1969).
149. J. M. Prausnitz, Molecular Thermodynamics of Fluid Phase Equilibria (Prentice-Hall, Englewood Cliffs, N. J., 1969): a) Chs. 5-7; b) §5.10; c) §6.15; d) §7.6; e) §7.7; f) §7.10; g) §7.11; h) 239; i) §10.8
150. J. S. Rowlinson, Liquids and Liquid Mixtures (Batterworths, London, 1959): a) Ch. 5; b) 230; c) 181; d) 183.
151. Hirschfelder, Curtiss, and Bird, op. cit., §7.6d; and numerous recent articles.
152. R. G. Gordon, J. Chem. Phys. 44,1830(1966).
153. J. C. Light, Adv. Chem. Phys. 19,1(1971); M. Karplus,

- R. N. Porter, and R. D. Sharma, J. Chem. Phys. 43, 3259(1965).
154. D. R. Herschbach, Adv. Chem. Phys. 10, 319(1966); R. J. Beuhler, Jr. and R. B. Bernstein, Chem. Phys. Lett. 2, 166(1968); Y. T. Lee, et. al., J. Chem. Phys. 51, 455(1969); 53, 3385(1970); F. P. Tully, Y. T. Lee, and R. S. Berry, Chem. Phys. Lett. 9, 80(1971); J. Geddes, H. F. Krause, and W. L. Fite, J. Chem. Phys. 52, 3296(1970); C. Maltz, Chem. Phys. Lett. 9, 251(1971), refs. 1-3.
 155. W. P. Mason, Trans. Amer. Soc. Mech. Eng. 69, 359(1947); Piezoelectric Crystals and Their Application to Ultrasonics (D. van Nostrand, Princeton, N. J., 1950); the first actual use in the critical region is under way in the laboratory of C. J. Pings at this institution.
 156. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water (Oxford, London, 1969): a) 148, and Tables 3.18, 4.2; b) §4.2; c) 222; d) §4.6e; e) §2.1b; f) 56, 257, 190ff.; g) §§4.4b, 4.6b; h) §4.7; i) §5.2; j) §4.6a; k) §5.3; l) §4.8a; m) §4.7, esp. 240; n) 112; o) 219 ff.; p) §4.6d
 157. A. Eucken, Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl. 38(1946); 1(1949); Z. Electrochem. 52, 255 (1948).
 158. L. Hall, Phys. Rev. 73, 775(1948).
 159. D. Sette, Phys. Rev. 78, 476(1950); E. H. Carnevale and T. A. Litovitz, J. Acoust. Soc. Am. 27, 547 (1955).
 160. A. Ben-Naim, J. Chem. Phys. 52, 5531(1970).
 161. G. H. Haggis, J. B. Hasted, and T. J. Buchanan, ibid. 20, 1452(1952).
 162. J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes (Dover, N. Y., 1964), 41, and Ch. 16.
 163. J. H. Andreae, P. D. Edmonds, and J. F. McKellar, Acustica 15, 74(1965).
 164. D. Sette, op. cit., §27.
 165. T. L. Hill, An Introduction to Statistical Thermodynamics (Addison-Wesley, Reading, Mass., 1960), §20.2.

166. J. L. Lebowitz, Phys. Rev. 133A, 895(1964); with J. S. Rowlinson, J. Chem. Phys. 41, 133(1964).
167. E. A. Guggenheim, Mixtures (Oxford, London, 1952); Applications of Statistical Mechanics (Oxford, London, 1966).
168. R. L. Scott, J. Chem. Phys. 25, 193(1956).
169. H. Renon and J. M. Prausnitz, Chem. Eng. Sci. 22, 299, errata 1891(1967).
170. G. Thomaes and J. van Itterbeek, Mol. Phys. 2, 372 (1959); J. P. Boon and G. Thomaes, Physica 28, 1074 (1962); 29, 208(1963).
171. E. McLaughlin, Chem. Rev. 64, 389(1964).
172. A. V. Anantaraman, A. B. Walters, P. D. Edmonds, and C. J. Pings, J. Chem. Phys. 44, 2651(1966); M. P. Puls, op. cit.
173. J. D. Cox and E. F. G. Herington, Trans. Far. Soc. 52, 926(1956).
174. M. Cevolani and S. Petralia, Atti Accad. Naz. Lincei 2, 674(1952).
175. R. B. Griffiths and J. C. Wheeler, Phys. Rev. A2, 1047 (1970).

Rederivation and Analysis of Fixman's Theory of Excess
Sound Absorption Near Fluid Critical Points*

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We retrace the thermodynamic and hydrodynamic analysis used by M. Fixman (J. Chem. Phys. 36, 1961 (1962)) in the first quantitative explanation of the anomalously large sound absorption near fluid critical points. With some oversights and ambiguities corrected, the basic theory is seen to be firmly based in classical thermodynamics and hydrodynamics. The use of the Ornstein-Zernike, Debye, and Flory-Huggins models for reduction of key quantities appears necessary for thermodynamic consistency. For analysis of experimental data, Fixman's theory is preferred over alternative theories, though no one theory is truly satisfactory. With a view toward interpreting our data presented in the following paper (J. Chem. Phys. xx, xxxx, (1971)), we argue the applicability of Fixman theory in systems having a strong background of additional (thermal) relaxation.

* Research sponsored by AFOSR (SRC)-OAR, USAF Grant No. AFOSR-68-1382.

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Introduction

As a probe of energy exchange, especially in simple fluid systems, measurement of the ultrasonic pressure amplitude attenuation or absorption coefficient α and of the sound velocity β has shown much utility. 'Thermal' relaxation of internal degrees of freedom, such as vibrational, or of local structure, as in chemical association, causes absorption and dispersion behavior whose details of magnitude, temperature- and composition-dependence can often be correlated closely with kinetic and thermodynamic parameters of the system.¹ Near critical points - and here we speak specifically of gas-liquid and binary liquid-critical points - additional strong absorption arises,² somehow tied to the presence of strong fluctuations in density or composition, up to macroscopic size. Early attempts at an explanation included Lucas'³ proposal that the fluctuations undergo differential acceleration relative to the bulk fluid because of their different density, thus causing excess viscous losses; and work by Richardson and Brown⁴ ascribing it in at least one system to an apparent loss of energy by Rayleigh scattering. Both models fail quantitatively, for both give too small a magnitude for the absorption, and dependences on frequency not generally observed.

Using irreversible thermodynamics as a framework unifying our treatment with that of ordinary thermal relaxation, we shall retrace the approach of M. Fixman,⁵ which proved the first successful model. The primary thermodynamic quantity to relate to absorption and dispersion is the effective complex compressibility (adiabatic) \underline{K}_s^ω giving the volume response of the system to the periodic pressure perturbation of the sound wave, hence the measure of reversible and irreversible work done. Substituting a complex compressibility in the wave equation for the pressure variation δp ,

$$\frac{\partial^2 \delta p}{\partial t^2} - \frac{1}{\rho K} \nabla^2 \delta p = 0 , \quad (1)$$

where $(\rho K)^{-1} = \beta^2 = \text{squared sound velocity}, \quad (2)$

gives a solution

$$\delta p = \delta p_0 e^{-\alpha x} e^{i(kx - \omega t)} \quad (3)$$

with $\alpha = \frac{\omega \rho \beta}{2} \text{Im } K. \quad (4)$

To calculate \underline{K} , it is generally sufficient to assume expansions of the volume and entropy differentials $\underline{\delta V}$ and $\underline{\delta S}$ in the state variables⁶ (also sound wave progress variables)

δT , δp , and $\delta \xi$; the latter is some order parameter for the internal degrees of freedom:

$$\delta S = \frac{C_p^\infty}{T} \delta T - v \theta^\infty \delta p + \frac{H'}{T} \delta \xi \quad (5)$$

$$\delta V = v \theta^\infty \delta T - v K_T^\infty \delta p + v' \delta \xi. \quad (6)$$

The superscript ' ∞ ' refers to processes in the limit of infinite frequency, where the internal degree of freedom is frozen. The quantities C_p , θ , H' , K_T , and v' are respectively isobaric heat capacity, thermal expansivity, an internal enthalpy, isothermal compressibility, and an internal volume change. The first equation is used in the form $\delta S=0$ to eliminate one variable and to express the lack of spatial heat transfer to first order during sound passage. A simple $\delta V \leftrightarrow \delta p$ relation to obtain K_s^ω is obtained with the addition of kinetic equation for $\delta \xi$, assumed to be

$$\frac{d}{dT} \delta \xi \equiv \delta \dot{\xi} = -L \delta Z. \quad (7)$$

Here Z is some ordering force associated with $\delta \xi$,

$$\delta Z = -\frac{H'}{T} \delta T + v' \delta p + \phi \delta \xi, \quad (8)$$

and ϕ is defined by the above equation. The total solution is then

$$K_s^\omega = K_s^\infty + \left\{ \frac{[V' - V\theta^\infty H']^2}{V\phi[1 + (H')^2/TC_p^\infty\phi]} \right\} \frac{1}{1 + i\omega\tau}, \quad (9)$$

$$\text{with } \tau = (L\phi)^{-1}. \quad (10)$$

This yields

$$\text{Im } K_s^\omega = - \left\{ \right\} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (11)$$

and thus a typical relaxation curve for α , proportional to $\frac{\omega^2\tau}{1 + \omega^2\tau^2}$. We have throughout neglected the extra shear

viscous and thermal conduction losses, which require extra terms in Eq. (1), since these are always additive for our uses.⁷

For our purposes, the internal degree of freedom is the local density or concentration. Treating binary systems more specifically, this is the local concentration (by mass, volume, or mole fraction, as is convenient) \underline{c}_2 of component 2. Its kinetic equation (Eqs. 7 and 8 combined) is a dissipative diffusive equation whose form outside the critical region is taken as⁸

$$\rho \dot{c}_2 = \alpha \left(\frac{\partial \mu}{\partial c_2} \right) \nabla^2 c_2 + \left[\alpha \left(\frac{\partial \mu}{\partial T} \right) + \epsilon \right] \nabla^2 T + \alpha \left(\frac{\partial \mu}{\partial p} \right) \nabla^2 \delta p. \quad (12)$$

Here μ is a chemical potential $\mu_1 - \mu_2$, with μ_1, μ_2 the chemical potential per unit concentration, and α, ϵ are constants; also $\frac{\partial \mu}{\partial p} = \underline{v}'$ and $\frac{\partial \mu}{\partial c_2} = \phi$ in the terminology of Eq.(8). This choice of kinetic equation describes the baro-diffusion ($\delta T \equiv 0$) or thermal diffusion ($\delta p \equiv 0$) mechanisms. The former yields a response of

$$\delta c_2 = \frac{\alpha \underline{v}' k^2}{\rho (i\omega + D_{12} k^2)} \delta p, \quad (13)$$

where \underline{k} is the propagation vector magnitude as in Eq. (3), and an absorption

$$\alpha = \frac{\rho \beta}{2} \frac{(\underline{v}')^2}{V \phi} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (14a)$$

$$\tau = \alpha \phi / \rho \beta^2 \equiv D_{12} / \beta^2. \quad (14b)$$

While ϕ vanishes at the critical point, so does \underline{D}_{12} and the absorption is not only finite but negligibly small.

Fixman's Development

Clearly the diffusion of \underline{c}_2 follows a modified equation in the critical region. The thermodynamic equations (5) and (6) may also need to be taken to higher order. Fixman⁹ realized that the differential of the local Gibbs energy density $\delta \underline{G}$ from which (5) and (6) are derived must include a quadratic term in $(\delta \underline{c}_2)^2$, since the linear term is vanishing. Taking \underline{c}_2 as \underline{n}_2 , the molecular or molar density, he obtains

$$\begin{aligned} dG \Big|_{p,T} &= \mu_1 dn_1 + \mu_2 dn_2 \\ &= [\mu_1^0 + \left(\frac{\partial \mu_1}{\partial n_2} \right) \delta n_2] dn_1 + [\mu_2^0 + \left(\frac{\partial \mu_2}{\partial n_2} \right) \delta n_2] dn_2, \quad (15) \end{aligned}$$

where μ_1^0 is the bulk or average value of μ_1 . The Gibbs-Duhem relation $n_1 d\mu_1 + n_2 d\mu_2$ yields

$$dG = \mu_1^0 dn_1 + \mu_2^0 dn_2 + \left(\frac{\partial \mu_1}{\partial n_2} \right) \left[dn_1 \delta n_2 - \frac{n_1}{n_2} dn_2 \delta n_2 \right]. \quad (16)$$

The relation of \underline{dn}_1 and \underline{dn}_2 in the fluctuation is taken as preserving the molar volume,

$$dV = \frac{\partial V}{\partial n_1} dn_1 + \frac{\partial V}{\partial n_2} dn_2 \equiv \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \longrightarrow 0, \quad (17)$$

corresponding to isochoric propagation conditions which can be related later to the proper adiabatic conditions. Integration over the fluctuation volume yields

$$\delta G = \int dG = - \frac{1}{2n_2} \bar{V}_1 \left(\frac{\partial \mu_1}{\partial n_2} \right)_{p,T,n_1} (\delta n_2)^2 \quad (18)$$

for the anomaly-containing quadratic term. Additionally, Fixman notes that we should make the replacement,

$$(\delta n_2)^2 \longrightarrow (\delta n_2)^2 + \kappa^{-2} |\nabla \delta n_2|^2, \quad (19)$$

where κ is the inverse correlation length of the critical region pair distribution function $\underline{g(R)}$ in Ornstein-Zernike¹⁰ form,

$$G(R) = g(R) - 1 \xrightarrow{R \rightarrow \infty} \frac{a}{R} e^{-\kappa R}. \quad (20)$$

κ is very temperature-sensitive but $\left(\frac{\partial \mu_1}{\partial n_2} \right)$ in Eq. (18) is proportional to κ^2 so this extra term in $\underline{\delta G}$ is as a whole negligible. Now make the good approximation

$$\begin{aligned} \delta S &= \frac{\partial}{\partial T} \delta G \Big|_{p,T} \\ &\approx - \frac{1}{2n_2 \bar{V}_1} \left(\frac{\partial^2 \mu_1}{\partial n_2 \partial T} \right)_{p,n_1} (\delta n_2)^2. \end{aligned} \quad (21)$$

We take some liberties with Fixman's original presentation from here on, as by keeping $\underline{n_2}$ as the concentration variable rather than going over to the volume fraction ϕ_2 ; our final result is unchanged.

The dynamic response of $(\underline{\delta n_2})^2$ must now be computed from the diffusion equation with critical region corrections. Now, $(\underline{\delta n_2})^2$ is not the square of the sound-driven fluctuation, which can be made arbitrarily small by reducing the sound intensity. Rather, $(\underline{\delta n_2})^2$ has a finite equilibrium average related to the 2-2 pair distribution function $\underline{G^{22}(R)} \equiv \underline{G(R)}$:

consider

$$\langle \delta n_2(\vec{R}_1) \delta n_2(\vec{R}_2) \rangle = \frac{n_2}{V} \delta(\vec{R}_{12}) + n_2^2 G(\vec{R}_{12}). \quad (22)$$

Assuming Fourier decompositions of $\underline{\delta n_2(\vec{R})}$ and of $\underline{G(\vec{R})}$ as

$$\delta n_2(\vec{R}) = \int d\vec{k} \, n_{\vec{k}} e^{i\vec{k} \cdot \vec{R}} \quad (23a)$$

$$G(\vec{R}) = \int d\vec{k} \, G_{\vec{k}} e^{i\vec{k} \cdot \vec{R}}, \quad (23b)$$

a few manipulations yield

$$\langle \delta n_2(\vec{R})^2 \rangle = \frac{n_2}{V} \int d\vec{k} + n_2^2 \int d\vec{k} \, G_{\vec{k}}. \quad (24)$$

The first term is dropped if we are considering a volume considerably larger than the fluctuation.

The periodic temperature excursion δT due to the sound wave alters the dynamics of the spontaneous fluctuations, adding a correction to $(\delta n_2)^2$ that is correlated to the sound wave. The resulting energy exchange with the sound wave has a phase lag and causes a loss or absorption of energy. The dynamics of the decay of spontaneous fluctuations in the singlet distribution c_2 are given by Fixman's modified diffusion equation¹¹ (less the non-anomalous direct driving terms in δp , δT of the sound wave),

$$\rho \dot{c}_2 = - \frac{h\rho}{2} \kappa^2 [v^2 c_2 - \kappa^{-2} v^2 v^2 c_2] . \quad (25)$$

The diffusion constant product $\alpha\phi$ of Eq. (12) has been written in the new variables \underline{h} and κ^2 , from the thermodynamic expression for κ^2 in terms of $\partial\mu_1/\partial n_2$ in the Ornstein-Zernike model,

$$\frac{4\pi a}{\kappa^2} = - \frac{\bar{V}_1}{n_2} \left[\frac{kT}{(\partial\mu_1/\partial n_2)} + \frac{1}{\bar{V}_1} \right] . \quad (26)$$

The relation $\underline{d\mu} = (\rho/n_2 m_1 m_2) \underline{d\mu}_1$ is also used to express \underline{h} as¹³

$$h = \frac{\alpha \bar{V}_1^2 \bar{V}_2 k T \rho}{m_1^2 m_2 c_2^2 2\pi a \phi_2} , \quad (27)$$

where \bar{V}_i , m_i , c_i , and ϕ_i are respectively partial molar volume, molecular mass, weight- and volume-fraction concentrations, and a is as in Eq. (26). The second or correction term in Eq. (25) has been derived by Fixman¹¹ and justified as consistent with the critical-region form of the free-energy density in a fluctuation.

The dynamic response of $(\delta n_2)^2$ to the sound wave perturbation δT is more readily expressed in terms of the response of $G(R)$. Intuitively, Fixman adapts the diffusion equation (25) for the pair density $G(R)$ simply by doubling the diffusion constant $h/2$,

$$\dot{G} = h \kappa^2 [\nabla^2 G - \kappa^{-2} \nabla^2 \nabla^2 G] . \quad (28)$$

The equilibrium solution to Eq. (28) is the proper Ornstein-Zernike form,

$$G(R) \xrightarrow{R \rightarrow \infty} \frac{a}{R} e^{-\kappa R} . \quad (29)$$

The primary temperature sensitivity is in κ^2 , such that Fixman¹⁴ adds the term

$$h \left(\frac{\partial \kappa^2}{\partial T} \right) \delta T \nabla^2 G \quad (30)$$

to Eq. (28). There is no way to treat a spatial dependence of δT , so the implicit assumption is that the sound wavelength is very large relative to the fluctuation size, or

$$\lambda_{\text{sound}} \gg \kappa^{-1} ; \quad (31)$$

this is consistent with dropping the first term in Eq. (24). A perturbation solution in Fourier space yields a correction δG_k to the component $G_k^0 = a/(2\pi^2 [k^2 + \kappa^2])$, given by

$$\delta \dot{G}_k = i\omega \delta G_k = -h k^2 (k^2 + \kappa^2) \delta G_k - h k^2 \left(\frac{\partial \kappa^2}{\partial T} \right) \delta T G_k^0 . \quad (32)$$

The fluctuating excess entropy δS of Eq. (21) is, using Eqs. (21), (26) and (32),

$$\delta S = \delta T \frac{kT}{4\pi^2} h \left(\frac{\partial \kappa^2}{\partial T} \right)^2 \int dk \frac{k^4}{(k^2 + \kappa^2) [i\omega + h k^2 (k^2 + \kappa^2)]} . \quad (33)$$

This is equivalent to an excess heat capacity Δ_M per mole,

$$\Delta_M = T \frac{\delta S}{c \delta T} \frac{N_0}{(n_1 + n_2)} \quad (34)$$

N_0 = Avogadro's number

which is clearly complex. The compressibility is then computed from Eqs. (5) and (6) by altering C_p^∞ to $C_p^\infty + \Delta_M$ and neglecting the small direct driving terms in δp and

$\delta \xi = \delta n_2$, $\frac{(H'/T) \delta n_2}{\bar{V}_2 \delta n_2}$ and $\bar{V}_2 \delta n_2$. We have, dropping superscripts,

$$\delta V = V \theta \delta T - V K_T \delta P, \quad (35)$$

and from $\delta S = 0$,

$$\delta V = \left[T \frac{(V \theta)^2}{(C_p + \Delta_M)} - V K_T \right] \delta p. \quad (36)$$

Expanding $(C_p + \Delta_M)^{-1}$ with Δ_M assumed small and using

$$\frac{TV \theta^2}{C_p^2} = K_T \frac{(C_p - C_V)}{C_p^2}, \quad (37)$$

(equality holds for C_p replaced by the net $C_p + \Delta$), we obtain an absorption

$$\alpha = \frac{\omega}{2\beta} \frac{(\gamma-1)}{C_p} \text{Im } \Delta_M, \quad (38)$$

where $\gamma = C_p/C_V$ as usual. This is Fixman's result. More rigorous attention to the mathematics, esp. in Eq. (37), would show small differences for the true adiabatic propagation conditions.