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ABSTRACT

The theory of cluster expansions is studied by a new method. A general procedure for obtaining the thermal average of a many body function as a series in powers of density is derived. A recipe based on the Baker-Hausdorf theorem for reducing quantum thermal averages to their classical analogues is also described. These results are used to express the slow neutron cross sections of imperfect gases as power series in molecular density. Formulae are given for the leading contributions to both elastic and inelastic scattering.

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1. INTRODUCTION

The scattering of slow neutrons by nuclei subject to   chemical

forces in atomic and molecular systems can be used as a tool to study these

forces. This technique is being developed as a new and welcome supplement

to such well established methods as x-ray and electron diffraction. Consider-

able work has been done on neutron diffraction by crystals and within the

past few years, the use of neutrons in the study of gases and liquids has

been initiated.[1]

Methods have recently been developed[2] for the treatment of inelastic

as well as elastic scattering of neutrons by gaseous systems. Since the

effects of intermolecular interactions were considered quite crudely, and

only in connection with the "outer effect", the results are strictly valid

only in the limit of vanishing density. When scattering experiments are

performed at gas densities at which the departure from ideality is manifested

in other properties, corrections to the formulae previously given may be

required. From the investigation of such imperfect gas corrections, one may

hope to elicit information on the potentials which act between gas particles

and on other aspects of the behavior of dense gases.

In the present work, we extend the methods of reference 2 to obtain

the neutron cross section in a power series in the gas density, the leading

term of which is the ideal gas result. For this purpose, a method is

presented in the next section which both unifies and generalizes procedures

previously used for deriving density expansions in simpler contexts. We

shall confine our treatment to gases whose behavior approximates that of a

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[1] G. E. Bacon, Neutron Diffraction, Oxford, 1955.

[2] A. C. Zemach and R. J. Glauber, Phys. Rev. 101, 118, 129 (1956), hereafter called ZG.

classical ensemble of particles (a slight restriction in practice). A concise

technique for obtaining classical limits of averages over systems in thermal

equilibrium and quantum corrections to them is also explained in section 2.

We discuss first some aspects of the scattering formalism. The

excitations of a target system bombarded by a slow neutron beam remain, as a

rule, unobserved. We recall the optical theorem which relates a total cross

section, summed over all scattering processes, to a coherent scattering

amplitude, i.e. to an amplitude for the process which leaves the dynamical

system as a whole unaltered. An analogous result is achieved in the present

case where a summation is performed over the final states of the scattering

medium only. In the time dependent formulation of the diffraction problem,

the relation takes the form[3]

$$\sigma(\theta) = (2\pi)^{-1} \Sigma_{\nu\nu'}(A_\nu A_{\nu'} + \delta_{\nu\nu'} C_\nu^2) \iint (k/k_o) e^{-i\epsilon t} <X_{\nu,\nu'}> dt\, d\epsilon \ , \tag{1.1}$$

$$<X_{\nu\nu'}> = <\psi \mid e^{iHt} \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_\nu) e^{-iHt} \exp(-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_{\nu'}) \mid \psi > \tag{1.2}$$

for the differential cross section when the initial state of the scatterer

is ψ .

Thus the cross section, originally computed within the formalism of

the first Born approximation, may be reinterpreted in terms of a twofold

collision of the neutron and the scatterer following which the scatterer

returns to its initial state. Specifically, if the expression for $\langle X_{\nu\nu'}\rangle$

is read from right to left, we find that the scatterer, initially in state ψ,

loses momentum $\underset{\sim}{\kappa}$ in collision of the neutron with nucleus ν'; propogates

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[3] The reader is referred to ZG for definitions and notation. Boltzmann's

constant and $\hbar$ have unit magnitude in the system of units adopted.

through a time interval t, and regains the momentum $\underset{\sim}{K}$ in a collision

involving nucleus ν. The cross section depends upon the overlap of the

latter state with the state $e^{-iHt}\psi$ resulting from an uninterrupted temporal

development of ψ in the course of the "collision time" t. The final states

of the true scattering processes appear as intermediate states in the double

scattering picture. The presence of the phase factor $e^{-i\epsilon t}$ insures that in

the integration over collision times, contributions from intermediate states

which disobey the conservation condition

$$\epsilon = E_i - E_f$$

interfere destructively. Eq. (1.1) leads to compact and powerful methods for

the calculation of cross sections; in addition, the accompanying physical

interpretation is of great utility in appreciating the qualitative features

of the scattering.

The approximation method[2,4] based on an expansion of all or part of

the expectation values (1.2) in ascending powers of t is of particular

importance both because of its wide domain of validity and the comparative

simplicity of the ensuing computations. The procedure is applicable when the

variation in time of the expanded quantities is slow compared to the rate of

oscillation of $e^{-i\epsilon t}$. We shall employ it in treating the imperfect gas

problem. Work extending these calculations to denser systems such as liquids

is planned.

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[4] G. C. Wick, Phys. Rev. 94, 1228 (1954).

2. CLUSTER EXPANSIONS AND THERMAL AVERAGES

We present a theory of cluster expansions which unifies and extends the formalism originated by Ursell and Mayer[5] and which provides a foundation for our later calculations.

The central problem concerns the average of a many-particle operator Q,

$$< \psi \mid Q \mid \psi > = \int \psi^{*}(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_n) Q\psi(\underline{r}_1, \ldots \underline{r}_n) d\underline{r}_1, \ldots d\underline{r}_n ,$$

$$(2.1)$$

in some state or thermal ensemble of states of a gaseous system. The integrand above is a separable function, i.e., when the particles divide into isolated clusters,[6] the function itself separates into factors, each a function of the coordinates of particles in one cluster. Corrections to the ideal gas limit of (2.1) which account for interparticle collisions make up a series in powers of molecular density. Series of this type are closely related to the cluster expansions of separable functions.

A situation of complete symmetry will be examined first. For brevity, we designate a set of coordinates $\underline{r}_1, \underline{r}_2, \ldots \underline{r}_N$ by $\underline{r}^N$ and $d\underline{r}_1 d\underline{r}_2 \ldots d\underline{r}_N$ by $d\underline{r}^N$. For each integer N, let $W_N(\underline{r}^N)$ specify a symmetric coordinate function which is separable in the sense that if $\underline{r}^N$ divides into isolated clusters $\underline{r}'^n$ and $\underline{r}''^m$, $n + m = N$, then

$$W_N(\underline{r}^N) \longrightarrow W_n(\underline{r}'^n) W_m(\underline{r}''^m) . \qquad (2.2)$$

We introduce a parmetric function $a(\rho)$ of a single position coordinate and write $a^{(n)}$ in abbreviation of the product

[5] See, for example, Hirschfelder, et al., Molecular Theory of Gases and Liquids, Wiley, 1955. Also, J. deBoer, Dissertation, Amsterdam.

[6] That is, clusters whose physical separation exceeds the range of molecular forces.

$a(\underset{\sim}{\rho_1}) \, a(\underset{\sim}{\rho_2}) \, \ldots \, a(\underset{\sim}{\rho_n})$. A generator $G_W(\, a \,)$ for the W functions is then defined by

$$G_W(a) \; = \; \sum_{n=0}^{\infty} \; \frac{1}{n!} \; \int a^{(n)} \, W_n(\underset{\sim}{\rho}^n) \, d\underset{\sim}{\rho}^n \; . \tag{2.3}$$

In this equation, W_0 is taken to be unity. Employing the technique of functional differentiation with respect to the parametric function, as expressed by

$$\frac{\delta}{\delta \, a \, (\underset{\sim}{r})} \, a(\underset{\sim}{\rho}) \; = \; \delta \, (\underset{\sim}{r} - \underset{\sim}{\rho}) \, ,$$

$$\frac{\delta}{\delta \, a(\underset{\sim}{r})} \, \int a \, (\underset{\sim}{\rho}) \, W(\underset{\sim}{\rho}) d\underset{\sim}{\rho} \; = \; W(\underset{\sim}{r}), \text{ etc.,}$$

we recover each W_N from the generator by the recipe:

$$W_N(\underset{\sim}{r}^N) \; = \; \frac{\delta}{\delta \, a \, (\underset{\sim}{r_1})} \; \cdots \; \frac{\delta}{\delta \, a \, (\underset{\sim}{r_N})} \; G_W(a) \, \Big|_{a \, = 0} \; . \tag{2.4}$$

A many particle function which vanishes when its arguments separate into isolated clusters will be termed a cluster function. The expansion of W_N in terms of cluster functions will now be derived. Let us define, as in (2.3), a generator $G_U(a)$ for a set of functions $U_N(\underset{\sim}{r}^N)$ and consider the relation

$$G_W(a) \; = \; e^{G_U(a)} \tag{2.5}$$

which serves as a definition of the U functions in terms of the W functions. The fundamental property of Eq. (2.5) is that each U_N so defined is a cluster function if and only if each W_N is separable. A proof of this theorem is given in the Appendix. Applying (2.4) to (2.5), we infer

$$W_N(r^N) = U_N(r^N) + \Sigma_N U_{N-1} U_1 + \cdots + U_1(r_1) U_1(r_2) \cdots U_1(r_N),$$

$$(2.6)$$

The general term of (2.6) is

$$\Sigma_N U_{N_1} U_{N_2} \cdots U_{N_n} , \qquad\qquad \Sigma N_i = N ,$$

where the symbol Σ_N indicates summation over all ways of alloting N arguments to the functions which follow. For example,

$$\Sigma_3 U_2 U_1 = U_2(r_1, r_2) U_1(r_3) + U_2(r_1, r_3) U_1(r_2) + U_2(r_2, r_3) U_1(r_1).$$

Solving (2.6) for the U functions, one obtains

$$U_0 = 0, \quad U_1(r_1) = W_1(r_1) ,$$

$$U_2(r_1, r_2) = W_2(r_1, r_2) - W_1(r_1) W_1(r_2) ,$$

$$U_3(r_1, r_2, r_3) = W_3(r_1, r_2, r_3) - \Sigma_3 W_2 W_1 + 2W_1(r_1) W_1(r_2) W_1(r_3),$$

$$\text{etc.}$$

$$(2.7)$$

We suppose hereafter that the cluster functions of interest depend on coordinate differences only. When n is sufficiently small, a connected n-particle cluster will occupy a negligible fraction of the volume V which encloses the gas particles. In this case, the cluster integral $\int U_n(r^N) dr^N$ is proportional to V. For if the integrations over r^{N-1} are carried out with r_N fixed, the effective limits of integration are set by the range of molecular forces rather than the size of the enclosure. Then the result must be independent of both V and r_N, and the final integration over r_N supplies a factor of V.

We now consider separable functions $W_{M,N}(\underset{\sim}{r}^M, \underset{\sim}{s}^N)$ which are symmetric functions of the groups $\underset{\sim}{r}^M$ and $\underset{\sim}{s}^N$ separately. A second parmetric function $b(\underset{\sim}{\sigma})$ is required for the definition of the generator:

$$G_W(a, b) = \Sigma \frac{1}{m!} \frac{1}{n!} \int a^{(m)} b^{(n)} W_{m,n}(\underset{\sim}{\rho}^m, \underset{\sim}{\sigma}^n) d\underset{\sim}{\rho}^m d\underset{\sim}{\sigma}^n \, ,$$

where $W_{0,0} = 1$. It follows that

$$W_{M,N}(\underset{\sim}{r}^M, \underset{\sim}{s}^N) = \frac{\delta}{\delta \, a(\underset{\sim}{r}_1)} \cdots \frac{\delta}{\delta \, b(\underset{\sim}{s}_N)} \, G_W(a, b) \Big|_{a=b=0} \, .$$

With a similar definiton for the generator $G_U(a, b)$ of the cluster functions, we have

$$G_W(a, b) = e^{G_U(a, b)} \, . \tag{2.8}$$

The derivation of $U_{N,M}(\underset{\sim}{r}^N, \underset{\sim}{s}^M)$ in terms of the W functions closely resembles the method of the previous case.

The relations between the integrals of the functions at hand are also of interest. If we define

$$w_{M,N} = \frac{1}{M!} \frac{1}{N!} \int W_{M,N}(\underset{\sim}{r}^M, \underset{\sim}{s}^N) d\underset{\sim}{r}^M d\underset{\sim}{s}^N \, , \tag{2.9}$$

$$u_{M,N} = \frac{1}{M!} \frac{1}{N!} \int U_{M,N}(\underset{\sim}{r}^M, \underset{\sim}{s}^N) d\underset{\sim}{r}^M d\underset{\sim}{s}^N$$

and replace $a(\underset{\sim}{\rho})$ and $b(\underset{\sim}{\sigma})$ by the constants a and b, respectively, then (2.8) becomes

$$\Sigma \, a^m b^n w_{m,n} = \exp(\Sigma \, a^m b^n u_{m,n}) \, . \tag{2.10}$$

The extension to situations of still lower symmetry is obvious.

As an application of the foregoing work, we determine the density expansion for the thermal average $< O(\underset{\sim}{r}) >_T$ of an operator function $O(\underset{\sim}{r})$. The operator may depend, in general, on all molecular coordinates of the N particle assembly; the notation indicates, however, a lack of symmetry between $\underset{\sim}{r}$ and the remaining coordinates.

We define $W_{0,N}$[7] as the Slater sum over a complete set of molecular states ψ_i :

$$W_{0,N}(\underset{\sim}{s}^N) = \left(\frac{2\pi}{MT}\right)^{3N/2} \Sigma_i \psi_i^*(\underset{\sim}{s}^N) e^{-H(\underset{\sim}{s}^N)/T} \psi_i(\underset{\sim}{s}^N) \quad , \tag{2.11}$$

and $W_{1,N-1}$ as the generalized Slater sum:

$$W_{1,N-1}(\underset{\sim}{r}, \underset{\sim}{s}^{N-1}) = \left(\frac{2\pi}{MT}\right)^{3N/2} \Sigma_i \psi_i^*(\underset{\sim}{r}, \underset{\sim}{s}^{N-1}) O(\underset{\sim}{r}) e^{-H(\underset{\sim}{r}, \underset{\sim}{s}^{N-1})/T} \psi_i(\underset{\sim}{r}, \underset{\sim}{s}^{N-1}). \tag{2.12}$$

Functions $W_{M,N}$ with $M \geqslant 2$ remain undefined, but no definitions are needed. The relations implicit in (2.8) and (2.10) are still of value; one simply ignores all terms containing a power of a higher than the first. Utilizing the definitons above, we find that

$$< O(\underset{\sim}{r}) >_T = (1/N) (w_{1,N-1}/w_{0,N}) . \tag{2.13}$$

Equating coefficients of a in (2.10), we obtain

$$\Sigma b^n w_{1,n} = \Sigma b^n u_{1,n} \exp(\Sigma b^k u_{0,k})$$

$$= \Sigma b^n u_{1,n} \Sigma b^k w_{0,k} \quad ,$$

7 We omit consideration of quantum statistics in this paper. The Slater sums require an additional factor of N! if the wave functions represent Bose or Fermi systems.

whence

$$W_{1,N-1} = \sum_{n=0}^{N-1} u_{1,n} W_{0,N-1-n} \quad . \tag{2.14}$$

We introduce the quantities D_n,

$$D_n = (1/V) u_{1,n} \tag{2.15}$$

which, for small n, are essentially volume independent. The partition sums $W_{0,n}$ are connected with the fugacity z of the gas by[5]

$$W_{0,N-n} = z^n W_{0,N} \quad . \tag{2.16}$$

The substitution of (2.14) into (2.13) yields, in virtue of (2.15) and (2.16),

$$< 0(\underset{\sim}{r}) >_T = (V/N) \sum_{n=0}^{N-1} D_n z^{n+1} \tag{2.17}$$

Finally, we take advantage of the equation

$$z = (N/V) \exp\left[-\sum_{n=1}^{\infty} \beta_n (N/V)^n\right] \tag{2.18}$$

which expresses the fugacity in terms of the molecular density and the irreducible cluster integrals β_n. The latter are derivable from the molecular potential. With the help of (2.18), we conclude that

$$\langle 0(\underset{\sim}{r})\rangle_T = D_0 + (N/V)(D_1 - \beta_1 D_0) + (N/V)^2\left[D_2 - 2\beta_1 D_1 - (\beta_2 - \tfrac{1}{2}\beta_1^2)D_0\right] + \ldots \tag{2.19}$$

which is the desired density series.

In terms of the molecular potential $V(\underset{\sim}{r_i} - \underset{\sim}{r_j})$, the classical expressions for the first two irreducible cluster integrals are

$$\beta_1 = \int f(\underset{\sim}{r})d\underset{\sim}{r} \quad , \tag{2.20}$$

$$\beta_2 = \tfrac{1}{2} \int f(\underset{\sim}{r}) f(\underset{\sim}{r} - \underset{\sim}{s}) f(\underset{\sim}{s}) \, d\underset{\sim}{r} \, d\underset{\sim}{s} \quad ,$$

where $f(\underset{\sim}{r}) = e^{-V(\underset{\sim}{r})/T} - 1.$

For later use, we compute the thermal average $< O(\underset{\sim}{r}, \underset{\sim}{r}') >_T$ where no symmetry is assumed between $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ or between these coordinates and the others. We define $W_{0,0,N}$ by the expression (2.11), and $W_{1,1,N-2}$ by

$$W_{1,1,N-2} = \left(\frac{2\pi}{MT}\right)^{3N/2} \Sigma_i \psi_i^*(\underset{\sim}{r}, \underset{\sim}{r}', \underset{\sim}{s}^{N-2}) O(\underset{\sim}{r}, \underset{\sim}{r}')$$

$$\times e^{-H(\underset{\sim}{r}, \underset{\sim}{r}', \underset{\sim}{s}^{N-2})/T} \psi_i(\underset{\sim}{r}, \underset{\sim}{r}', \underset{\sim}{s}^{N-2}).$$

Additional functions $W_{0,1,N-1}$ and $W_{1,0,N-1}$ are inferred from the assumed separability of $W_{1,1,N-1}$. The cluster expansion of $W_{1,1,N-2}$ is obtained using generators which depend on three parametric functions, and integrals $w_{1,1,N-2}$, etc. are defined in analogy to (2.9). The equation corresponding to (2.10) is

$$\Sigma \ a^m \ b^n \ c^k \ w_{m,n,k} = \exp(\Sigma \ a^m \ b^n \ c^k \ u_{m,n,k}) \tag{2.22}$$

so that

$$w_{1,1,N-2} = \sum_{n=0}^{N-2} \left[u_{1,1,n} + \sum_{m=0}^{n} u_{1,0,m} u_{0,1,n-m} \right] w_{0,0,N-2-n}.$$

With the definitions

$$I_n = (1/V) u_{1,1,n} \quad ,$$

$$I_n^{(1)} = (1/V) u_{1,0,n} \quad , \qquad I_n^{(2)} = (1/V) u_{0,1,n} \quad ,$$

we get

$$< 0(\underset{\sim}{r}, \underset{\sim}{r'}) >_T \;=\; \left[N(N-1)\right]^{-1} w_{1,1,N-2} \,/\, w_{0,0,N}$$

$$=\; V\left[N(N-1)\right]^{-1} \sum_{n=0}^{N-2} \left(I_n + V\sum_{m=0}^{n} I_m^{(1)} I_{n-m}^{(2)}\right) z^{n+2}$$

$$=\; (1/V)\, I_0 + (N/V^2)(I_1 - 2\beta_1 I_0) + \ldots$$

$$+ I_0^{(1)} I_0^{(2)} + (N/V)\left[I_0^{(1)} I_1^{(2)} + I_1^{(1)} I_0^{(2)} - 2\beta_1 I_0^{(1)} I_0^{(2)}\right] + \ldots$$

$$(2.23)$$

To arrive at (2.23) from the preceding line, we have equated $N/(N-1)$ to unity.

The generator equations and the process of functional differentiation were of value in proving the cluster property of the U functions. We observe, however, that for the calculation of terms in the density series, the simpler relations among integrals, as expressed by (2.10) and (2.22), are sufficient.

At high temperatures, the thermal averages and Slater sums approximate their classical analogues. In concluding this section, we show how the Baker-Hausdorff theorem may be used to effect the passage to the classical limit in an elementary way. The quoted theorem is an operator identity which states that if

$$e^A \, e^B \;=\; e^C \tag{2.24}$$

then C is given by a series,

$$C \;=\; A + B + \frac{1}{2}\left[A, B\right] + \frac{1}{12}\left[A - B, \left[A, B\right]\right] - \frac{1}{24}\left[B, \left[A, \left[A, B\right]\right]\right] + \ldots \tag{2.25}$$

whose higher terms are successive commutators of A and B.

To illustrate the principle, we examine a two particle system with the Hamiltonian

$$H \;=\; (p_1^2 + p_2^2)\big/ 2M + V(\underset{\sim}{r}_1 - \underset{\sim}{r}_2). \tag{2.26}$$

The corresponding classical Hamiltonian H_c is formed by replacing the operator momenta in (2.26) by c-numbers $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$. Let $Z(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ denote the generalized Slater sum[7] over a complete set of states,

$$Z(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \left(\frac{2\pi}{MT}\right)^3 \sum_i \psi_i (\underset{\sim}{r}_1, \underset{\sim}{r}_2) Q(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{p}_1, \underset{\sim}{p}_2) e^{-H/T} \psi_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2) ,$$

$$(2.27)$$

whose integral, properly normalized, represents the thermal average of the operator Q. If a suitable classical analogue, $Q_c(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{q}_1, \underset{\sim}{q}_2)$ of Q can be defined, we expect (2.27) to reduce, at high temperatures, to $Z_c(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ where

$$Z_c(r_1, r_2) = (2\pi MT)^{-3} \int Q_c(r_1, r_2, q_1, q_2) e^{-H_c/T} d\underset{\sim}{q}_1 d\underset{\sim}{q}_2 .$$

Since the complete set of states ψ_i is arbitrary, we choose plane waves,

$$\psi_{q_1, q_2}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = V^{-1} \exp \left(i \underset{\sim}{q}_1 \cdot \underset{\sim}{r}_1 + i \underset{\sim}{q}_2 \cdot \underset{\sim}{r}_2 \right) ,$$

and replace the summation in (2.27) by $V^2(2\pi)^{-6} \int d\underset{\sim}{q}_1 d\underset{\sim}{q}_2$ in the usual way. In virtue of the translation property,

$$e^{-i(\underset{\sim}{q}_i \cdot \underset{\sim}{r}_i)} \underset{\sim}{p}_i e^{i(\underset{\sim}{q}_i \cdot \underset{\sim}{r}_i)} = \underset{\sim}{p}_i + \underset{\sim}{q}_i , \qquad\qquad i = 1, 2 .$$

Eq. (2.27) assumes the form

$$Z(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = (2\pi MT)^{-3} \int Q(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{p}_1 + \underset{\sim}{q}_1, \underset{\sim}{p}_2 + \underset{\sim}{q}_2) e^B d\underset{\sim}{q}_1 d\underset{\sim}{q}_2 \quad (2.28)$$

where

$$B = -(p_1 + q_1)^2/2MT - (p_2 + q_2^2)/2 MT - V/T .$$

The operator momenta appearing as arguments of Q in (2.28) are now to be commuted to the extreme left where they disappear, leaving a function $Q_c(r_1, r_2, q_1, q_2)$. The occurrences of p_1 and p_2 in the exponential are to be commuted to the extreme right with the aid of (2.24). Thus if we set $A = H_c/T$, then

$$e^B = e^{-H_c/T} \exp\left[\frac{-\nabla^2 V}{2MT^2} + \frac{(\nabla V)^2}{3MT^3} - \frac{i(q_1 - q_2)\cdot\nabla V}{2MT^2} + \frac{[(q_1 - q_2)\cdot\nabla]^2 V}{6MT^3} + \ldots\right]$$

(2.29)

$$= e^{-H_c/T}\left[1 - \frac{\nabla^2 V}{2MT^2} + \frac{(\nabla V)^2}{3MT^3} - \frac{i(q_1 - q_2)\cdot\nabla V}{2MT^2}\right.$$

$$\left. + \frac{[(q_1 - q_2)\cdot\nabla^2]V}{6M^2T^3} - \frac{[(q_1 - q_2)\cdot\nabla V]^2}{8M^2T^4} + \ldots\right]. \quad (2.30)$$

The gradients are with respect to r_1.

In the calculation of the bracketed series in (2.29) via (2.25), each additional commutation supplies another gradient applied to V. Thus, e^B is equal to $\exp(-H_c/T)$ multiplied by a series of powers of the gradient. Each gradient carries with it a factor of $\hbar$, although this is not evident in our notation. Then the series proceeds in powers of $\hbar$. The use of (2.30) in (2.28) yields the classical limit with quantum corrections. Since, however, Q_c may itself contain a dependence on $\hbar$, the so-called quantum corrections are not always smaller than all contributions from the leading term, even in the limit of large T. (Compare the treatment of interference scattering in Sec. 4 where these corrections cancel against other terms.) The effects of quantum statistics may also be computed by this formalism without difficulty.

3. ELASTIC SCATTERING

In the absence of extensive experimental information on neutron scattering by imperfect gases, we shall be content to mark out the general features of the problem rather than essay an exhaustive treatment of different examples. For this purpose, we neglect the role of internal degrees of freedom which formed the principal concern of ZG. A temperature sufficiently high to permit an approximately classical evaluation of thermal averages (including lowest order quantum corrections) will be assumed.

The initial term arising from the time expansion procedure is treated in the present section. This forms the static approximation which is valid when the scattering is predominantly elastic. The direct scattering is then found to be independent of molecular coordinates. Accordingly, imperfect gas corrections to elastic scattering must be sought in the interference terms.

Let $\sigma_{1,2}(\theta)$ represent one of the two terms of the elastic cross section due to interference between molecules (1) and (2):

$$\sigma_{1,2}(\theta) = A^2 < \chi_{1,2} > = A^2 < \exp i\, \underset{\sim}{K} \cdot (\underset{\sim}{r}_1 - \underset{\sim}{r}_2) >_T \quad , \qquad (3.1)$$

where $\underset{\sim}{K}$ is evaluated with $k = k_o$. Then the elastic interference cross section per molecule is given by

$$\sigma_{int}^{(0)}(\theta) = \sum_{n=2}^{N} \sigma_{1,n}(\theta) \quad . \qquad (3.2)$$

We suppose that molecular interaction is due to a spherically symmetric two particle potential $V(\underset{\sim}{r}_i - \underset{\sim}{r}_j)$. We shall frequently write $\underset{\sim}{r}_{ij}$ for $\underset{\sim}{r}_i - \underset{\sim}{r}_j$ and V_{ij} for $V(\underset{\sim}{r}_i - \underset{\sim}{r}_j)$. Averaging classically, we have

$$< X_{1,2} >_T \; = \; \frac{\int \exp \left(- \Sigma \, V_{ij} / T + i \kappa \cdot r_{1\,2} \right) \; dr^N}{\int \exp \left(- \Sigma \, V_{ij} / T \right) \; dr^N} \; . \tag{3.3}$$

Quantum corrections to (3.3) are considered together with inelastic corrections in the next section. Eq. (3.3) leads to the Zernike-Prins formula[8] and the final result below can be obtained from the known density expansion of the pair distribution function. The treatment here illustrates the methods of Sec. 2 and serves as an introduction to the work of the next section.

The first two terms in the density series for (3.3) will be determined. We define the separable functions:

$$W_{1,0,0}(r_1) = \exp(i\kappa \cdot r_1) \; , \qquad\qquad W_{0,1,0}(r_2) = \exp(-i\kappa \cdot r_2) \; ,$$

$$W_{1,1,0}(r_1, \, r_2) = e^{-V_{12}/T} \, \exp(i\kappa \cdot r_{12})$$

and

$$W_{1,0,1}(r_1, \, r_3) \; = \; e^{-V_{13}/T} \; \exp(i\kappa \cdot r_1) \; ,$$

$$W_{0,1,1}(r_2, \, r_3) \; = \; e^{-V_{23}/T} \; \exp(-i\kappa \cdot r_2) \; ,$$

$$W_{1,1,1}(r_1, \, r_2, \, r_3) \; = \; e^{-(V_{12} + V_{23} + V_{31})/T} \; \exp(i\kappa \cdot r_{12}) \; .$$

The u integrals are now deduced from (2.22). Thus,

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[8] J. deBoer, Reports on Progress in Physics XII, 305 (1949);

N. S. Gingrich, Revs. of Modern Physics 15, 90 (1943).

$$u_{1,1,0} = w_{1,1,0} - w_{0,1,0}\, w_{1,0,0} = \int (e^{-V_{12}/T} - 1)\,\exp(i\kappa\cdot r_{12})dr_1\, dr_2$$

$$(3.4)$$

$$u_{1,1,1} = w_{1,1,1} - w_{1,1,0}\, w_{0,0,1} - w_{1,0,1}\, w_{0,1,0} - w_{1,1,0}\, w_{0,0,1}$$

$$+\ 2\,w_{1,0,0}\, w_{0,1,0}\, w_{0,0,1}$$

$$= \int \Big[e^{-(V_{12} + V_{23} + V_{31})/T} - e^{-V_{12}/T} - e^{-V_{23}/T}$$

$$-\ e^{-V_{13}/T} + 2 \Big]\, \exp(i\kappa\cdot r_{12})dr_1\, dr_2,\ \text{etc.}$$

$$(3.5)$$

The terms $I_n^{(1)}$ and $I_n^{(2)}$ are seen to be proportional to the integrals

$$V^{-1} \int \exp(i\kappa\cdot r_1)dr_1\ , \qquad\qquad V^{-1} \int \exp(-i\kappa\cdot r_2)dr_2\ ,$$

$$(3.6)$$

respectively and may be dropped. For when the volume of integration is macroscopically large, one readily confirms that for scattering angles differing even minutely from the precise forward direction, the integrals (3.6) are vanishingly small.

We get, by (2.19) and (3.4),

$$I_0 = \int f(r)\,\exp(i\kappa\cdot r)dr\ .$$

Further, by (3.5) and (2.18), we have

$$I_1 = \int e^{-V(r)/T} f(\underset{\sim}{r} - \underset{\sim}{s}) \, f(\underset{\sim}{s}) \, \exp(i \, \underset{\sim}{\kappa} \cdot \underset{\sim}{r}) d\underset{\sim}{r} \, d\underset{\sim}{s} + 2 \, \beta_1 \, I_0 \; .$$

It follows from (2.25) and (3.2) that

$$\sigma_{int}^{(0)}(\theta) = A^2 \left\{ (N/V) \int f(\underset{\sim}{r}) \, \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}) d\underset{\sim}{r} \right.$$

$$+ (N/V)^2 \int e^{-V(r)/T} f(\underset{\sim}{r} - \underset{\sim}{s}) f(\underset{\sim}{s})$$

$$\left. \times \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}) d\underset{\sim}{r} \, d\underset{\sim}{s} \; + \; \ldots \right\} \qquad .$$

Using the notation

$$< F(\underset{\sim}{r}^N) > = \int F(\underset{\sim}{r}^N) \, \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_1) d\underset{\sim}{r}^N \Big/ \int F(\underset{\sim}{r}^N) d\underset{\sim}{r}^N \; ,$$

and the definitions (2.16), (2.17), we obtain for the interference cross section in the present approximation:

$$\sigma_{int}^{(0)}(\theta) = A^2 \left\{ (N/V)\beta_1 < f(r) > + (N/V)(2\beta_2 + \beta_1^2) < e^{V(r)/T} f(\underset{\sim}{r}-\underset{\sim}{s}) f(\underset{\sim}{s}) > \right.$$

$$\left. + \ldots \right\} . \tag{3.7}$$

The expressions in angular brackets above are essentially weighted averages of $\exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r})$. They are equal to unity for $\kappa = 0$ (forward scattering) and oscillate with decreasing amplitude as κ increases. For molecular potentials of the Lennard-Jones type, these functions can be computed, for example, by the method Kihara employed for the virial coefficients.[9]

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[9] T. Kihara, J. Phys. Soc. Japan 3, 265 (1948) and 6, 184 (1951).

Quantitative statements are more easily made if the molecules are assumed to be hard spheres. In terms of the hard sphere diameter, we have $\beta_1 = -(4\pi/3)d^3$, $\beta_2 = -(5\pi^2/12)d^6$. The coefficients of the angular brackets are conveniently expressed in terms of the ratio V_0/V where $V_0 = (4\pi/3)N d^3$ is the total "interaction volume." If a hard sphere is introduced into a rare gas of N hard spheres, V_0 is essentially the volume from which the first sphere is excluded in virtue of the particle interactions. The coefficients of the first and second angular brackets are then $-(V_0/V)$ and $(17\ 32)(V_0/V)^2$, respectively. The first term of (3.7) is simply the Debye formula for the outer effect. The second bracket is reducible to the form

$$< e^{-V(\underset{\sim}{r})}\ {}^T f(\underset{\sim}{r} - \underset{\sim}{s})\ f(\underset{\sim}{s}) > \ = \ (6/25) \int_1^2 (\kappa a)^{-1} \sin(\kappa a z)(z^4 - 12\ z^2 + 16\ z)dz,$$

which, if desired, can be integrated in terms of elementary functions.

The terms which appear in the density expansion for the cross section are quite similar to the cluster integrals and the virial coefficients. Their evaluation presents difficulties of a comparable order of magnitude and the domain of convergence is probably equivalent to that of the virial expansion.

4. INELASTIC CORRECTIONS

We have observed that apart from the first term the terms of the density series for the expectation values $< X_{\nu\nu} >_T$ yield only inelastic corrections to the direct scattering. To investigate the relative importance of the succeeding part we examine the portion which is linear in (N/V) and compute the leading terms obtained by the time expansion method.

The development of $< X_{\nu\nu} >_T$ in powers of t gives rise to terms of two types. From the classical evaluation of the thermal averages, we obtain spatial integrals of $\nabla^2 V$, $(\nabla V)^2$, and higher derivatives, multiplied by certain powers of t. The latter cause the appearance of inverse powers of $\mathcal{E}_o$, the incident neutrons energy, in the cross section. In addition, we have the quantum corrections to the classical averaging process which contain similar integrals over derivatives of the potential, divided by powers of T. Since the two kinds of terms may be of comparable magnitude, it is necessary to consider them together in a consistent calculation. It is then natural to order the various quantities according to the number of derivatives applied to the potential that they contain and to study, in a first approximation, the initial terms of the resulting series.

This procedure is quite analogous to the familiar method for approximating the partition function which was discussed earlier, and may be expected to have the same validity; that is, the series in powers of $\nabla^2 V/\mathcal{E}_o$, $\nabla^2 V/T$, etc. is presumably asymptotic, and its leading terms yield an adequate approximation when $\mathcal{E}_o$ and T are not much lower than ordinary thermal energies.

We consider now the direct scattering by a gas particle specified by the coordinate r_1. We seek to determine the linear term in the density expansion of the thermal average of the operator

$$e^{iHt} \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_1) \, e^{-iHt} \, \exp(-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_1) = e^{iHt} \, e^{-iH_{(1)}'t} \quad . \tag{5.1}$$

The operator $H_{(1)}'$, as defined in ZG, is obtained from H by replacing the the momentum $\underset{\sim}{p}_1$ with $\underset{\sim}{p}_1 - \underset{\sim}{\kappa}$. If the particle at $\underset{\sim}{r}_1$ is free, we have, simply, $H = p_1^2/2M$ and (5.1) reduces to a quantity we denote by $X_o(t)$:

$$X_o(t) = \exp\left[i\,t(2\,\underset{\sim}{p}_1\cdot\underset{\sim}{\kappa} - \kappa^2)/2M\right] \quad . \tag{5.2}$$

But if the first particle interacts with a second through a potential, then

$$H = p_1^2/2M + p_2^2/2M + V(\underset{\sim}{r}_1 - \underset{\sim}{r}_2) \quad , \tag{5.3}$$

whence

$$H_{(1)}' = (\underset{\sim}{p}_1 - \underset{\sim}{\kappa})^2/2M + p_2^2/2M + V(\underset{\sim}{r}_1 - \underset{\sim}{r}_2) \quad .$$

In the latter case, (5.1) is a function of greater complexity which we shall call $X_1(t)$. Hereafter, the symbol H will be reserved for the two particle Hamiltonian (5.3). and we shall write H_0 for $(p_1^2 + p_2^2)/2M$.

Following the prescription of Sec. 3, we have

$$D_0 = (1/V)(2\pi/MT)^{3/2} \int \left\{ \Sigma_i \; \psi_i^*(\underset{\sim}{r}_1) \; X_o(t) e^{-p_1^2/2MT} \; \psi_i(\underset{\sim}{r}_1) \right\} d\underset{\sim}{r}_1 \quad ,$$

$$D_1 = (1/V)(2\pi/MT)^3 \int \left\{ \Sigma_i \; \psi_i^*(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \left[X_1(t) e^{-H/T} - X_0(t) e^{-H_0/T} \right] \right.$$

$$\left. \times \psi_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \right\} d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \quad .$$

Then the latter equation can be rewritten

$$D_1 = \beta_1 D_0 + (1/V)(2\pi/MT)^3 \int \Big\{ \Sigma_i \, \psi_i^* (\underset{\sim}{r}_1, \underset{\sim}{r}_2) \big[\chi_1(t) e^{-H/T}$$

$$- (1 + \beta) \chi_0 e^{-H_0/T} \big] \psi_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \Big\} \, d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \tag{5.4}$$

where β_1 is the quantum version of the first irreducible cluster integral.[*]

The identity (2.25) allows us to express $\chi_1(t)$ as the exponential of a series in ascending powers of t. A factor of $\chi_0(t)$ can then be separated from $\chi_1(t)$ by a second application of (2.25) so that

$$\chi_1(t) = e^{+iHt} \, e^{-iH(1)'t} =$$

$$= \chi_0(t) \big[1 + c_2(-it)^2 + c_3(-it)^3 + c_4(-it)^4 + \dots \big] \tag{5.5}$$

where

$$c_2 = \frac{1}{2} \, i(\underset{\sim}{\kappa} \cdot \underset{\sim}{\nabla})/M \quad,$$

$$c_3 = \big[2(\underset{\sim}{\kappa} \cdot \underset{\sim}{\nabla})^2 V + (\underset{\sim}{p}_1 - \underset{\sim}{p}_2) \cdot \underset{\sim}{\nabla} \big] /6 \, M^2 \quad,$$

$$c_4 = -\frac{1}{8} (\underset{\sim}{\kappa} \cdot \underset{\sim}{\nabla})^2 / M^2 \quad.$$

The gradients occurring above are with respect to $\underset{\sim}{r}_1$. In computing the coefficients c_i, we have discarded terms containing more than two derivatives. We now insert (5.5) into (5.4), use momentum eigenfunctions for the $\psi_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ and reduce $e^{-H/T}$ to the form (2.30). Upon integration over momentum and space coordinates, we find

$$D_1 - \beta_1 D_0 = \overset{4}{\underset{n=2}{\Sigma}} c_n' (-it)^n \exp \Big[\frac{-it\kappa^2}{2M} - \frac{t^2 T\kappa^2}{2M} \Big] \quad, \tag{5.6}$$

[*] $\beta_1 = (1/V)(2\pi/MT)^3 \int \Big\{ \Sigma_i \, \psi_i^*(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \big[e^{-H/T} - e^{-H_0/T} \big] \psi_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \Big\} d\underset{\sim}{r}_1 \, d\underset{\sim}{r}_2 \quad.$

where

$$c_2' = (\kappa^2/18\ M^2 T)\mathcal{V}_1 - (\kappa^2/24\ M^2 T^2)\mathcal{V}_2 \ .$$

$$c_3' = -(\kappa^2/9\ M^2)\mathcal{V}_1 + (\kappa^2/12\ M^2 T)\mathcal{V}_2$$

$$c_4' = (\kappa^2 T/18\ M^2)\mathcal{V}_1 - (\kappa^2/24\ M^2)\mathcal{V}_2 \ .$$

and

$$\mathcal{V}_1 = \int e^{-V(\underset{\sim}{r})/T}\ \vec{\nabla}^2\ V\ d\underset{\sim}{r}\ ,$$

$$\mathcal{V}_2 = \int e^{-V(\underset{\sim}{r})/T}\ (\underset{\sim}{\nabla}V)^2\ d\underset{\sim}{r}\ .$$

As was shown in ZG, the exponential in (5.6) produces corrections to the cross section of relative order (m/M) and α^2 where

$$\alpha^2 = mT/M\mathcal{E}_0 \ .$$

Although their calculation involves no special difficulty, they are best omitted in a first estimate of inter-molecular effects. Accordingly, we replace the exponential by unity.

Let us write $\sigma_{dir}^{(1)}(\theta)$ for the part of the direct cross section under calculation. Then, by (2.19) and (ZG. I, 4.7),

$$\sigma_{dir}^{(1)}(\theta) = B^2(N/V) \iint (k/2\pi\ k_0)e^{-i\epsilon t}(D_1 - \beta_1\ D_0)dt\ d\epsilon$$

$$= \frac{B^2(N/V)}{k_0}\ \Sigma_m(\frac{m}{k}\ \frac{d}{dk})^n\ (k\ c_n')\ \Big|_{k=k_0} \qquad (5.7)$$

where B^2, apart from a faster of 4π, is the incoherent cross section for a gas particle. Consequently, we obtain

$$\sigma_{dir}^{(1)}(\theta) = B^2 \, \alpha^2 \, \frac{N}{V} (1 - \frac{7}{8} \frac{T^2}{\mathcal{E}_o^2}) (\frac{\mathcal{V}_1}{18 \, MT^2} - \frac{\mathcal{V}_2}{24 \, MT^3}) \; . \tag{5.8}$$

In order to estimate the magnitude of (5.8), we choose for V the Lennard-Jones potential

$$V(r) = V_o \left[(\frac{r_o}{r})^{12} - (\frac{r_o}{r})^6 \right] \tag{5.9}$$

and suppose the scattering to be performed at room temperature. The values $r_o = (3.5) \times 10^{-8}$ cm, $V_o = 0.05$ ev are typical of the magnitudes assumed by the Lennard-Jones parameters. One may show, very approximately, that $\mathcal{V}_1 \approx 100 \, V_o \, r_o$, $\mathcal{V}_2 \approx 40 \, V_o^2 \, r_o$. For $\mathcal{E}_o \approx T$, (5.8) becomes

$$\sigma_{dir}^{(1)}(\theta) \approx B^2 \, (N/V) \, (m/M)^2 (4 \times 10^{-23} \, cm^3) \; . \tag{5.10}$$

Equation (5.10) is to be compared with the leading term in the direct cross section which is of the order of B^2. Thus, the calculated correction is too small to be of importance at standard conditions of temperature and pressure where, for a gas, $N/V \approx 3 \times 10^{19}$ cm^{-3}, but it may be of significance under other circumstances.

Our methods are not powerful enough to analyze in detail the convergence properties of either the density expansion or the time expansion. But it is probably safe to assert that for gas densities which are not too great and neutron energies which are not too small, the development presented here is valid. Equation (5.8) contains the largest imperfect gas corrections to the direct cross section in this development.

We turn now to a consideration of inelastic effects in the (N/V) part of the interference cross section. Again, only terms having fewer than three derivatives applied to the potential are to be retained, and quantum modifications of the classically computed thermal averages are included to this order. As in the previous section, we may drop all interference terms involving $I_m^{(1)}$ and $I_\eta^{(2)}$. The latter are, in fact, identical to their time independent analogues and do not contribute noticeably to the cross section.

We observe that

$$e^{iHt} \exp(i\kappa \cdot r_1) e^{-iHt} \exp(-i\kappa \cdot r_2) = e^{iHt} e^{-iH(1)'t} \exp(i\kappa \cdot r_{12})$$

$$= \chi_1(t) \exp(i\kappa \cdot r_{12}) \ .$$

Proceeding as before, we obtain for the cross section $\sigma_{int}(\theta)$, including presently calculated corrections,

$$\sigma_{int}(\theta) = A^2 (N/V) \iint (k/2\pi k_0) e^{-i\epsilon t} I_0 \ dt \ d\epsilon \ ,$$

where

$$I_0 = (1/V)(2\pi/MT)^3 \int \Big\{ \Sigma_\iota \ \psi_\iota^*(r_1, r_2) \Big[\chi_1(t)\exp(i\kappa \cdot r_{12}) \ e^{-H/T}$$

$$- \exp(i\kappa \cdot r_{12}) \ e^{-H_0/T} \Big] \psi_\iota(r_1, r_2) \Big\} \ dr_1 \ dr_2 \ . \tag{5.11}$$

The reduction of (5.11) will yield a single spatial integral whose integrand contains the factor $e^{-V/T} \exp(i\kappa \cdot r)$. Since

$$\nabla \big[e^{-V/T} \exp(i\kappa \cdot r) \big] = \big[-(\nabla V)/T + i\kappa \big] e^{-V/T} \exp(i\kappa \cdot r) \ ,$$

it follows that by an integration by parts, factors of κ can be replaced by derivatives of V inside the integral. Accordingly, such factors of κ are to be counted equivalent to derivatives for the purpose of determining

which terms in the expansion are to be retained or rejected. Hence, from (5.11), we derive

$$I_0 = \int (e^{-V(\underset{\sim}{r}) \, T} - 1) \, \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}) \, d\underset{\sim}{r}$$
$$+ \int e^{-V(\underset{\sim}{r})/T} \, \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}) \, \Big[\quad d_0 + d_1 t + d_2 t^2 \Big] \, d\underset{\sim}{r} \tag{5.12}$$

with

$$d_0 = (\underset{\sim}{\nabla}V)^2 \Big/ 12 \, MT - (\nabla^2 V) \Big/ 6 \, MT^2 \;,$$

$$d_1 = (\underset{\sim}{\kappa}\cdot\underset{\sim}{\nabla}V)/2 \, MT - i\kappa^2/2M \;,$$

$$d_2 = -i(\underset{\sim}{\kappa}\cdot\underset{\sim}{\nabla}V)\Big/2 \, M - T \, \kappa^2/2 \, M \;.$$

But when the suggested integrations by parts are performed in (5.12) the t and t^2 terms disappear. All that is left is the term which represents the quantum correction to the classically evaluated $\sigma_{int}^{(0)}(\theta)$:

$$\sigma_{int}(\theta) = \sigma_{int}^{(0)}(\theta) + A^2(N/V) \int e^{-V/T} \exp(i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}) \left\{ \frac{(\underset{\sim}{\nabla}V)^2}{12MT} - \frac{\nabla^2 V}{6MT^2} \right\} d\underset{\sim}{r}.$$

Nothing remains of the inelastic corrections, to the order considered. Thus, in neutron diffraction by imperfect gases as in diffraction by free molecules, inelastic effects are much less prominent in the interference terms than in the direct scattering.

APPENDIX

For a given integer N, consider the proposition $P(N)$ that for all $n < N$, each U_n defined by Eq. (2.5) is a cluster function if and only if each W_n is separable. The truth of $P(N)$ for the smallest values of N is inferred directly from (2.7). Assuming $P(N)$, we shall prove $P(N + 1)$ and so establish, by mathematical induction, the fundamental relation between U and W functions for clusters of arbitrary size.

Let $\underset{\sim}{r}^N$ be composed of two clusters $\underset{\sim}{r}^{N_1}$ and $\underset{\sim}{r}^{N_2}$, $N_1 + N_2 = N$, with the coordinates of $\underset{\sim}{r}^{N_2}$ labeled $\underset{\sim}{r}_{N_1+1}, \cdots, \underset{\sim}{r}_N$. Then

$$\frac{\delta}{\delta a(\underset{\sim}{r}_1)} \cdots \frac{\delta}{\delta a(\underset{\sim}{r}_N)} \, e^{G_U(a)} = e^{G_U(a)} \left[W_{N_1}(\underset{\sim}{r}^{N_1}) \right.$$

$$+ (N_1!/N!) \int a(\underset{\sim}{\rho}^{N_2}) \, U_N(\underset{\sim}{r}^{N_1}, \underset{\sim}{\rho}^{N_2}) d\underset{\sim}{\rho}^{N_2} + \text{other terms} \left. \right]. \tag{A.1}$$

We note that the right side of (A.1) reduces to $W_{N_1}(\underset{\sim}{r}^{N_1})$ when $a = 0$.

Let (A.1) be differentiated with respect to each of the functional variables $a(\underset{\sim}{r}_i)$ with $N_1 + 1 \leq i \leq N$, and the parametric function then set equal to zero. We find that

$$W_N(\underset{\sim}{r}^N) = W_{N_1}(\underset{\sim}{r}^{N_1}) \, W_{N_2}(\underset{\sim}{r}^{N_2}) + U_N(\underset{\sim}{r}^N) + \text{other terms.} \tag{A.2}$$

where the "other terms" in (A.2) consist of certain products containing functions U_n with $n < N$. At least one U_n in each product has arguments drawn from both the groups $\underset{\sim}{r}^{N_1}$ and $\underset{\sim}{r}^{N_2}$. If $\underset{\sim}{r}^{N_1}$ and $\underset{\sim}{r}^{N_2}$ are now isolated from each other and the inductive hypothesis $P(N)$ is invoked,

the "other terms" vanish. The validity of P(N + 1) follows immediately.

The extension of this proof to cases of lower symmetry requires only notational changes.