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LINKED-DIAGRAM EXPANSION FOR THE EQUATION OF STATE OF A GAS OF MOLECULES

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$$A^N = [(NZ)!]^{-1} \Sigma_\alpha \delta_\alpha P_\alpha . \tag{2.18}$$

Since the states $| \Lambda^N (0) \rangle$ form a complete (unsymmetrized) set, the states $A^N | \Lambda^N (0) \rangle$ form a complete antisymmetrized set. The trace may thus be written

$$\begin{aligned} \mathrm{Tr} \exp(-\beta H^N) &= \Sigma_\Lambda \langle \Lambda^N(0) | A^N \exp(-\beta H^N) A^N | \Lambda^N(0) \rangle \\ &= \Sigma_\Lambda \langle \Lambda^N(0) | A^N \exp(-\beta H^N) | \Lambda^N(0) \rangle \end{aligned}$$

(since A^N and H^N commute, and $(A^N)^2 = A^N$)

$$= [(NZ)!]^{-1} \Sigma_\Lambda \Sigma_\alpha \delta_\alpha \langle \Lambda^N(\alpha) | \exp(-\beta H^N) | \Lambda^N(0) \rangle \tag{2.19}$$

For every electron reassignment from the original assignment (0), there are $(Z!)^N$ permutations P_α, representing further permutations within molecules. If we restrict the set $\{\alpha\}$ to the set of reassignments from the assignment (0), we may write (2.19) as

$$\mathrm{Tr} \exp(-\beta H^N) = (Z!)^N [(NZ)!]^{-1} \Sigma_\Lambda \Sigma_\alpha \delta_\alpha \langle \Lambda^N(\alpha) | \exp(-\beta H^N) | \Lambda^N(0) \rangle . \tag{2.20}$$

LINKED-DIAGRAM EXPANSION FOR THE EQUATION OF STATE OF A GAS OF MOLECULES

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ABSTRACT

The method of the linked-diagram expansion is applied to the equilibrium statistical mechanics of a nondegenerate gas of molecules, taking into account the structure of the molecules, and using the Pauli principle for all the electrons. The equation of state is obtained in the form of a virial expansion analogous to that of Ursell and Mayer.

LINKED-DIAGRAM EXPANSION FOR THE EQUATION OF STATE OF A GAS OF MOLECULES*

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I. INTRODUCTION

A gas is a many-body system of interacting molecules which are themselves structured systems. The interaction between molecules is due to Coulomb forces and the Pauli principle, both of which are responsible as well for the structure of the molecules themselves. Most previous treatments of the equation of state of a gas, such as the classical Ursell-Mayer expansion,[1] have attacked the problem in two steps: first, use of quantum mechanics or experimental data to obtain the molecular interaction; and second, application of statistical mechanics to the gas, treating the molecules as simple particles with a given interaction.

Recently there have been several derivations[2-5] of linked-cluster expansions valid for a quantum-mechanical system of interacting particles. In this paper the techniques developed by Glassgold, Heckrotte, and Watson[4] are generalized to handle the problem of a gas of interacting molecules, using the Coulomb interaction and the Pauli principle throughout. Molecular interactions, including the effects of exchange, are thus obtained from first principles.

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II. FORMULATION

To simplify the presentation, we shall assume that the gas is composed of N identical molecules, in a box of volume $\mathcal{V}$. (The extension to several species of molecules is described in Section V.) Each molecule contains Z electrons and Z' atomic nuclei. The set of Z' nuclei will be referred to as a "molecular ion." Then we assume that the gas is nondegenerate, in the sense that exchange of nuclei between different molecular ions is negligible. However, we shall consider the possibility of electron exchange.

The Hamiltonian for the N molecules is[6]

$$H^N = \Sigma_\rho T_\rho + \Sigma_{\rho<\sigma} q_\rho q_\sigma / s_{\rho\sigma} \quad . \tag{2.1}$$

The sum is over all the electrons and nuclei of the system. T_ρ is the kinetic energy operator for particle ρ, q_ρ its charge, and $s_{\rho\sigma}$ the distance between particles ρ and σ. The second term of Eq. (2.1) is thus the total Coulomb energy.[7]

Let us consider a specific assignment of electrons and nuclei to molecules; we denote this assignment by the symbol (0). Then we may write H^N as the sum of two terms: $K^N(0)$, the total Hamiltonian for N noninteracting molecules, and $V^N(0)$, their total Coulomb interaction:

$$K^N(0) = \Sigma_i^N h_i(0) \ , \tag{2.2}$$

$$h_i(0) = \Sigma_\rho^i T_\rho + \Sigma_{\rho<\sigma}^i q_\rho q_\sigma / s_{\rho\sigma} \ , \tag{2.3}$$

$$V^N(0) = \Sigma_{i<j}^N V_{ij}(0) \ , \tag{2.4}$$

$$V_{ij}(0) = \Sigma_\rho^i \Sigma_\sigma^j q_\rho q_\sigma / s_{\rho\sigma} \ . \tag{2.5}$$

The symbol $\Sigma_\rho^{\,i}$ means to sum over all particles in molecule i. The symbol (0) determines which ρ and σ appear in the sums of (2.3) and (2.5). The Hamiltonian of the single molecule i is $h_i(0)$, and its interaction energy with molecule j is $V_{ij}(0)$.

Since the molecules are identical, the eigenstates and eigenvalues of $h_i(0)$ are independent of i and (0):

$$h \mid \lambda \rangle = \epsilon \mid \lambda \rangle . \tag{2.6}$$

Then $\mid \lambda_i(0) \rangle$ denotes the state of molecule i for the assignment (0), and ϵ_i its energy. We assume that the set $\mid \lambda_i(0) \rangle$ is complete for the particles in molecules i; then the N-molecule states

$$\mid \Lambda^N(0) \rangle \equiv \prod_{i=1}^{N} \mid \lambda_i(0) \rangle \tag{2.7}$$

form a complete set for all the particles of the system. These are eigenstates of $K^N(0)$:

$$K^N(0) \mid \Lambda^N(0) \rangle = E_\Lambda \mid \Lambda^N(0) \rangle , \tag{2.8}$$

$$E_\Lambda = \Sigma_i^{\,N} \epsilon_i . \tag{2.9}$$

We shall suppose that the single-molecule states $\mid \lambda \rangle$ are properly symmetrized. Let us now apply a permutation (of electrons) P_α to the system state $\mid \Lambda^N(0) \rangle$:

$$P_\alpha \mid \Lambda^N(0) \rangle \equiv \mid \Lambda^N(\alpha) \rangle . \tag{2.10}$$

The state $\mid \Lambda^N(\alpha) \rangle$ has the same $\mid \lambda_i \rangle$ as $\mid \Lambda^N(0) \rangle$, but $\mid \lambda_i(\alpha) \rangle$ and $\mid \lambda_i(0) \rangle$ are different in the sense that the electrons of molecule i

are, in general, different in (α) and (0). Only if P_α permutes electrons within the same molecule does one have

$$| \Lambda^N(\alpha)\rangle = \delta_\alpha \, | \Lambda^N(0) \rangle , \tag{2.11}$$

where δ_α is ± 1, depending on the number of interchanges in P_α; in general one has

$$| \Lambda^N(\alpha) \rangle = \Sigma_{\Lambda'} \, a_{\Lambda'} \, | \Lambda'^N(0) \rangle . \tag{2.12}$$

Although H^N commutes with P_α, $K^N(0)$ does not; in fact we have

$$P_\alpha \, K^N(0) \, P_\alpha^{-1} = K^N(\alpha) \tag{2.13}$$

and

$$K^N(\alpha) \, | \Lambda^N(\alpha) \rangle = E_\Lambda \, | \Lambda^N(\alpha) \rangle . \tag{2.14}$$

For any assignment α we may decompose H^N into

$$H^N = K^N(\alpha) + V^N(\alpha) , \tag{2.15}$$

with

$$V^N(\alpha) = \Sigma_{i<j}^{N} \, V_{ij}(\alpha) . \tag{2.16}$$

Because the N molecular ions will be treated as distinguishable, the grand partition function is

$$\mathcal{Z}(\theta, \mu, \mathcal{V}) = \Sigma_N (N!)^{-1} \, e^{\beta\mu N} \, \mathrm{Tr} \exp(-\beta H^N) , \tag{2.17}$$

where $\theta \equiv \beta^{-1}$ is the temperature, and μ is the chemical potential. The trace is to be taken over states antisymmetric with respect to electron interchange.

Now for every permutation P_α which exchanges electrons between molecules, there are $(Z!)^N$ permutations with the same reassignment of electrons among molecules, but with further permutations within molecules. Since there are $(NZ)!$ permutations altogether, the number of reassignments is $(NZ)!/(Z!)^N$. The operator which projects from any (unsymmetrized) state the antisymmetric part is thus

$$A^N \equiv \frac{(Z!)^N}{(NZ)!} \sum_\alpha \delta_\alpha P_\alpha , \tag{2.18}$$

where the sum is over different reassignments (α). Since the states $| \Lambda^N(0) \rangle$ form a complete (unsymmetrized) set, the states $A^N | \Lambda^N(0) \rangle$ form a complete antisymmetrized set.

The trace may thus be written

$$\begin{aligned} \mathrm{Tr}\, \exp(-\beta H^N) &= \Sigma_\Lambda \langle \Lambda^N(0) | A^N \exp(-\beta H^N) A^N | \Lambda^N(0) \rangle \\ &= \Sigma_\Lambda \langle \Lambda^N(0) | A^N \exp(-\beta H^N) | \Lambda^N(0) \rangle \end{aligned}$$

(since A^N and H^N commute, and $(A^N)^2 = A^N$)

$$= \frac{(Z!)^N}{(NZ)!} \sum_\Lambda \sum_\alpha \delta_\alpha \langle \Lambda^N(\alpha) | \exp(-\beta H^N) | \Lambda^N(0) \rangle . \tag{2.19}$$

III. DEVELOPMENT

We wish to make a perturbation expansion in the interaction between molecules. To accomplish this, we first express $\exp(-\beta H^N)$ as

$$\exp(-\beta H^N) = (2\pi i)^{-1} \int dE\, (E - H^N)^{-1} \exp(-\beta E) , \tag{3.1}$$

with the contour of Fig. 1, which crosses the real axis to the left of all the eigenvalues of H^N. With the notation

$$J_\Lambda^\alpha(E) \equiv \delta_\alpha \langle \Lambda^N(\alpha) \mid (E - H^N)^{-1} \mid \Lambda^N(0) \rangle , \tag{3.2}$$

we can then write the partition function (2.17) as

$$\mathcal{Z} = \sum_N (Z!\, e^{\beta\mu})^N [N!\, (ZN)!]^{-1} \Sigma_\Lambda (2\pi i)^{-1} \int dE\, e^{-\beta E} \Sigma_\alpha J_\Lambda^\alpha(E). \tag{3.3}$$

For any assignment γ, we may express $(E - H^N)^{-1}$ as

$$(E - H^N)^{-1} = [E - K^N(\gamma)]^{-1}[1 + V^N(\gamma)(E - H^N)^{-1}] \tag{3.4a}$$

or

$$(E - H^N)^{-1} = [1 + (E - H^N)^{-1} V^N(\gamma)][E - K^N(\gamma)]^{-1} , \tag{3.4b}$$

corresponding to the decomposition (2.15), and then can iterate by using (3.4) again on the right-hand side. Because $\langle \Lambda^N(\alpha) \mid$ appears on the left of the matrix element of (3.2), it is convenient first to use (3.4a) with $(\gamma) = (\alpha)$, to obtain

$$J_\Lambda^\alpha(E) = \delta_\alpha (E - E_\Lambda)^{-1} \left[\langle \Lambda^N(\alpha) \mid \Lambda^N(0) \rangle + \langle \Lambda^N(\alpha) \mid V^N(\alpha)(E - H^N)^{-1} | \Lambda^N(0) \rangle \right] . \tag{3.5}$$

In the second term of (3.5) we next use (3.4b) with $(\gamma) = (0)$ to obtain

$$J_\Lambda^\alpha(E) = \delta_\alpha(E - E_\Lambda)^{-1} \langle \Lambda^N(\alpha) \mid \Lambda^N(0) \rangle$$

$$+ \delta_\alpha(E - E_\Lambda)^{-2} \langle \Lambda^N(\alpha) \mid V^N(\alpha) \mid \Lambda^N(0) \rangle$$

$$+ \delta_\alpha(E - E_\Lambda)^{-2} \langle \Lambda^N(\alpha) \mid V^N(\alpha)(E - H^N)^{-1} V^N(0) \mid \Lambda^N(0) \rangle . \tag{3.6}$$

In the last term of this expression, we may then use either (3.4a) or (3.4b) successively, with arbitrary γ each time, but for concreteness and simplicity we shall set $(\gamma) = (0)$ in each iteration. We then have the infinite series

$$(E - H^N)^{-1} = \left[\sum_{n=0}^{\infty} \left\{ [E - K^N(0)]^{-1} V^N(0) \right\}^n \right] [E - K^N(0)]^{-1} .$$

For each value of n, there is a contribution to (3.6):

$$\delta_\alpha(E - E_\Lambda)^{-2} \langle \Lambda^N(\alpha) \mid V^N(\alpha)[E - K^N(0)]^{-1} V^N(0)[E - K^N(0)]^{-1} \ldots$$

$$\ldots[E - K^N(0)]^{-1} V^N(0) \mid \Lambda^N(0) \rangle . \tag{3.7}$$

In this term we insert unity in the form $\Sigma_{\Lambda'} \mid \Lambda'^N(0) \rangle\langle \Lambda'^N(0) \mid$ at the appropriate places:

$$\delta_\alpha(E - E_\Lambda)^{-2} \sum_{\Lambda'\Lambda''\ldots\Lambda'''}$$

$$\times \frac{\langle \Lambda^N(\alpha) | V^N(\alpha) | \Lambda'^N(0) \rangle \langle \Lambda'^N(0) | V^N(0) | V''^N(0) \rangle \ldots \langle \Lambda'''^N(0) | V^N(0) | \Lambda^N(0) \rangle}{(E - E_{\Lambda'})(E - E_{\Lambda''})\ldots(E - E_{\Lambda'''})} . \tag{3.8}$$

Then for each $V^N(\alpha)$ and $V^N(0)$ in (3.8) or (3.6) we use (2.16) or (2.4), and obtain a sum of terms of the type

$$\delta_\alpha (E - E_\Lambda)^{-2} \sum_{\Lambda'\Lambda''\ldots\Lambda'''}{}' \times \frac{\langle \Lambda^N(\alpha) \mid V_{ij}(\alpha) \mid \Lambda'^N(0)\rangle\langle \Lambda'^N(0) \mid V_{k\ell}(0) \mid \Lambda''^N(0)\rangle \ldots \langle \Lambda'''^N(0) \mid V_{mn}(0) \mid \Lambda^N(0)\rangle}{(E - E_{\Lambda'})(E - E_{\Lambda''}) \ldots (E - E_{\Lambda'''})} . \tag{3.9}$$

Each such term may (in principle) be explicitly evaluated, and can be represented by a graph.

For each (α), we have such an expansion; let us denote by $J_{\Lambda u}(E)$ the value of a single term of the expansion, such as (3.9). Then we have, for (3.3),

$$\Sigma_\alpha J_\Lambda^\alpha(E) = \Sigma_u J_{\Lambda u}(E) . \tag{3.10}$$

The sum over u will be called a "sum over all graphs."

We illustrate these graphs for the example $(\alpha) = (1, 9, 2)(6, 7)$, by which we mean that P_α permutes electrons among molecules (1, 9, 2) and between molecules (6, 7). A graph shows which interactions V_{ij} and which permutations appear in $J_{\Lambda u}(E)$. Thus the first term of (3.6) is shown in Fig. 2a. Only the molecules concerned are represented, by vertical lines. The horizontal dotted lines represent P_α. Such a graph is called "unlinked"; this one consists of two linked parts.

Let us specialize further to the example of a gas of hydrogen atoms, with (1, 9, 2) representing a cyclic permutation of the electrons. Then for this graph u we have

$$J_{\Lambda u}(E) = -(E - E_\Lambda)^{-1} \langle \lambda_1(9)\, \lambda_9(2)\, \lambda_2(1) \mid \lambda_1(1)\, \lambda_9(9)\, \lambda_2(2) \rangle$$

$$\times \langle \lambda_6(7)\, \lambda_7(6) \mid \lambda_6(6)\, \lambda_7(7) \rangle ,$$

where $\lambda_1(9)$, for example, is the state of molecule 1 as a function of proton 1 and electron 9. If the states λ_i occurring in Λ^N are low-lying electron states, this term gets appreciable contributions only when the molecules (1, 9, 2) are near each other. However, since the set $|\Lambda^N\rangle$ must be complete, this graph, for other Λ^N, may represent continuum states $|\lambda\rangle$.

Figure 2b illustrates a graph contributing to the second term of (3.6), with (α) the same and with $V_{9,2}(\alpha)$ appearing as a term of $V^N(\alpha)$. The intermolecular interaction $V_{9,2}$ is represented by a solid horizontal line. The value of this graph is (for hydrogen atoms)

$$J_{\Lambda u}(E) = -(E - E_\Lambda)^{-2} \langle \lambda_1(9)\, \lambda_9(2)\, \lambda_2(1) \mid V_{9,2}(2,1) \mid \lambda_1(1)\, \lambda_9(9)\, \lambda_2(2) \rangle$$

$$\times \langle \lambda_6(7)\, \lambda_7(6) \mid \lambda_6(6)\, \lambda_7(7) \rangle ,$$

where $V_{9,2}(2, 1)$ denotes the interaction between atom (proton 9, electron 2) and atom (proton 2, electron 1).

Finally we show, in Fig. 2c, a term of the type (3.9) with five interactions and the same α as above. The ordering of the V's in the graph from bottom to top corresponds to the order in (3.9) from right to left, and will be referred to as if it were chronological, although of course time does not enter into the picture. We note that the "initial" and "final" states are the same Λ^N (with different assignments, however), while the

intermediate states (represented by the portions of the diagram between successive interactions) are to be summed over.

As a first step in evaluation, it is convenient to eliminate the effect of those molecules which do not appear in a given graph u. The states $|\Lambda^N\rangle$ and energies E_Λ which appear in (3.6) and (3.9) refer to the whole system of N molecules. Let us factor $|\Lambda^N\rangle$:

$$|\Lambda^N\rangle \equiv |\Lambda^u\rangle\,|\Lambda^f\rangle \quad , \tag{3.11a}$$

where $|\Lambda^u\rangle$ is a state of the molecules appearing in the graph u, and $|\Lambda^f\rangle$ a state of the other (free) molecules. Similarly, we write

$$E_\Lambda \equiv E_\Lambda{}^u + E_\Lambda{}^f \quad , \tag{3.11b}$$

$$E_{\Lambda'} \equiv E_{\Lambda'}{}^u + E_\Lambda{}^f \quad , \tag{3.11c}$$

and

$$E \equiv W + E_\Lambda{}^f \quad , \tag{3.11d}$$

to define a new complex variable W, since $E_\Lambda{}^f$ and $|\Lambda^f\rangle$ are constant in u.

With these substitutions in $J_{\Lambda u}(E)$ [see (3.9)], the latter retains the same form, except that all $|\Lambda^N\rangle$'s are replaced by $|\Lambda^u\rangle$'s, all E_Λ's are replaced by $E_\Lambda{}^u$'s, and E is replaced by W. Let us call the resulting expression $J_{\Lambda u}(W)$. Since it is independent of $|\Lambda^f\rangle$ and $E_\Lambda{}^f$, we have, for each graph u,

$$\Sigma_\Lambda (2\pi i)^{-1} \int dE\, e^{-\beta E}\, J_{\Lambda u}(E) = [\Sigma_{\Lambda^f} \exp(-\beta E_\Lambda{}^f)][\Sigma_{\Lambda^u} (2\pi i)^{-1} \int dW e^{-\beta W}\, J_{\Lambda u}(W)] \quad , \tag{3.12}$$

to be used in (3.3), with (3.10).

Since E_Λ^f is just a sum of free-molecule energies [see (2.9)], we may immediately evaluate the first factor of (3.12),

$$\Sigma_{\Lambda^f} \exp(-\beta E_\Lambda^f) = (\Sigma_\lambda e^{-\beta\epsilon})^{n_1} \equiv g_1^{n_1} , \tag{3.13}$$

where g_1 is the single-molecule partition function, and $n_1(u)$ is the number of molecules not in the graph u. Thus the partition function (3.3) is

$$\mathcal{Z} = \Sigma_N (Z!\, e^{\beta\mu})^N [N!(ZN)!]^{-1} \Sigma_u g_1^{n_1(u)} \Sigma_{\Lambda^u} (2\pi i)^{-1} \int dW e^{-\beta W} J_{\Lambda u}(W) . \tag{3.14}$$

Let us now select, from the set of all graphs $\{u\}$, subsets whose graphs all have the same molecules linked together. A group of linked molecules will be called a "cluster" ℓ, and a group of clusters will be called a "clustering" C. For example, graph Fig. 2c contains three clusters. If there were an additional interaction V_{19}, the new graph would belong to the same clustering, but an interaction V_{84} would produce a different clustering. To obtain a graph u belonging to C, one does not need the complete Hamiltonian H^N, but only the clustering Hamiltonian

$$H^C \equiv \Sigma_\ell H_\ell , \tag{3.15}$$

where H_ℓ is the complete Hamiltonian for the molecules of the ℓth cluster. Because the clusters are not linked to each other, the interaction between molecules in different clusters may be omitted from H^C.

We may sum over all graphs u belonging to a given C:

$$J_{\Lambda C}(W) \equiv \Sigma_u^C J_{\Lambda u}(W) = \mathcal{L}_C [\Sigma_\alpha^C \delta_\alpha \langle \Lambda^C(\alpha) \mid (W - H^C)^{-1} \mid \Lambda^C(0) \rangle] . \tag{3.16}$$

The matrix element has the same form as (3.2); upon expansion one obtains all the graphs u of the clustering C, and others. The sum over α includes only those reassignments that preserve the clustering, i.e., reassignments within clusters. The operator $\mathcal{L}_C$ then selects graphs belonging to C, and drops those in which one or more clusters are unlinked (and therefore are no longer clusters). The partition function now reads

$$\mathcal{Z} = \Sigma_N (Z!\, e^{\beta\mu})^N [N!(ZN)!]^{-1} \Sigma_C\, g_1^{n_1(C)} \Sigma_{\Lambda^C} (2\pi i)^{-1} \int dW e^{-\beta W} J_{\Lambda C}(W) \,. \tag{3.17}$$

The integration over W can now be performed:

$$(2\pi i)^{-1} \int dW e^{-\beta W} J_{\Lambda C}(W) = \mathcal{L}_C [\Sigma_\alpha{}^C\, \delta_\alpha \langle \Lambda^C(\alpha) | (2\pi i)^{-1} \int dW e^{-\beta W} (W - H^C)^{-1} | \Lambda^C(0) \rangle$$

$$= \mathcal{L}_C [\Sigma_\alpha{}^C\, \delta_\alpha \langle \Lambda^C(\alpha) \mid \exp(-\beta H^C) \mid \Lambda^C(0) \rangle] \,.$$

Because the H_ℓ commute with each other, this becomes

$$\mathcal{L}_C [\Sigma_\alpha{}^C\, \delta_\alpha \langle \Lambda^C(\alpha) \mid \Pi_\ell \exp(-\beta H_\ell) \mid \Lambda^C(0) \rangle]$$

$$= \Pi_\ell\, \mathcal{L}_\ell [\Sigma_\alpha{}^\ell\, \delta_\alpha \langle \Lambda^\ell(\alpha) \mid \exp(-\beta H_\ell) \mid \Lambda^\ell(0) \rangle] \,,$$

where $\mathcal{L}_\ell$ selects graphs in which the molecules of cluster ℓ are all linked. Upon summing over Λ^C, as required by (3.17), we obtain

$$\Pi_\ell\, \mathcal{L}_\ell [\Sigma_{\Lambda^\ell} \Sigma_\alpha\, \delta_\alpha \langle \Lambda^\ell(\alpha) \mid \exp(-\beta H_\ell) \mid \Lambda^\ell(0) \rangle \quad] \,,$$

$$\text{or} \quad \Pi_\ell\, \mathcal{L}_\ell\, [(N_\ell Z)!\, (Z!)^{-N_\ell}\, \mathrm{Tr} \exp(-\beta H_\ell)] \tag{3.18}$$

by analogy to (2.19). The trace is here taken over antisymmetrized states

of the N_ℓ molecules in cluster ℓ.

Let us introduce the notation

$$g_\ell \equiv (N_\ell Z)!\,(Z!)^{-N_\ell}\,\mathcal{L}_\ell\,[\mathrm{Tr}\,\exp(-\beta H_\ell)]\,, \tag{3.19}$$

so that the partition function can be written as

$$\mathcal{Z} = \Sigma_N (Z!\,e^{\beta\mu})^N\,[N!\,(ZN)!]^{-1}\,\Sigma_C\, g_1^{\,n_1(C)}\,\Pi_\ell\, g_\ell\,. \tag{3.20}$$

We note that although g_ℓ is defined for the particular group of molecules in the ℓth cluster, its value depends only upon N_ℓ, the number of molecules in the cluster. Thus we have

$$\Pi_\ell\, g_\ell = \Pi_{m=2}\,(g_m)^{n_m(C)}\,, \tag{3.21}$$

where g_m now denotes g_ℓ for any m-molecule cluster:

$$g_m = (mZ)!\,(Z!)^{-m}\,\mathcal{L}_m[\mathrm{Tr}\,\exp(-\beta H^m)]\,, \tag{3.22}$$

and n_m is the number of such clusters in C. We note that our definition (3.13) for g_1 is consistent with (3.22). Thus the partition function is

$$\mathcal{Z} = \Sigma_N (Z!\,e^{\beta\mu})^N\,[N!\,(ZN)!]^{-1}\,\Sigma_C\,\Pi_{m=1}\,(g_m)^{n_m(C)}$$

$$= \Sigma_N\,[N!\,(ZN)!]^{-1}\,\Sigma_C\,\Pi_{m=1}\,[(Z!\,e^{\beta\mu})^m\,g_m]^{n_m(C)}\,, \tag{3.23}$$

where we have used

$$N = \Sigma_{m=1}\, m\, n_m\,. \tag{3.24}$$

We are still distinguishing between clusterings in which the labels of the molecules involved are different. Now the number of clusterings with

the same "partitioning" into n_m groups of m-molecule clusters is

$$\frac{N!}{\prod_{m=1} (m!)^{n_m} \; n_m!} \quad , \tag{3.25}$$

so that we have

$$\mathcal{Z} = \sum_N \frac{1}{(ZN)!} \sum_{\{n_m\}} \prod_{m=1} \frac{1}{n_m!} \left[\frac{(Z!\; e^{\beta\mu})^m \; g_m}{m!} \right]^{n_m} \quad , \tag{3.26}$$

where the sum over $\{n_m\}$ is a sum over partitionings, subject to (3.24). It is now convenient to introduce what we shall call the m-molecule linked partition function

$$f_m \equiv (m!)^{-1} \; e^{\beta\mu m} \; \mathcal{L}_m \; [\mathrm{Tr}\, \exp(-\beta H^m) \;] \quad , \tag{3.27}$$

which differs from the form (2.17) in that there is no sum over m, and in that the linkage operator $\mathcal{L}_m$ is included. Upon comparison with (3.22), we see that

$$f_m = \frac{(Z!)^m}{m!\; (mZ)!} \; e^{\beta\mu m} \; g_m \quad . \tag{3.28}$$

By analogy to (2.19) and (3.1), we see that another form is

$$f_m = (m!)^{-1} \; e^{\beta\mu m} \; \Sigma_\Lambda (2\pi i)^{-1} \int dW \; e^{-\beta W} \; \mathcal{L}_m [\; \langle \; \Lambda^m(0) \; | \; A^m (W - H^m)^{-1} | \; \Lambda^m(0) \; \rangle \;]. \tag{3.29}$$

In terms of f_m, the partition function (3.26) is

$$\mathcal{Z} = \sum_N \frac{1}{(NZ)!} \sum_{\{n_m\}} \prod_m \frac{1}{n_m!} \; [\; (mZ)! \; f_m \;]^{n_m} \quad . \tag{3.30}$$

From the analogy of f_m (3.27) to $\mathcal{Z}$ (2.17), we can immediately write down a recursion relation for f_m. The linkage operator $\mathcal{L}_m$ just subtracts off the effects of clusterings into more than one cluster. Noting the form (3.30), we thus have

$$f_m = \frac{1}{m!} e^{\beta\mu m} \operatorname{Tr} \exp(-\beta H^m) - \frac{1}{(mZ)!} \sum_{\{n_{m'}\}} \prod_{m'} \frac{1}{n_{m'}!} [(m'Z)!\, f_{m'}]^{n_{m'}} , \tag{3.31}$$

with

$$\Sigma_{m'}\ m'\, n_{m'} = m$$

and

$$\Sigma_{m'}\ n_{m'} > 1 .$$

Let us now realize that our mathematical definition of a linked graph includes terms representing physically unlinked molecules. Consider, for example, $m = 2$ for the case of hydrogen atoms. If electron 1 interacts with proton 2, this is represented by a graph linked by either V_{12} or an exchange. However, the state of electron 1 interacting <u>only</u> with proton 2(and not with proton 1), and electron 2 interacting <u>only</u> with proton 1, is included in f_2, although it is not manifest in our representation. It is convenient to subtract off such "physically" unlinked graphs; their contributions are of course each the same as those of the corresponding "mathematically" unlinked graphs.

Let L_m denote the operator that subtracts off all such unlinked graphs, and let

$$F_m \equiv (m!)^{-1} e^{\beta\mu m} L_m [\operatorname{Tr} \exp(-\beta H^m)] \tag{3.32}$$

be the analogue to f_m. For each mathematical clustering $\{n_{m'}\}$ there are

$$\frac{(mZ)!}{\prod_{m'} [m'Z)!]^{n_{m'}}} \tag{3.33}$$

physical clusterings, since this is the number of assignments of the electrons to the clusters. If we insert this factor in the second term of (3.31), that equation then applies to F_m :

$$F_m = \frac{1}{m!} e^{\beta\mu m} \operatorname{Tr} \exp(-\beta H^m) - \sum_{\{n_{m'}\}} \prod_{m'} \frac{1}{n_{m'}!} (F_{m'})^{n_{m'}} . \tag{3.34}$$

Similarly, we modify (3.30) with the corresponding factor

$$\frac{(NZ)!}{\prod_m (mZ!)^{n_m}} ,$$

and obtain

$$\begin{aligned} \mathcal{Z} &= \sum_N \sum_{\{n_m\}} \prod_m \frac{1}{n_m!} (F_m)^{n_m} \\ &= \prod_m \sum_{n_m} \frac{1}{n_m!} (F_m)^{n_m} \\ &= \prod_m \exp F_m \end{aligned}$$

or

$$\ln \mathcal{Z} = \sum_{m=1}^{\infty} F_m . \tag{3.35}$$

Thus the logarithm of the grand partition function is expressed as the sum of the F_m's, which are evaluated from (3.34) and its graphical representation.

The pressure and density may now be obtained:

$$p = \theta \mathcal{V}^{-1} \ln \mathcal{Z} = \theta \mathcal{V}^{-1} \Sigma_m F_m , \tag{3.36}$$

$$n = \theta \mathcal{V}^{-1} \partial \ln \mathcal{Z}/\partial\mu = \theta \mathcal{V}^{-1} \Sigma_m \partial F_m/\partial\mu = \mathcal{V}^{-1} \Sigma_m m F_m , \tag{3.37}$$

where (3.32) was used in the last step of (3.37). These are converted to the conventional form[1] by introducing the activity

$$z \equiv F_1/\mathcal{V} = f_1/\mathcal{V} = e^{\beta\mu} g_1/\mathcal{V} \tag{3.38}$$

and the "cluster integrals"

$$b_m \equiv (F_1/\mathcal{V})^{-m} (F_m/\mathcal{V}) = z^{-m} F_m/\mathcal{V} . \tag{3.39}$$

Then we have

$$F_m = \mathcal{V} z^m b_m , \tag{3.40}$$

and

$$p/\theta = \Sigma_m z^m b_m , \tag{3.41}$$

$$n = \Sigma_m m z^m b_m . \tag{3.42}$$

(We note that $b_1 = 1$, so that in the limit of low density, $z \rightarrow n$.)

IV. THE CLASSICAL VIRIAL EXPANSION

The quantity g_1 was defined in (3.13) as the single-molecule partition function

$$g_1 = \Sigma_\lambda \; e^{-\beta\epsilon} \; , \tag{4.1}$$

where the sum is over properly antisymmetrized states. Let us separate the center-of-mass motion from the internal coordinates:

$$\epsilon = e + k^2/2M \; , \tag{4.2}$$

$$|\lambda\rangle = |\lambda^{cm}\rangle \; |\lambda^{int}\rangle \; , \tag{4.3}$$

$$g_1 = \left\{ \Sigma_{\lambda^{cm}} \; e^{-\beta k^2/2M} \right\} \left\{ \Sigma_{\lambda^{int}} \; e^{-\beta e} \right\} . \tag{4.4}$$

The center-of-mass partition function may be evaluated classically:

$$\mathcal{V}(2\pi)^{-3} \int d^3k \; e^{-\beta k^2/2M} = \mathcal{V}\lambda^{-3} \; , \tag{4.5}$$

where

$$\lambda \equiv (2\pi/M\theta)^{1/2} \tag{4.6}$$

is the "thermal wave length." We shall denote the single-molecule internal partition function by γ :

$$\gamma \equiv \Sigma_{\lambda^{int}} \; e^{-\beta e} \; . \tag{4.7}$$

We then have the relations

$$g_1 = \mathcal{V}\lambda^{-3}\gamma \; , \tag{4.8}$$

$$z = e^{\beta\mu}\lambda^{-3}\gamma \; . \tag{4.9}$$

At temperatures low compared with the excitation potential of the first excited internal state, we have

$$\gamma \approx e^{-\beta e_0} , \tag{4.10}$$

$$z \approx \lambda^{-3} e^{\beta\mu'} , \tag{4.11}$$

with

$$\mu' \equiv \mu - e_0 , \tag{4.12}$$

the conventional molecular chemical potential.[1]

In evaluating F_m for $m > 1$, the kinetic energy of the molecular centers of mass cannot be separated out, because it does not commute with the potential energy, which is a function of the center-of-mass positions (as well as of the internal coordinates). However, for large molecular mass (or high temperature), the center-of-mass motion may be treated classically.[8] We shall assume that this is the case, so that F_m (3.32) becomes

$$F_m = (m!)^{-1} (e^{\beta\mu}/\lambda^3)^m \; L_m \left\{ \int d^3R^{(m)} \; \mathrm{Tr} \exp[-\beta \, H^m(\underset{\sim}{R}^{(m)}) \,] \right\} ; \tag{4.13}$$

here the center-of-mass kinetic partition function has been evaluated to yield λ^{-3m}. Integration over the positions of the centers of mass $\underset{\sim}{R}^{(m)}$ of the m molecules remains to be done. The trace now refers only to internal coordinates;

$$H^m(\underset{\sim}{R}^{(m)}) \equiv H^m - \sum_{i=1}^{m} (k_i^2/2M) \tag{4.14}$$

depends parametrically on $\underset{\sim}{R}^{(m)}$, and includes the internal kinetic energies and the total potential energy of the m molecules. Since only the relative positions of the centers of mass enter into the latter, one integration can

be immediately performed to yield a factor $\mathcal{V}$. Thus the cluster integral b_m (3.39) is, from (4.13) and (4.9),

$$b_m = (m!)^{-1} \gamma^{-m} L_m \left\{ \int d^3R^{(m-1)} \, \mathrm{Tr} \exp[-\beta H^m(\underset{\sim}{R}^{(m)})] \right\} . \tag{4.15}$$

The recursion formula (3.34) now reads, for the cluster integrals,

$$b_m = \frac{1}{m! \, \gamma^m} \int d^3R^{(m-1)} \, \mathrm{Tr} \exp [-\beta H^m(\underset{\sim}{R}^{(m)})] - \frac{1}{\mathcal{V}} \sum_{\{n_{m'}\}} \prod_{m'} \frac{1}{n_{m'}!} (\mathcal{V} b_{m'})^{n_{m'}} . \tag{4.16}$$

Let us introduce the exact eigenstates and eigenvalues of $H^m(\underset{\sim}{R}^{(m)})$,

$$H^m(\underset{\sim}{R}^{(m)}) \mid \mu (\underset{\sim}{R}^{(m)}) \rangle = \mathcal{E}(\underset{\sim}{R}^{(m)}) \mid \mu (\underset{\sim}{R}^{(m)}) \rangle , \tag{4.17}$$

so that we have

$$\mathrm{Tr} \exp[-\beta H^m(\underset{\sim}{R}^{(m)})] = \Sigma_\mu \exp[-\beta \mathcal{E} (\underset{\sim}{R}^{(m)})] . \tag{4.18}$$

For temperatures low compared with excitation energies, this is approximately

$$\exp [-\beta \mathcal{E}_0(\underset{\sim}{R}^{(m)})] , \tag{4.19}$$

where $\mathcal{E}_0(\underset{\sim}{R}^{(m)})$ is the ground-state energy for fixed molecular centers of mass. In this approximation we may use (4.10), and introduce

$$\phi^m(\underset{\sim}{R}^{(m)}) \equiv \mathcal{E}_0(\underset{\sim}{R}^{(m)}) - m e_0 , \tag{4.20}$$

the m-molecule ground-state interaction energy. The recursion relation (4.16) now reads

$$b_m = \frac{1}{m!} \int d^3R^{(m-1)} \exp\left[-\beta \phi^{m}(\underline{R}^{(m)})\right] - \frac{1}{\mathcal{V}} \sum_{\{n_{m'}\}} \prod_{m'} \frac{1}{n_{m'}!} (\mathcal{V}\, b_{m'})^{n_{m'}} . \tag{4.21}$$

This form is equivalent to the Ursell-Mayer virial expansion.[1]

V. GENERALIZATION

We have supposed above that only internal interactions are present in the system. Suppose now that there is additionally an interaction, with a static external field, of the form

$$V^{ext} = \Sigma_i \; V_i \quad , \tag{5.1}$$

where V_i is the external interaction energy of molecule i. We must now include graphs for which there are a number of external interactions, as in Fig. 3. The arguments leading to Eqs. (3.32), (3.34), and (3.35) are clearly still valid; H^m is now the total m-molecule Hamiltonian, including the external interaction. It is convenient (for future applications[9]) to write

$$F_m = \Sigma_{r=0}^{\infty} \; F_m^{\;r} \quad , \tag{5.2}$$

where $F_m^{\;r}$ is the resultant of m-molecule linked graphs with r external interactions. (Fig. 3 corresponds to $r = 2$.) This provides a perturbation expansion in the strength of the external field.

If there are several species of particles, with chemical potentials μ_s $(s = 1, \cdots, S)$, the grand partition function (2.17) becomes

$$\mathcal{Z}(\theta, \{\mu_s\}, \mathcal{V}) = \sum_{\{N_s\}} \left[\prod_s (N_s!)^{-1}\right] \exp(\beta \, \Sigma_s \, \mu_s \, N_s) \; \mathrm{Tr} \exp[-\beta \, H\{N_s\} \;] \; . \tag{5.3}$$

The antisymmetrization operator (2.18) becomes

$$A^{\{N_s\}} = \frac{\Pi_s (Z_s!)^{N_s}}{(\Sigma_s \, Z_s \, N_s)!} \; \Sigma_\alpha \; \delta_\alpha \; P_\alpha \quad . \tag{5.4}$$

Other changes are self-evident. Equation (3.35) becomes

$$\ln \mathcal{Z} = \sum_{\{m_s\}} F\{m_s\} \quad , \tag{5.5}$$

where (3.32) is generalized to

$$F\{m_s\} = [\Pi_s \; m_s!\,]^{-1} \exp(\beta \Sigma_s \mu_s m_s) \, L[\mathrm{Tr} \exp(-\beta H\{m_s\})] \; . \tag{5.6}$$

FOOTNOTES AND REFERENCES

1. For expositions see, e.g., J. De Boer, Reports on Progress in Physics 12, 305 (1948-49), or T. L. Hill, Statistical Mechanics (McGraw-Hill Book Co., New York, 1956), Chap. 5. For a derivation of the virial expansion under the same general conditions as in this paper, but by a simple algebraic method of S. Ono and J. E. Kilpatrick, see T. L. Hill, op. cit., pp. 134-136.
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4. A. E. Glassgold, W. Heckrotte, and K. M. Watson, Phys. Rev. 115, 1374 (1959). The present paper may be considered as a generalization and correction of Sec. IV of this reference, and may be understood even if the reference has not been read. D. J. Thouless, Phys. Rev. 116, 21 (1959).
5. T. D. Lee and C. N. Yang, Phys. Rev. 113, 1165 (1959).
6. In Sec. V we indicate the generalization to the presence of an external field.
7. Our treatment is thus nonrelativistic. We plan to discuss effects due to interaction with the transverse electromagnetic field in a subsequent paper.
8. R. W. Zwanzig, Phys. Rev. 106, 13 (1957).
9. A. N. Kaufman and K. M. Watson (submitted to Physics of Fluids).

FIGURE CAPTIONS

Fig. 1. Contour for E-integration.

Fig. 2. Examples of unlinked graphs.

Fig. 3. A graph with external interaction.

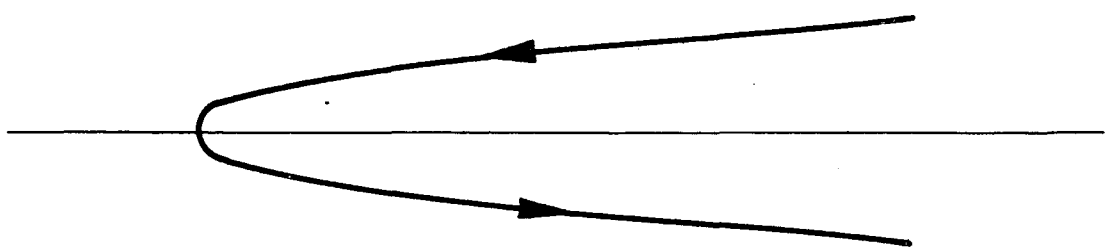

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Fig. 1.

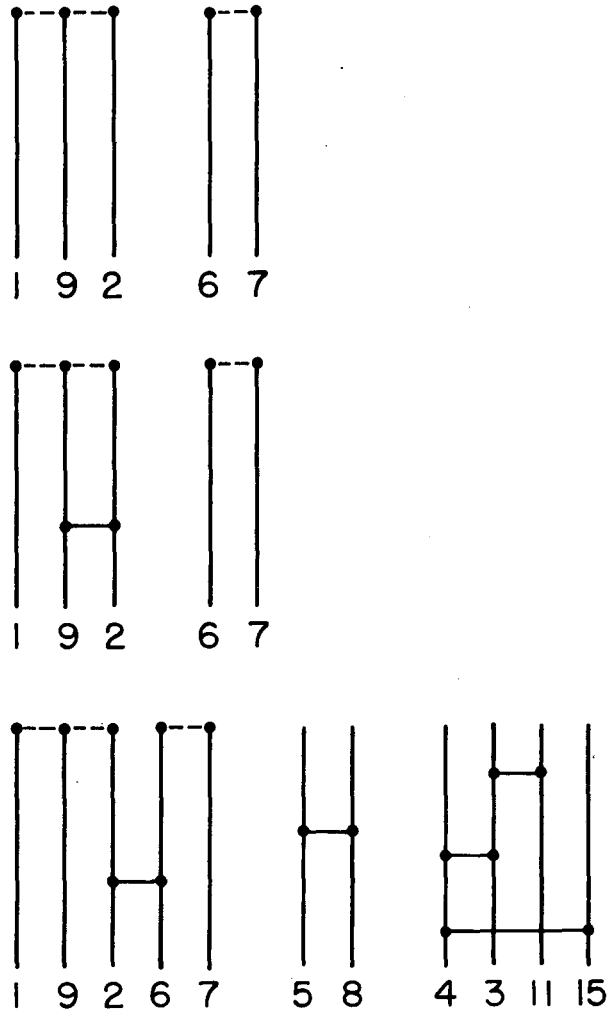

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Fig. 2

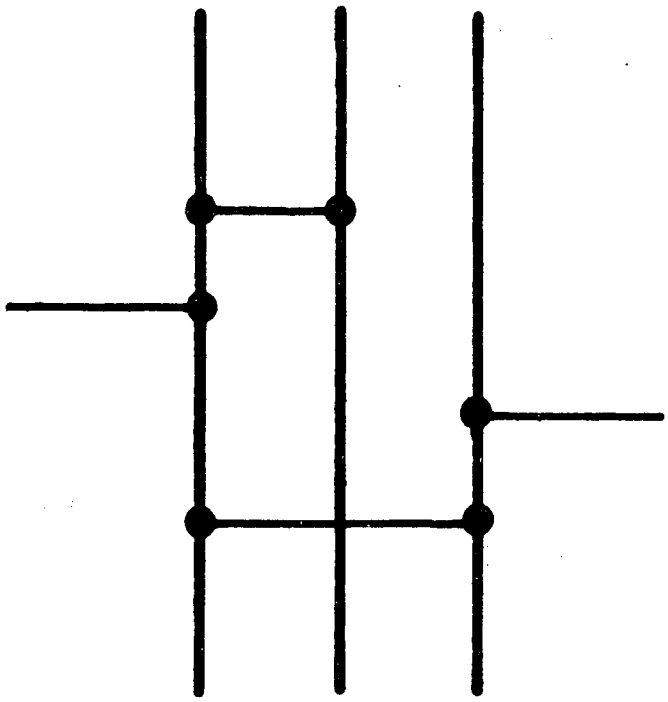

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Fig. 3.

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