

Neutron Scattering by Fluids and the Law of Corresponding States*

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It is shown that the classical law of corresponding states implies correspondences in the time-displaced pair correlations of fluids, and also in the cross sections for neutron and x-ray scattering. A measurement of the scattering at one temperature and pressure by one fluid of a class of fluids can thus be used to determine the scattering at corresponding temperatures and pressures of all fluids of the class. Other applications, in the study of molecular fluids and in the separation of the self-correlation from the general correlation, are pointed out.

INTRODUCTION

THE law of corresponding states shows how the thermodynamic and transport properties of a family of fluids can be determined from the properties of one member of the family.¹⁻³ As has been known for many years, the principle applies to any class of substances for which the laws of intermolecular potential can be brought into coincidence by changes of length and energy scales. In this note it is pointed out that the law of corresponding states can be readily extended to cover the scattering of neutrons (and x rays) by fluids,⁴ and some ways are suggested in which this extension may be useful.

BASIC THEORY

We restrict our attention at first to classical, monomolecular fluids in which the intermolecular force is central and two-body. It will be assumed, in the conventional way,² that for a class of fluids the intermolecular potentials have the form

$$\phi = \epsilon f(r/\alpha). \quad (1)$$

Here r is the separation of centers of two molecules; α is a length and ϵ is an energy characteristic of a particular fluid in the class. f is an arbitrary function, but is the same for all fluids of the class.

The Hamiltonian for a fluid of the class is then

$$H = \sum_{j=1}^N \frac{1}{2M} \mathbf{p}_j^2 + \sum_{j>l=1}^N \epsilon f(r_{jl}/\alpha), \quad (2)$$

where M is the molecular mass, \mathbf{p}_j the momentum of the j th molecule, and r_{jl} the separation of a pair. The

neutron scattering is determined completely by the time-displaced pair correlation function⁵ $G(\mathbf{r}, t)$ and the time displaced self-correlation $G_s(\mathbf{r}, t)$. Consider the first of these which, for classical systems, is defined as the average number density of molecules at \mathbf{r} after a time t if a molecule was at the origin at time 0. From Eq. (10) of reference 5, specialized to a classical monomolecular fluid, one has

$$G(\mathbf{r}, t) = \sum_{j=1}^N Z^{-1} \int e^{-\beta H} \delta[\mathbf{r} + \mathbf{r}_1(0) - \mathbf{r}_j(t)] d\Gamma. \quad (3)$$

Here Z is the partition function, δ is a three-dimensional Dirac delta function, $\beta = (kT)^{-1}$, $\mathbf{r}_j(t)$ is the position of the j th molecule at time t , and H is given by (2) with the dynamical variables taken at time 0. The integration in (3) is over all of Γ space consistent with the volume V of the system.

One now introduces units of length, mass, and energy appropriate to the particular fluid; the unit of length is α , of mass is M , and of energy is ϵ . The unit of time $[t]$ becomes $\alpha(M/\epsilon)^{1/2}$. Reduced variables, identified by asterisks, are introduced as follows:

$$\mathbf{r}^* = \mathbf{r}/\alpha, \quad (4)$$

$$M^* = 1, \quad (5)$$

$$t^* = t/[t] = t/\alpha(M/\epsilon)^{1/2}, \quad (6)$$

$$T^* = kT/\epsilon, \quad (7)$$

$$V^* = V/\alpha^3, \quad (8)$$

$$P^* = P\alpha^3/\epsilon. \quad (9)$$

(P is pressure, T is temperature.) In Eq. (3), $\mathbf{r}_j(t)$ depends on V , $\mathbf{r}_1(0) \cdots \mathbf{r}_N(0)$, and $\mathbf{p}_1(0) \cdots \mathbf{p}_N(0)$, as well as on t , through the equations of motion of the system. If reduced variables are introduced $\mathbf{r}_j^*(t^*)$ will be a universal (i.e., the same for all fluids of the class) function of the corresponding reduced variables V^* , $\mathbf{r}_1^*(0) \cdots \mathbf{p}_N^*(0)$. Similarly, all of the other functions in the integrand of (3) are seen to be universal functions of the reduced variables. Thus the result of the integration, $G(\mathbf{r}, t)$, will be given in terms of a universal func-

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¹ H. Kammerlingh Onnes and W. H. Keesom, *Enzyklopädie der Mathematischen Wissenschaften* (B. G. Teubner, Leipzig-Berlin, 1912), Vol. V, Part 10, pp. 26, 27.

² D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), Chap. VIII.

³ J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, New York, 1954).

⁴ Note added in proof. The law of corresponding states for transport properties, as derived from time-dependent correlations, has been discussed recently by E. Helfand and S. A. Rice, *J. Chem. Phys.* (to be published).

⁵ L. Van Hove, *Phys. Rev.* **95**, 249 (1954).

tion of the reduced variables \mathbf{r}^* , t^* , and V^* , and of the number of molecules N . For large systems V^* and N will enter only in the combination V^*/N , which will depend on P^* and T^* . It is thus permissible and convenient to consider the state variables to be T^* and P^* , and to write G in terms of a dimensionless universal function G^* of the reduced state variables and the reduced microscopic variables \mathbf{r}^* and t^* :

$$G(\mathbf{r}, t) = \alpha^{-3} G^*(\mathbf{r}^*, t^*; T^*, P^*). \quad (10)$$

An exactly similar argument relates the self-correlation function⁵ to a universal self-correlation G_s^* , as follows:

$$G_s(\mathbf{r}, t) = \alpha^{-3} G_s^*(\mathbf{r}^*, t^*; T^*, P^*). \quad (11)$$

The Van Hove formulas⁶ giving the differential cross section for single scattering of neutrons by a monatomic fluid in terms of the Fourier transforms of the pair correlations may now be invoked. The cross section $\sigma_{\text{coh}}''(\mathbf{k}, \omega)$ for coherent scattering with loss of neutron momentum $\hbar\mathbf{k}$ and loss of energy $\hbar\omega$, per unit solid angle and per unit energy range, is

$$\sigma_{\text{coh}}''(\mathbf{k}, \omega) = \frac{a_{\text{coh}}^2 k}{\hbar k_0} \int \int \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] G(\mathbf{r}, t) d\mathbf{r} dt, \quad (12)$$

where a_{coh} is the coherent scattering length, $\hbar\mathbf{k}_0$ is the momentum of the incoming neutron and $\hbar\mathbf{k}$ is the momentum of the scattered neutron. Using (10) in (12), and reducing the other variables appearing in the integration, one finds

$$\sigma_{\text{coh}}''(\mathbf{k}, \omega) = \frac{a_{\text{coh}}^2 k}{\hbar k_0} \alpha \left(\frac{M}{\epsilon} \right)^{\frac{1}{2}} \int \int \exp[i(\mathbf{k}^* \cdot \mathbf{r}^* - \omega^* t^*)] \times G^*(\mathbf{r}^*, t^*; T^*, P^*) d\mathbf{r}^* dt^*, \quad (13)$$

or

$$\sigma_{\text{coh}}''(\mathbf{k}, \omega) = \frac{a_{\text{coh}}^2 k}{\hbar k_0} \alpha \left(\frac{M}{\epsilon} \right)^{\frac{1}{2}} F(\mathbf{k}^*, \omega^*; T^*, P^*). \quad (14)$$

Here F designates a dimensionless universal function of the four reduced variables, defined by the reduced Fourier transform of G^* in (13). Similarly, the incoherent part of the scattering cross section, $\sigma_{\text{inc}}''(\mathbf{k}, \omega)$, is found from G_s and the incoherent scattering length a_{inc} :

$$\sigma_{\text{inc}}''(\mathbf{k}, \omega) = \frac{a_{\text{inc}}^2 k}{\hbar k_0} \alpha \left(\frac{M}{\epsilon} \right)^{\frac{1}{2}} F_s(\mathbf{k}^*, \omega^*; T^*, P^*), \quad (15)$$

where

$$F_s(\mathbf{k}^*, \omega^*; T^*, P^*) = \int \int \exp[i(\mathbf{k}^* \cdot \mathbf{r}^* - \omega^* t^*)] \times G_s^*(\mathbf{r}^*, t^*; T^*, P^*) d\mathbf{r}^* dt^*. \quad (16)$$

Equations (14) and (15) show how the coherent and incoherent cross sections of all members of a class of fluids obeying a law of corresponding states can be ex-

pressed in terms of nuclear parameters and universal functions of certain reduced variables. Thus a measurement of the scattering at one temperature and pressure by one fluid of a class determines the scattering at corresponding temperatures and pressures by all fluids of that class.

If the time dependence of the correlation functions is sufficiently slow compared with certain characteristic times of the scattering,⁵ $G^*(\mathbf{r}^*, t^*; T^*, P^*)$ in (13) can be replaced with $G^*(\mathbf{r}^*, 0; T^*, P^*)$ and an integration of both sides of the equation with respect to ω^* can be carried out. This gives the differential cross section for coherent scattering (without regard to energy changes), per unit solid angle,

$$\sigma_{\text{coh}}'(\mathbf{k}_0) = a_{\text{coh}}^2 \int \exp(i\mathbf{k}_0 \cdot \mathbf{r}^*) G^*(\mathbf{r}^*, 0; T^*, P^*) d\mathbf{r}^*. \quad (17)$$

Here $\mathbf{k}_0 = \mathbf{k}_0 - \mathbf{k}$ with $\omega = 0$. Recognizing that $G(\mathbf{r}, 0) = \delta(\mathbf{r}) + g(\mathbf{r})$, where $g(\mathbf{r})$ is the ordinary radial density of the fluid, (17) is seen to be a reduced form of the scattering expression first derived by Zernicke and Prins⁶ for the case of x-ray diffraction. Successful use of the Zernicke-Prins equation with a law of corresponding states to correlate x-ray scattering data from different fluids has been made by Ricci.⁷

It should be noted that the microscopic parameters ϵ and α do not need to be known for the application of a law of corresponding states, since the critical pressure, P_c , and critical temperature, T_c , of a fluid will serve as well. One has, from dimensional considerations,

$$\epsilon \propto kT_c,$$

and

$$\alpha \propto (kT_c/P_c)^{\frac{1}{2}}.$$

Thus, if kT_c is substituted for ϵ and $(kT_c/P_c)^{\frac{1}{2}}$ is substituted for α throughout Eqs. (4) through (17), equally valid reduced expressions will be obtained.

QUANTUM AND MOLECULAR CONSIDERATIONS

For systems of very light molecules the classical law of corresponding states is inadequate, and, as is well known,² the universal functions come to depend on an additional parameter $\Lambda^* = \hbar\alpha^{-1}(M\epsilon)^{-\frac{1}{2}}$. In the absence of theoretical information on the dependence of the reduced correlation functions on Λ^* , one does not have any general way to use the reduced scattering cross-section formulas. Corresponding-state considerations can be helpful, however, with systems of polyatomic molecules that fulfill two conditions: (a) the molecular mass M is great enough that the translational motions of the molecule can be treated classically, and (b) the internal degrees of freedom are virtually independent of the translational degrees of freedom. Condition (a)

⁶ F. Zernicke and J. A. Prins, *Z. Physik* **41**, 184 (1927).

⁷ The author is indebted to Dr. Ricci for communicating his results before publication.

requires that Λ^* be somewhat less than one. Condition (b) would seem to be satisfied by molecules of nearly spherical shape. Assuming these two conditions, one separates the dynamical variables of molecular translation from the variables of internal motion. The contribution of the translational motions to the scattering can then be expressed in a "universal" way with the aid of the law of corresponding states, and can be evaluated by measurements on any other scatterer of the same family. The remaining contribution is from internal motions, and in some cases can be evaluated forthwith. The ideas will be illustrated by treating a simple case, that in which one or more incoherently scattering atoms has a large cross section compared with all other atoms in the molecule. This is the case with molecules containing hydrogen, and the law of corresponding states has already been applied successfully to thermodynamic properties of several of these.

Consider now a molecule containing one or more hydrogen atoms and no other atoms of large scattering cross section. Employing the general results of Van Hove,⁵ Glauber,⁸ Zemach and Glauber,⁹ and others the scattering cross section is proportional to the Fourier transform of the expectation value of the operator $\Omega(\mathbf{r}, t)$, where

$$\Omega(\mathbf{r}, t) = \sum_{\nu} \exp[-i\mathbf{r} \cdot \mathbf{r}_{\nu}(0)] \exp[i\mathbf{r} \cdot \mathbf{r}_{\nu}(t)]. \quad (18)$$

Here $\mathbf{r}_{\nu}(t)$ is the Heisenberg operator representing the position of the ν th hydrogen atom in a molecule at time t , and the summation is over all hydrogen atoms in one molecule. Put

$$\mathbf{r}_{\nu}(t) = \mathbf{R}(t) + \mathbf{b}_{\nu}(t), \quad (19)$$

where $\mathbf{R}(t)$ is the position of the center of gravity of a molecule and $\mathbf{b}_{\nu}(t)$ is the position of the ν th hydrogen atom in that molecule with respect to the center of gravity. Assumption (b) above allows one to treat \mathbf{R} and \mathbf{b}_{ν} as statistically independent, and thus to split out a factor containing $\mathbf{R}(0)$ and $\mathbf{R}(t)$ from the right side of (18) and to average it separately. One then finds

$$\langle \Omega(\mathbf{r}, t) \rangle = \langle \Omega_{e.m.}(\mathbf{r}, t) \rangle \langle \Omega_{int}(\mathbf{r}, t) \rangle, \quad (20)$$

where

$$\Omega_{e.m.}(\mathbf{r}, t) = \exp[-i\mathbf{r} \cdot \mathbf{R}(0)] \exp[i\mathbf{r} \cdot \mathbf{R}(t)], \quad (21)$$

and

$$\Omega_{int}(\mathbf{r}, t) = \sum_{\nu} \exp[-i\mathbf{r} \cdot \mathbf{b}_{\nu}(0)] \exp[i\mathbf{r} \cdot \mathbf{b}_{\nu}(t)]. \quad (22)$$

All information pertaining to the internal motions of a molecule is contained in Ω_{int} , and all information on the translational motions is contained in $\Omega_{e.m.}$. Under assumption (a) above the latter motion can be treated classically and subjected to a law of corresponding states. Because Ω has been decomposed into a product in Eq. (20), the scattering cross section to which it leads can, by a familiar theorem in Fourier transforms,

be expressed as a convolution of cross sections associated independently with $\Omega_{e.m.}$ and Ω_{int} . Thus, the cross section per molecule is given by

$$\sigma_{inc}''(\mathbf{r}, \omega) = \frac{a_{inc}^2 k}{2\pi \hbar k_0} \int s_{int}''(\mathbf{r}, \omega - \omega') s_{e.m.}''(\mathbf{r}, \omega') d\omega', \quad (23)$$

where

$$s_{int}''(\mathbf{r}, \omega) = \int \langle \Omega_{int}(\mathbf{r}, t) \rangle \exp(-i\omega t) dt, \quad (24)$$

and

$$s_{e.m.}''(\mathbf{r}, \omega) = \int \langle \Omega_{e.m.}(\mathbf{r}, t) \rangle \exp(-i\omega t) dt. \quad (25)$$

Apart from the factor $a_{inc}^2 k / \hbar k_0$, $s_{int}''(\mathbf{r}, \omega)$ is precisely the cross section for scattering by the same molecule, with all its internal motions (vibration and rotation), but with its center of mass rigidly fixed, and $s_{e.m.}''(\mathbf{r}, \omega)$ is the cross section for incoherent scattering by a single atom moving with the center of gravity of the molecule. If the substance belongs to a family obeying a law of corresponding states, $s_{e.m.}''(\mathbf{r}, \omega)$ obeys such a law, being related to the $s_{e.m.}''$ for other members of the family in precisely the way the σ_{inc}'' are interrelated, as given by Eq. (15). Thus, if the incoherent scattering by another member of the family (possibly a monatomic substance) can be measured, $s_{e.m.}''$ can be determined and, through (23) or (20), s_{int}'' can be found. This idea has been used in a more or less intuitive form before; the above reasoning gives it a more satisfactory foundation.

FURTHER APPLICATIONS

Two further applications of these principles can now be suggested. The first possibility is to explore how far correspondence of states can actually be found in new families of fluids, particularly families for which thermodynamic and transport data have been insufficient to make the conventional tests. Finding a correspondence of states implies a similarity of intermolecular forces; lack of correspondence implies essential differences. The liquid metals would seem particularly deserving of such attention.

A second application allows one to separate the coherent from the incoherent scattering in a fluid, and thus to determine both the self-correlation G_s and the general correlation G .¹⁰ Consider two monatomic fluids of different elements, A and B , which are known to obey a law of corresponding states. The scattering cross section for substance A will be proportional to

$$(a_{coh}^A)^2 s_{coh}''^A(\mathbf{r}, \omega) + (a_{inc}^A)^2 s_{inc}''^A(\mathbf{r}, \omega),$$

¹⁰ B. N. Brockhouse and N. K. Pope [Phys. Rev. Letters **3**, 259 (1959)] have been able to find G_s at small times by determining G and extracting the peak near the origin of the time axis. This procedure cannot be used at longer times where the interesting diffusive behavior of G_s sets in. In some systems isotopic substitution that alters the relative amounts of coherent and incoherent scattering could be employed to make this separation.

⁸ R. J. Glauber, Phys. Rev. **98**, 1692 (1955).

⁹ A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956); **101**, 129 (1956).

where $s_{\text{coh}}''^A(\mathbf{k}, \omega)$ is the coherent cross section of A , apart from the factors of scattering length and $k/(hk_0)$, a_{coh}^A is the coherent scattering length for A atoms, and the second term in the expression involves the corresponding incoherent quantities. For B the scattering is proportional to the same expression with A replaced by B throughout.

Now by use of the principle of corresponding states, $s_{\text{coh}}''^B(\mathbf{k}, \omega)$ can be expressed theoretically in terms of $s_{\text{coh}}''^A(\mathbf{k}, \omega)$, and $s_{\text{inc}}''^B(\mathbf{k}, \omega)$, can be expressed in terms of $s_{\text{inc}}''^A(\mathbf{k}, \omega)$. Assuming that

$$(a_{\text{coh}}^A/a_{\text{inc}}^A)^2 \neq (a_{\text{coh}}^B/a_{\text{inc}}^B)^2,$$

measurement of the scattering from both A and B at corresponding conditions of temperature and pressure allows immediate determination of *both* $s_{\text{coh}}''^A(\mathbf{k}, \omega)$ and $s_{\text{inc}}''^A(\mathbf{k}, \omega)$, rather than just their weighted sum. Fourier inversion then determines G and G_s for substance A .

The corresponding substances liquid argon and liquid krypton would seem to be well suited for an experiment of this type. Theoretical approximations which have been suggested¹¹ for G_s and for relating G_s to G could be tested most effectively by such a determination.

¹¹ G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

Fermi Surface and Some Simple Equilibrium Properties of a System of Interacting Fermions*

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It is shown that certain analytical properties of the propagators of many-fermion systems lead rigorously to the existence of sharp discontinuities of the momentum distribution at absolute zero. This discontinuity in the momentum distribution is used to define a Fermi surface for a system of interacting fermions. It is shown that the volume of this surface in momentum space is unaffected by the interaction. The same analytic properties are shown to lead, by direct statistical mechanical arguments, to simple expressions for the low-temperature heat capacity, the spin paramagnetism, and the compressibility of the system. These expressions are very analogous to the corresponding expressions for noninteracting particles. Finally, it is shown how the whole formalism may be generalized when an external periodic potential is present (band case).

I. INTRODUCTION

IN this paper we shall be concerned with the existence and characteristics of the Fermi surface (FS) for a system of interacting fermions, as well as some simple equilibrium properties of such a system. Usually such a surface is introduced into momentum space only for a system of noninteracting fermions. In that case this surface represents the limit of occupation of the different single-particle momentum states in the ground state of the system. All the states with momentum contained within this surface are occupied, all those with momentum outside this surface are unoccupied. As soon as one considers interaction between the particles the above definition of the FS becomes meaningless. None the less, we shall show that with a suitable definition, and under certain conditions, such a surface can be given a rigorous meaning for a system of interacting fermions. This possibility was first pointed out by Migdal,¹ who noticed that under some circumstances it

could be so that the *mean* occupation number of different single-particle momentum states in the true ground state still possesses a discontinuity. Migdal's argument can certainly not be general, i.e., it cannot be valid for all systems of interacting fermions. Consider, for example, a collection of interacting deuterium atoms. These obey Fermi statistics. However, the ground state of this system is certainly a molecular crystal made up of D_2 molecules, and has no trace of a FS in its momentum distribution. Therefore the existence of a FS depends on the nature of the forces between the fermions. We shall investigate the problem here under the assumption that the forces between particles are such as to allow a power series expansion in their strength to give a good representation of certain properties of the system. We cannot expect that such a power series will be truly convergent, but rather that it is at most an asymptotic expansion. This was already clear from the difficulties which arise in the theory of superconductivity when one has even arbitrarily weak attractive forces. More recently Van Hove² has indicated how

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¹ A. B. Migdal, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 399 (1957) [translation: Soviet Phys.—JETP **5**, 333 (1957)]. See also

V. M. Galitsky and A. B. Migdal, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 139 (1958) [translation: Soviet Phys.—JETP **7**, 96 (1958)].

² L. Van Hove, Physica **25**, 849 (1959).