

Statistical Theory of Magnetic Susceptibility of an Imperfect Gas

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The linear response of an imperfect gas in thermal equilibrium to a nonuniform external magnetostatic field is studied, using a linked-diagram evaluation of the grand partition function. Account is taken of the molecular structure, of short-range molecular interaction and correlation, and of the long-range dipole-dipole interaction. In addition, a multipole expansion of the molecular interaction leads to the consideration of interaction terms, not heretofore studied, of order lower than or the same as that of the well-known dipole-dipole terms. The contributions of these terms are eliminated by a summation of graphs, which is an operational generalization of the conventional gauge transformation. The final result is a virial expansion of the Clausius-Mossotti function.

I. INTRODUCTION

IN a recent paper,¹ to be referred to as KW, Kaufman and Watson calculated the linear response of an imperfect gas of molecules, in thermal equilibrium, to a nonuniform external *electrostatic* field. The result was expressible as a virial expansion of the Clausius-Mossotti function:

$$\frac{K-1}{K+2} = \frac{4\pi}{3} [n\alpha_1(\Theta) + n^2\alpha_2(\Theta) + \dots], \quad (1.1)$$

where $K(n, \Theta)$ is the dielectric constant, n is the molecular density, Θ is the temperature (in energy units), and $\alpha_1, \alpha_2, \dots$ are polarizability coefficients with a simple physical interpretation.²

It was at first thought that the treatment of the corresponding *magnetostatic* problem would be entirely analogous. However, our investigation uncovered many novel features, and the present paper is devoted to an exposition of these. Those aspects of the problem which *are* analogous are omitted, with a suitable reference to KW. (Hence a familiarity with KW is helpful for an understanding of the present paper, but is not essential.)

The system to be studied is a gas of real molecules (of a single species, for simplicity), enclosed by a container of volume V with fixed walls, in thermal equilibrium at temperature Θ , and acted upon by a nonuniform external magnetostatic field $\mathbf{B}_0(\mathbf{R})$. The linear response is characterized by the permeability $\mu(n, \Theta)$, which relates the macroscopic fields \mathbf{B} and \mathbf{H} (to be defined in Sec. III). We shall study the linear response

for a *dilute* imperfect gas, by which we mean that in the Clausius-Mossotti expansion to be derived

$$\frac{\mu-1}{\mu+2} = \frac{4\pi}{3} [n\alpha_1(\Theta) + n^2\alpha_2(\Theta) + \dots] \quad (1.2)$$

(now $\alpha_1, \alpha_2, \dots$ represent *magnetic* polarizabilities), only terms to order n^2 are treated. This allows a simplification of treatment, in that only *binary* molecular encounters need to be studied.

The de Broglie wavelength of the molecular center-of-mass motion is assumed to be small compared to molecular size. Thus this motion is treated classically, and the molecules are considered distinguishable. Let \mathbf{R}_l denote the position of the center of mass of the l th molecule. The set $\{\mathbf{R}_l\}$ (for all l) is called a "configuration." For a criterion of molecular contact, we introduce a length R_0 , much larger than molecular size a_0 , and much smaller than the mean nearest-neighbor distance $n^{-1/3}$. Then, if the molecular separation R_{lm} of molecules l and m is less than R_0 , they are said to be in contact.

Each configuration can be partially characterized by the numbers N_1, N_2, N_3, \dots ; where N_1 is the number of "free" molecules, i.e., molecules not in contact with others, N_2 is the number of pairs of molecules in contact, N_3 is the number of triplets, etc. The total number of molecules is $N = \sum m N_m$. For a dilute gas we have the relation

$$N_1 \gg N_2 \gg N_3 \dots$$

for nearly all configurations. Hence we shall neglect N_3 , and shall treat each configuration as if only free molecules and pairs were present.

We introduce the term "quasimolecule" for either a free molecule or a pair. (We shall use the symbols a, b, \dots to label quasimolecules; l, m, \dots to label real molecules; and i, j, \dots to label their constituent particles, i.e., electrons and nuclei.) In Sec. II we shall derive a Hamiltonian for the system in a given configura-

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¹ A. N. Kaufman and K. M. Watson, *Phys. Fluids* **4**, 931 (1961).

² A. N. Kaufman and K. M. Watson, *J. Chem. Phys.* **36**, 439 (1962).

tion. It can be expressed in the form

$$H = \sum_a H_a + \sum_{a < b} H_{ab}; \quad (1.3)$$

H_a involves operators of particles in quasimolecule a only, while H_{ab} involves those of a and b . Because of the separation of quasimolecules implicit in their definition, a multipole expansion is possible for the interaction H_{ab} . We find that, in addition to the magnetic dipole-dipole interaction (which falls off as R_{ab}^{-3}), there are many other terms of order R_{ab}^{-n} , with $n=1, 2, \text{ or } 3$, involving other electric and magnetic multipoles.

Section III is devoted to an exposition of the statistical-mechanical formalism based on the quasimolecule concept. This is then utilized in Sec. IV to evaluate the magnetization, with only the magnetic dipole-dipole interactions considered. Finally, in Sec. V, the other interaction terms are treated, and it is shown that, as expected, they make no contribution to the magnetization. Finally, Sec. VI summarizes the concepts studied, and the reasons for the approach used here.

II. THE HAMILTONIAN

The magnetic interaction between particles is relativistic in nature, being of order v^2/c^2 compared to the Coulomb interaction. In the present section we wish to find the particle Hamiltonian which includes the magnetic interaction between the molecules of the macroscopic system to be studied. A possible starting point is the Hamiltonian of relativistic electrodynamics, whereby the particles interact via the radiation field. It is shown by Bethe and Salpeter,³ using lowest order perturbation theory, that the effective interaction between particles is given by the Breit Hamiltonian if the particle separation r_{ij} is small relative to an electromagnetic wavelength λ characteristic of the virtual transitions between unperturbed states of the Coulomb Hamiltonian. The Breit Hamiltonian, in turn, can be reduced to the Darwin Hamiltonian^{4,5} if the particle speeds v are small compared to c .

Hence we utilize the Darwin approximation, valid to order v^2/c^2 and if $r_{ij} \ll \lambda$. Our discussion of it will be classical for the time being. At any stage it may be thrown into quantum operator form by means of the Weyl prescription.⁶ Further, the nonclassical spin contributions to the interaction, being well understood, can be postponed until the end of the calculation, and then included in an obvious way. Later in this section we shall discuss the interaction between distant particles, i.e., separations violating the condition $r_{ij} \ll \lambda$.

³ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 38 α .

⁴ C. G. Darwin, *Phil. Mag.* **39**, 537 (1920).

⁵ J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962), Sec. 12.6

⁶ H. Weyl, *Theory of Groups and Quantum Mechanics* (Methuen and Company Ltd., London, 1932), p. 275.

In a previous paper,⁷ we have discussed the classical Darwin approximation for a macroscopic body with both internal and external magnetic interaction, and have deduced various thermodynamic expressions for magnetic energy and work. Quoting from Eq. (11) of that paper, the Darwin Lagrangian is

$$L = \sum_i K_i - \sum_{i < j} C_{ij} + \sum_{i < j} M_{ij} + \sum_i q_i c^{-1} \mathbf{v}_i \cdot \mathbf{A}_0(\mathbf{r}_i), \quad (2.1)$$

where

$$K_i \equiv \frac{1}{2} m_i v_i^2 \quad (2.2)$$

is the kinetic energy of a particle;

$$C_{ij} \equiv q_i q_j r_{ij}^{-1} \quad (2.3)$$

is the Coulomb interaction energy of a pair of particles;

$$M_{ij} \equiv c^{-2} q_i q_j \mathbf{v}_i \cdot \mathbf{v}_j \cdot \mathbf{T}_{ij} \quad (2.4)$$

is their magnetic interaction energy, with

$$\mathbf{T}_{ij} \equiv \frac{1}{2} (\mathbf{I} + \hat{r}_{ij} \hat{r}_{ij}) r_{ij}^{-3}; \quad (2.5)$$

and \mathbf{A}_0 is the externally applied time-independent vector potential. (The external scalar potential is taken to be zero in this paper.) The canonical momentum of a particle is

$$\mathbf{p}_i = m_i \mathbf{v}_i + q_i c^{-1} \mathbf{A}^i, \quad (2.6)$$

where \mathbf{A}^i is the *total* vector potential, in the Coulomb gauge, acting on particle i :

$$\mathbf{A}^i \equiv \mathbf{A}_0(\mathbf{r}_i) + \sum_j q_j c^{-1} \mathbf{T}_{ij} \cdot \mathbf{v}_j. \quad (2.7)$$

(It is to be understood that $\mathbf{T}_{ij} \equiv 0$ for $i=j$.)

The corresponding Hamiltonian is⁷

$$H = \sum_i K_i + \sum_{i < j} (C_{ij} + M_{ij}). \quad (2.8)$$

For canonical or quantum calculations, it is convenient to eliminate the velocities in favor of the momenta. Solving Eqs. (2.6) and (2.7), we obtain

$$m_i \mathbf{v}_i = \mathbf{P}_i - (q_i/c) \sum_j (q_j/m_j c) \mathbf{S}_{ij} \cdot \mathbf{P}_j, \quad (2.9)$$

where

$$\mathbf{P}_i \equiv \mathbf{p}_i - q_i c^{-1} \mathbf{A}_0(\mathbf{r}_i) \quad (2.10)$$

and

$$\mathbf{S}_{ij} \equiv \mathbf{T}_{ij} - \sum_k (q_k^2/m_k c^2) \mathbf{T}_{ik} \cdot \mathbf{T}_{kj} + \dots \quad (2.11)$$

Substituting into (2.8), we find

$$H = \sum_i \frac{1}{2m_i} P_i^2 + \sum_{i < j} C_{ij} - \sum_{i < j} (q_i q_j / m_i m_j c^2) \mathbf{P}_i \cdot \mathbf{P}_j \cdot \mathbf{S}_{ij}. \quad (2.12)$$

From the definition of \mathbf{S}_{ij} , we see that the last term of

⁷ A. N. Kaufman and T. Soda, *J. Chem. Phys.* **37**, 1988 (1962).

H includes *many-body* interactions. However, in the series (2.11), the relative order of successive terms is $\epsilon \equiv Nr_0/R$, where N is the total number of interacting particles, r_0 is the classical electron radius, and R is a typical interparticle distance; thus $\epsilon \sim nr_0R^2$. Now, since the applicability of the Darwin approximation is limited to $R \ll \lambda$, we have $\epsilon \ll nr_0\lambda^2$. Estimating $r_0 \sim (137)^{-2}a_0$, and $\lambda \sim 137a_0$, we find $\epsilon \ll na_0^3$. Our diluteness assumption implies $na_0^3 \ll 1$, hence $\epsilon \ll 1$. Therefore \mathbf{S}_{ij} may be replaced by \mathbf{T}_{ij} in (2.9) and (2.12), and the interaction reduces to a sum of two-body interactions. Also ϵ represents the order of the ratio of the second term to the first term on the right side of (2.9). Therefore we may, when convenient, replace the \mathbf{P} 's in the last term of (2.12) by $m\mathbf{v}$'s, obtaining

$$H = \sum_i \frac{1}{2m_i} P_i^2 + \sum_{i < j} (C_{ij} - M_{ij}). \quad (2.13)$$

[Note the difference in sign of the magnetic term in the two equivalent forms (2.8) and (2.13).]

As explained in Sec. I, for each configuration $\{\mathbf{R}_i\}$, we assign the particles to quasimolecules; thus (2.13) can be written in the form (1.3), with

$$H_a \equiv \sum_i^a \frac{1}{2m_i} P_i^2 + \sum_{i < j}^a (C_{ij} - M_{ij}) \quad (2.14)$$

the Hamiltonian for quasimolecule a , and

$$\begin{aligned} H_{ab} &\equiv C_{ab} - M_{ab} \\ &\equiv \sum_i^a \sum_j^b (C_{ij} - M_{ij}) \end{aligned} \quad (2.15)$$

the interaction Hamiltonian of two quasimolecules.

Because two quasimolecules a and b are by definition far apart ($R_{ab} \gg a_0$), their interaction H_{ab} may be expanded in a multipole series. The leading term of the Coulomb interaction, for uncharged quasimolecules, is well known:

$$C_{ab}^{\pi\pi} \equiv \boldsymbol{\pi}_a \boldsymbol{\pi}_b : \mathbf{A}_{ab}, \quad (2.16)$$

where

$$\boldsymbol{\pi}_a \equiv \sum_i^a q_i \mathbf{s}_i \quad (2.17)$$

is the electric dipole moment of quasimolecule a ,

$$\mathbf{A}_{ab} \equiv \nabla_a \nabla_b R_{ab}^{-1} \equiv (\mathbf{I} - 3\hat{R}_{ab}\hat{R}_{ab})R_{ab}^{-3} \quad (2.18)$$

is the dipole-dipole tensor, \mathbf{R}_a is the position of the center of mass of a quasimolecule, and \mathbf{s}_i is the position of a particle relative to its quasimolecular center of mass:

$$\mathbf{s}_i \equiv \mathbf{r}_i - \mathbf{R}_a. \quad (2.19)$$

Because of the inequality $a_0 \ll R_0$, the next terms in the multipole expansion are relatively small, and because they fall off as R_{ab}^{-4} , they have no long-range effect.

The multipole expansion of the magnetic interaction is well known only for the case of time-independent charge distributions. Since quantum fluctuations (of electric dipole moments, for example) are large, the assumption of time independence cannot be made here. To our knowledge, the general case has not previously been discussed in the literature. From (2.15) and (2.5), we have

$$M_{ab} = c^{-2} \sum_i^a \sum_j^b q_i q_j \mathbf{v}_i \mathbf{v}_j : \mathbf{T}_{ij}. \quad (2.20)$$

Since the nuclear velocities are small compared to the electronic velocities, we may with negligible error restrict the sums in (2.20) to the electrons; correspondingly, we may replace \mathbf{v}_i by $\dot{\mathbf{s}}_i$. The expansion of M_{ab} in powers of (s/R_{ab}) is straightforward, and we find, to terms of order R_{ab}^{-3} ,

$$M_{ab} = M_{ab}^{(1)} + M_{ab}^{(2)} + M_{ab}^{(3)}, \quad (2.21)$$

where

$$M_{ab}^{(1)} = c^{-2} \dot{\boldsymbol{\pi}}_a \dot{\boldsymbol{\pi}}_b : \mathbf{T}_{ab}, \quad (2.21a)$$

with

$$\mathbf{T}_{ab} \equiv \frac{1}{2}(\mathbf{I} + \hat{R}_{ab}\hat{R}_{ab})R_{ab}^{-1}; \quad (2.21b)$$

$$M_{ab}^{(2)} = c^{-2} \sum_i^a q_i \dot{\mathbf{s}}_i (\mathbf{s}_i \cdot \nabla_a) \dot{\boldsymbol{\pi}}_b : \mathbf{T}_{ab} + (a \leftrightarrow b); \quad (2.21c)$$

$$\begin{aligned} M_{ab}^{(3)} &= c^{-2} \sum_i^a q_i \dot{\mathbf{s}}_i (\mathbf{s}_i \cdot \nabla_a) \sum_j^b q_j \dot{\mathbf{s}}_j (\mathbf{s}_j \cdot \nabla_b) : \mathbf{T}_{ab} \\ &+ \frac{1}{2} c^{-2} \left[\sum_i^a q_i \dot{\mathbf{s}}_i (\mathbf{s}_i \cdot \nabla_a)^2 \dot{\boldsymbol{\pi}}_b : \mathbf{T}_{ab} + (a \leftrightarrow b) \right]. \end{aligned} \quad (2.21d)$$

(The superscript on M refers to the negative exponent of R_{ab} .)

It is desirable to express the interaction in terms of the irreducible multipole moments. Thus the moment appearing in (2.21c) is separated into symmetric and antisymmetric parts

$$\sum_i^a q_i \dot{\mathbf{s}}_i \mathbf{s}_i \equiv \frac{1}{2} \mathbf{Q}_a' - c \mathbf{u}_a', \quad (2.22)$$

where

$$\begin{aligned} \mathbf{Q}_a' &\equiv \sum_i^a q_i \mathbf{s}_i \mathbf{s}_i \\ &\equiv \mathbf{Q}_a + \mathbf{I} \omega_a, \end{aligned} \quad (2.22a)$$

with

$$\mathbf{Q}_a \equiv \sum_i^a q_i (\mathbf{s}_i \mathbf{s}_i - \frac{1}{3} s_i^2 \mathbf{I}) \quad (2.22b)$$

the electric quadrupole moment, and

$$\omega_a \equiv \frac{1}{3} \sum_i^a q_i s_i^2 \quad (2.22c)$$

the second scalar electric moment; and

$$\mathbf{u}_a' \equiv \frac{1}{2}c^{-1} \sum_i^a q_i (\mathbf{s}_i \dot{\mathbf{s}}_i - \dot{\mathbf{s}}_i \mathbf{s}_i) \quad (2.22d)$$

is the dual to the magnetic dipole moment:

$$\mathbf{u}_a \equiv \frac{1}{2}c^{-1} \sum_i^a q_i \mathbf{s}_i \times \dot{\mathbf{s}}_i. \quad (2.22e)$$

Substitution of (2.22) into (2.21c) yields

$$M_a^{(2)} = M_{ab}^{\mu\pi} + M_{ab}^{Q\pi}, \quad (2.23)$$

where

$$M_{ab}^{\mu\pi} \equiv -c^{-1} [(\mathbf{u}_a' \cdot \nabla_a) \dot{\pi}_b \cdot \mathbf{T}_{ab} + (a \leftrightarrow b)] \quad (2.23a)$$

ouples the electric and magnetic dipole moments, while $M_{ab}^{Q\pi}$ couples electric quadrupole and dipole moments. (That the scalar moment ω does not appear follows from the identity $\nabla_a \cdot \mathbf{T}_{ab} = 0$, which is a reflection of the Coulomb gauge condition.) Expression (2.23a) may be simplified, by using the identity

$$\mathbf{T}_{ab} \equiv \mathbf{I}R_{ab}^{-1} + \nabla_a \nabla_b R_{ab}, \quad (2.24)$$

to the form

$$M_{ab}^{\mu\pi} = c^{-1} \dot{\pi}_b \cdot \mathbf{A}_a^b + (a \leftrightarrow b), \quad (2.23b)$$

where

$$\mathbf{A}_a^b \equiv -\mathbf{u}_a \times \nabla_b R_{ab}^{-1} \quad (2.25)$$

is the vector potential at \mathbf{R}_b due to only the magnetic dipole moment of a .

Substitution of (2.22) into the *first* term of (2.21d) yields

$$M_{ab}^{\mu\mu} + M_{ab}^{\mu Q} + M_{ab}^{Q Q}, \quad (2.26a)$$

in obvious notation. The magnetic dipole-dipole term is

$$\begin{aligned} M_{ab}^{\mu\mu} &= (\mathbf{u}_a' \cdot \nabla_a)(\mathbf{u}_b' \cdot \nabla_b) : \mathbf{T}_{ab} \\ &= -\mathbf{u}_a \mathbf{u}_b : \mathbf{A}_{ab}, \end{aligned} \quad (2.26b)$$

where we have again used (2.24). [Noting the minus sign of (2.15), we recognize this as the conventional magnetic interaction term.] The (magnetic dipole)—(electric quadrupole) term is

$$\begin{aligned} M_{ab}^{\mu Q} &= -\frac{1}{2}c^{-1} [(\mathbf{u}_a' \cdot \nabla_a)(\mathbf{Q}_b \cdot \nabla_b) : \mathbf{T}_{ab} + (a \leftrightarrow b)] \\ &= \frac{1}{2}c^{-1} \dot{\mathbf{Q}}_b : (\nabla_b \mathbf{A}_a^b)^S + (a \leftrightarrow b), \end{aligned} \quad (2.26c)$$

the superscript S indicating the symmetric part of the dyad. The term $M_{ab}^{Q Q}$ couples electric quadrupole moments.

The *second* term of (2.21d) couples the electric dipole moment to the reducible third moment $\sum_i q_i \mathbf{s}_i \mathbf{s}_i \dot{\mathbf{s}}_i$. Introducing tensor subscripts for the cartesian coordinates, and suppressing the particle subscript i and the symbol q , we have

$$C_{\mu\nu\sigma} \equiv s_\mu s_\nu \dot{s}_\sigma \quad (2.27a)$$

$$\equiv \frac{1}{3} \dot{O}_{\mu\nu\sigma} + \frac{2}{3} (\epsilon_{\nu\sigma\lambda} K_{\mu\lambda} + \epsilon_{\mu\sigma\lambda} K_{\nu\lambda}), \quad (2.27b)$$

where

$$O_{\mu\nu\sigma} \equiv s_\mu s_\nu s_\sigma \quad (2.27c)$$

is a completely symmetric third-rank tensor, and

$$K_{\mu\nu} \equiv \frac{1}{2} \epsilon_{\nu\rho\tau} s_\mu s_\rho \dot{s}_\tau \quad (2.27d)$$

is a second-rank traceless pseudotensor. The decomposition of O and K to irreducible tensors is as follows:

$$O_{\mu\nu\sigma} \equiv R_{\mu\nu\sigma} + \frac{1}{3} (\delta_{\mu\nu} V_\sigma + \delta_{\nu\sigma} V_\mu + \delta_{\mu\sigma} V_\nu), \quad (2.27e)$$

where $V_\sigma \equiv O_{\mu\mu\sigma}$ is a polar vector, and $R_{\mu\nu\sigma}$ is the traceless part of $O_{\mu\nu\sigma}$, i.e., $R_{\mu\mu\sigma} = R_{\mu\nu\nu} = R_{\mu\nu\mu} = 0$;

$$K_{\mu\nu} \equiv L_{\mu\nu} + \epsilon_{\mu\nu\rho} \Gamma_\rho, \quad (2.27f)$$

where \mathbf{L} is the symmetric part of \mathbf{K} (thus \mathbf{L} is a symmetric traceless second-rank pseudotensor), and $\mathbf{\Gamma}$ is the polar vector dual to the antisymmetric part of \mathbf{K} . In summary, \mathbf{C} is reducible to the irreducible tensors \mathbf{R} , \mathbf{V} , \mathbf{L} , and $\mathbf{\Gamma}$, none of which transforms under rotations and reflections like the axial vector magnetic dipole moment. (This fact will be of use in Sec. V.)

There are thus three types of interaction terms in the multipole expansion to order R_{ab}^{-3} : (a) the magnetic dipole-dipole interaction (2.26b); (b) the terms which couple the magnetic dipole to other moments, namely $M^{\mu\pi}$ and $M^{\mu Q}$; and (c) terms which couple two moments, neither of which is or transforms as a magnetic dipole moment. In the following sections, we shall proceed as if only (a) existed; then in Sec. V we shall eliminate (b) by the equivalent of a unitary transformation, and finally shall show that the terms (c) do not contribute to the magnetization.

It remains to discuss the magnetic interaction for the cases $R_{ab} \sim \lambda$ and $R_{ab} \gg \lambda$. In the latter case, we start with the Hamiltonian H^{ed} of electrodynamics, in the Coulomb gauge and the nonrelativistic limit⁸:

$$H^{\text{ed}} \equiv \sum_i K_i + \sum_{i<j} C_{ij} + H_r, \quad (2.28)$$

where H_r is the Hamiltonian of the transverse radiation field

$$H_r \equiv \int d^3r (E_r^2 + B_r^2) / 8\pi, \quad (2.28a)$$

and \mathbf{E}_r , \mathbf{B}_r are expressed in terms of the transverse ($\nabla \cdot \mathbf{A}_r = 0$) radiation potential

$$\mathbf{E}_r = -c^{-1} \dot{\mathbf{A}}_r, \quad \mathbf{B}_r = \nabla \times \mathbf{A}_r. \quad (2.28b)$$

The velocities \mathbf{v}_i in K_i [see (2.2)] are again to be eliminated in favor of the momenta \mathbf{p}_i by Eq. (2.6), but now the Darwin form (2.7) is replaced by

$$\mathbf{A}^i \equiv \mathbf{A}_0(\mathbf{r}_i) + \mathbf{A}_r(\mathbf{r}_i). \quad (2.29)$$

The Hamiltonian then reads

$$\begin{aligned} H^{\text{ed}} &= \sum_i P_i^2 / 2m_i + \sum_{i<j} C_{ij} + H_r \\ &\quad - \sum_i \{ (q_i / m_i c) \mathbf{P}_i \cdot \mathbf{A}_r(\mathbf{r}_i) \\ &\quad \quad - (q_i^2 / 2m_i c^2) [\mathbf{A}_r(\mathbf{r}_i)]^2 \}. \end{aligned} \quad (2.30)$$

⁸ Cf., for example, W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, England, 1954), 3rd ed., Sec. 6.4.

Following the method of Bethe and Salpeter³ (who treated the other limit $r_{ij} \ll \lambda$), we select those terms of (2.30), which correspond to two noninteracting quasimolecules, as an unperturbed Hamiltonian, and treat the remaining terms as perturbations. Second-order perturbation theory is then used to compute the shift in energy of an unperturbed state resulting from the $\mathbf{P}_i \cdot \mathbf{A}_r(\mathbf{r}_i)$ terms only. This energy change is then considered to be the effective magnetic interaction Hamiltonian. (The \mathbf{A}_r^2 terms and the higher order perturbation effects are ignored; they lead to infinities and must be treated with care.⁹)

Let $|\xi_a\rangle$ and $|\xi_b\rangle$ be unperturbed states of the two quasimolecules, while $|0\rangle$ and $|\mathbf{k}, \mathbf{e}\rangle$ represent respectively the vacuum radiation state and the one-photon (of momentum $\hbar\mathbf{k}$ and polarization \mathbf{e}) state. The second-order energy shift is due to the emission of a photon by either of the quasimolecules and its absorption by the other, without any molecular transition. Thus we have

$$\Delta E = \sum_{\mathbf{k}, \mathbf{e}} |\langle \xi_a \xi_b 0 | H' | \xi_a \xi_b \mathbf{k}, \mathbf{e} \rangle|^2 / (-\hbar c k), \quad (2.31)$$

with

$$H' \equiv - \sum_i^a (q_i/m_i c) \mathbf{P}_i \cdot \mathbf{A}_r(\mathbf{r}_i) - \sum_j^b (q_j/m_j c) \mathbf{P}_j \cdot \mathbf{A}_r(\mathbf{r}_j). \quad (2.32)$$

The reduction of (2.31) to

$$\Delta E = - \frac{4\pi}{c^2} \int \frac{d^3 k}{(2\pi)^3} \frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{k^2} : \langle \sum_i^a q_i m_i^{-1} \mathbf{P}_i e^{i\mathbf{k} \cdot \mathbf{s}_i} \rangle_a \times \langle \sum_j^b q_j m_j^{-1} \mathbf{P}_j e^{-i\mathbf{k} \cdot \mathbf{s}_j} \rangle_b e^{i\mathbf{k} \cdot \mathbf{R}_{ab}} \quad (2.33)$$

is straightforward; here $\langle \dots \rangle_a$ stands for $\langle \xi_a | \dots | \xi_a \rangle$. In the matrix elements, we replace $m_i^{-1} \mathbf{P}_i$ by \mathbf{v}_i , we ignore nuclear motion, and expand the exponential

$$\sum_i^a q_i \mathbf{v}_i e^{i\mathbf{k} \cdot \mathbf{s}_i} = \dot{\pi}_a + i\mathbf{k} \cdot (\frac{1}{2} \dot{\mathbf{Q}}_a' - c \mathbf{u}_a') + O(k^2 s^2), \quad (2.34)$$

where we have used (2.22). To this order of perturbation theory, the dotting operation is equivalent to commutation with the unperturbed Hamiltonian; thus the diagonal elements of the dotted terms vanish, and we have

$$\langle \sum_i^a q_i \mathbf{v}_i e^{i\mathbf{k} \cdot \mathbf{s}_i} \rangle_a = -i c \mathbf{k} \cdot \langle \mathbf{u}_a' \rangle_a + O(k^2). \quad (2.35)$$

Substituting into (2.33), we obtain finally

$$\Delta E = \langle \mathbf{u}_a \rangle_a \langle \mathbf{u}_b \rangle_b : \mathbf{A}_{ab} + O(R_{ab}^{-4}). \quad (2.36)$$

Hence we shall take the interaction of two distant

⁹ For an analogous problem, see the treatment of the Coulomb interaction between atoms for $R_{lm} \gg \lambda$: H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948); I. E. Dzyaloshinskii, Zh. Eksperim. i Teor. Fiz. **30**, 1152 (1956) [English transl: Soviet Phys.—JETP **3**, 977 (1957)].

($R_{ab} \gg \lambda$) molecules to be

$$H_{ab} = \mathbf{u}_a \mathbf{u}_b : \mathbf{A}_{ab}. \quad (2.37)$$

(The Coulomb interaction [cf. (2.15) and (2.16)] is of no importance for the present problem.) For the intermediate case ($R_{ab} \sim \lambda$), we shall adopt, without derivation, the same interaction, inasmuch as it is valid in both limiting cases. In conclusion, then, we use (2.37) for all R_{ab} in Secs. III and IV, and in Sec. V eliminate the other interaction terms for the case $R_{ab} \ll \lambda$.

III. STATISTICAL MECHANICS

The thermodynamic properties of the system studied are obtainable from the grand partition function

$$\mathfrak{z} = \sum_N \frac{1}{N!} e^{\beta \mu N} \text{Tr} e^{-\beta H^N}, \quad (3.1)$$

where H^N is the N -molecule Hamiltonian. As in KW, we treat the momenta and coordinates of the molecular centers of mass classically, obtaining

$$\mathfrak{z} = \sum_N \frac{y^N}{N!} \int d^3 R^{(N)} \text{Tr} e^{-\beta H^N(\mathbf{R}_i)}, \quad (3.2)$$

where

$$y \equiv \lambda^{-3} e^{\beta \mu}, \quad (3.3)$$

$$\lambda \equiv h(2\pi M \Theta)^{-1/2} \quad (3.4)$$

is the molecular thermal wavelength, and $H^N\{\mathbf{R}_i\}$ is the Hamiltonian, less the molecular centers-of-mass kinetic energy, for fixed configuration $\{\mathbf{R}_i\}$.

As discussed in Sec. I, for each configuration we assign the molecules to quasimolecules, and then ignore the contributions of quasimolecules consisting of more than two molecules. In Eq. (3.2), the integration over configuration space and the sum over N may then be replaced by, first, a restricted integration (denoted by a prime) over all configurations corresponding to a given assignment to quasimolecules; second, multiplication by the number $[N!/(N_1!N_2!2^{N_2})]$ of assignments for fixed (N_1, N_2) , and finally, a sum over (N_1, N_2)

$$\mathfrak{z} = \sum_{N_1, N_2} \frac{y^N}{N_1! N_2! 2^{N_2}} \int' d^3 R^{(N)} \text{Tr} e^{-\beta H^N(\mathbf{R}_i)}. \quad (3.5)$$

The trace operation in (3.2) and (3.5) is a sum over internal molecular states. We replace it by the operation Tr' , which includes additionally integration over the vector separation \mathbf{R}_{lm} (with $R_{lm} < R_0$) of the molecular members of each pair. Correspondingly, the remaining integration is then only over the $N' \equiv N_1 + N_2$ quasimolecule positions \mathbf{R}_a , subject to the restriction $R_{ab} > R_0$. (The restriction is of importance and valid in this simple form only when the quasimolecules a, b are free molecules.) The restriction on the integration can be lifted, if one introduces an additional fictitious hard-sphere

quasimolecule interaction of range R_0

$$\psi(R_{ab}) = \begin{cases} \infty & R_{ab} < R_0, \\ 0 & R_{ab} > R_0. \end{cases} \quad (3.6)$$

With the notations

$$H(N_1, N_2) \equiv H^N\{\mathbf{R}_i\} + \sum_{a < b} \psi(R_{ab}) \quad (3.7)$$

and

$$y_2 \equiv \frac{1}{2} y^2, \quad (3.8)$$

we may write the grand partition function in the simple form

$$\mathfrak{z} = \sum_{N_1, N_2} \frac{y^{N_1} y_2^{N_2}}{N_1! N_2!} \int d^3 R^{(N')} \text{Tr}' e^{-\beta H(N_1, N_2)}. \quad (3.9)$$

This bears a formal resemblance to the partition function of a two-species gas.

In an earlier paper,¹⁰ to be referred to as KW', it was shown how to express such a quantity in terms of "linked diagrams." We quote from that paper (Sec. V):

$$\ln \mathfrak{z} = \sum_{N_1, N_2} F(N_1, N_2), \quad (3.10a)$$

where

$$F(N_1, N_2) \equiv \frac{y^{N_1} y_2^{N_2}}{N_1! N_2!} \times \int d^3 R^{(N')} L_{N'} \text{Tr}' e^{-\beta H(N_1, N_2)}. \quad (3.10b)$$

The only difference between (3.10b) and the summand of (3.9) is the operator $L_{N'}$, which selects, from a diagrammatic representation of the trace, those diagrams in which all N' quasimolecules are linked.

We shall use (3.10) to calculate, now, the relation between density and activity (3.14) in the absence of an external field, and later, to obtain the linear relation between magnetization and applied field, making use of the first result. When the applied field \mathbf{B}_0 vanishes, the long-range quasimolecular interactions are ineffective, as will be seen in Sec. IV when the case $\mathbf{B}_0 \neq 0$ is studied. Thus the effective Hamiltonian (3.7) reduces to

$$H(N_1, N_2) = \sum_{a=1}^{N'} H_a + \sum_{a < b} \psi(R_{ab}). \quad (3.11)$$

Since ψ is of finite range, there are no many-body ($N' \gg 1$) contributions to $\ln \mathfrak{z}$ at low density. We shall see *a posteriori* that we need only the following F 's:

$$\ln \mathfrak{z} = F(1, 0) + F(2, 0) + F(0, 1), \quad (3.12)$$

i.e., contributions from one free molecule, two free molecules, and one pair.

From Eq. (3.10b), we have

$$F(1, 0) = Vz, \quad (3.13)$$

where

$$z \equiv y\gamma \quad (3.14)$$

is the activity, γ is the internal partition function for a free molecule, and V is the volume of the container. Letting \mathbf{R}_{12} be the separation of two free molecules, we have

$$F(2, 0) = \frac{1}{2} z^2 V \int d^3 R_{12} (e^{-\beta \psi(R_{12})} - 1), \quad (3.15)$$

the term (-1) being the effect of the linkage operator. It follows from (3.6) that

$$F(2, 0) = -\frac{1}{2} z^2 V V_0, \quad (3.16)$$

where $V_0 \equiv \frac{4}{3} \pi R_0^3$. Finally, in analogy to (3.13) and (3.14), we have

$$F(0, 1) = Vz_2, \quad (3.17a)$$

where

$$z_2 \equiv y_2 \gamma_2 \quad (3.17b)$$

is the "activity" of a pair, and

$$\gamma_2 \equiv \int_{R < R_0} d^3 R \text{Tr} e^{-\beta H_p(\mathbf{R})} \quad (3.17c)$$

is its internal partition function, with $H_p(\mathbf{R})$ its Hamiltonian for fixed molecular separation \mathbf{R} .

Collecting terms into (3.12) and using (3.8), we obtain [to $O(z^2)$]

$$V^{-1} \ln \mathfrak{z} = z - \frac{1}{2} z^2 \int_{R < R_0} d^3 R (1 - e^{-\beta \phi(\mathbf{R}, \Theta)}), \quad (3.18)$$

where we have introduced the molecular interaction free energy¹¹

$$\phi(\mathbf{R}, \Theta) \equiv -\Theta \text{Tr} \exp\{-\beta[H_p(\mathbf{R}) - H_p(\infty)]\}. \quad (3.19)$$

The mean density n is related to the activity by

$$n = z \partial(V^{-1} \ln \mathfrak{z}) / \partial z = z - 2z^2 b(\Theta) + O(z^3), \quad (3.20)$$

with

$$b(\Theta) \equiv \frac{1}{2} \int d^3 R (1 - e^{-\beta \phi}). \quad (3.21)$$

Incidentally, the equation of state is

$$\begin{aligned} p &= \Theta V^{-1} \ln \mathfrak{z} \\ &= \Theta [z - z^2 b(\Theta) + O(z^3)] \\ &= \Theta [n + n^2 b(\Theta) + O(n^3)], \end{aligned} \quad (3.22)$$

the well-known virial expansion, with the second virial coefficient including the effects of molecular structure.¹⁰

We now consider the system in the presence of the applied magnetostatic field $\mathbf{B}_0(\mathbf{R})$. Although the partition function \mathfrak{z} is gauge-invariant, the Hamiltonian de-

¹⁰ A. N. Kaufman and K. M. Watson, Phys. Fluids 4, 655 (1961).

¹¹ R. W. Zwanzig, Phys. Rev. 106, 13 (1957).

depends on \mathbf{B}_0 only through \mathbf{A}_0 , and always in the combination $\mathbf{p}_i - (q_i/c)\mathbf{A}_0(\mathbf{r}_i) \equiv \mathbf{P}_i$. It is convenient to choose a gauge which exhibits the \mathbf{B}_0 dependence explicitly.

Let us expand $\mathbf{A}_0(\mathbf{r}_i)$ about the center-of-mass position \mathbf{R}_a of the quasimolecule containing particle i . (Because the quasimolecules do not overlap, it is allowable to assign an electron to a definite quasimolecule, and require antisymmetry of the state function under exchange of electrons only within the same quasimolecule.)

$$\begin{aligned} \mathbf{A}_0(\mathbf{r}_i) &= \mathbf{A}_0(\mathbf{R}_a) + \mathbf{s}_i \cdot \nabla_a \mathbf{A}_0(\mathbf{R}_a) + O(s^2) \\ &= \mathbf{A}_0(\mathbf{R}_a) + \mathbf{s}_i \cdot (\nabla_a \mathbf{A}_0)^s \\ &\quad - \frac{1}{2} \mathbf{s}_i \times \mathbf{B}_0(\mathbf{R}_a) + O(s^2). \end{aligned} \quad (3.23)$$

Whereas the conventional gauge transformation, $\mathbf{A}_0(\mathbf{r}) \rightarrow \mathbf{A}_0'(\mathbf{r}) \equiv \mathbf{A}_0(\mathbf{r}) - \nabla \chi(\mathbf{r})$, utilizes a single gauge function χ (thereby leaving the state function completely antisymmetric), our treatment of the quasimolecules as distinguishable allows us to use a different gauge function χ_a for each quasimolecule. Referring to (3.23), we see that the choice

$$\chi_a(\mathbf{s}) \equiv \mathbf{s} \cdot \mathbf{A}_0(\mathbf{R}_a) + \frac{1}{2} \mathbf{s} \cdot \nabla_a \mathbf{A}_0(\mathbf{R}_a) \quad (3.24)$$

leads to

$$\begin{aligned} \mathbf{A}_0'(\mathbf{r}_i) &\equiv \mathbf{A}_0(\mathbf{r}_i) - \nabla_s \chi_a(\mathbf{s}_i) \\ &= -\frac{1}{2} \mathbf{s}_i \times \mathbf{B}_0(\mathbf{R}_a) + O(s^2). \end{aligned} \quad (3.25)$$

The terms $O(s^2)$ are of relative order a_0/L , where L is the spatial scale, assumed macroscopic, of $\mathbf{B}_0(\mathbf{R})$. Hence we drop these terms, and in the new gauge (dropping the prime), we use

$$\mathbf{A}_0(\mathbf{r}_i) = -\frac{1}{2} \mathbf{s}_i \times \mathbf{B}_0(\mathbf{R}_a). \quad (3.25a)$$

Consider the effect of a small change $\delta \mathbf{B}_0(\mathbf{R})$, of the external field, on the partition function (3.1)

$$\delta \bar{\partial} = -\beta \sum_N \frac{1}{N!} e^{\beta \mu N} \text{Tr}[e^{-\beta H^N} \delta H^N]. \quad (3.26a)$$

Since \mathbf{B}_0 appears in H^N only through the \mathbf{P} 's, we have

$$\begin{aligned} \delta H^N &= \sum_i \delta \mathbf{P}_i \cdot \partial H^N / \partial \mathbf{P}_i \\ &= \sum_i [-(q_i/c) \delta \mathbf{A}_0(\mathbf{r}_i)] \cdot \partial H^N / \partial \mathbf{p}_i \\ &= \sum_i [\frac{1}{2} (q_i/c) \mathbf{s}_i \times \delta \mathbf{B}_0(\mathbf{R}_a)] \cdot \mathbf{v}_i \\ &= -\sum_a \mathbf{u}_a \cdot \delta \mathbf{B}_0(\mathbf{R}_a). \end{aligned} \quad (3.26b)$$

We introduce the magnetization, or magnetic dipole density

$$\mathbf{M}(\mathbf{R}) \equiv \sum_a \mathbf{u}_a \delta(\mathbf{R} - \mathbf{R}_a), \quad (3.26c)$$

and express (3.26b) as

$$\delta H^N = - \int d^3 R \mathbf{M}(\mathbf{R}) \cdot \delta \mathbf{B}_0(\mathbf{R}). \quad (3.26d)$$

Substituting into (3.26a), we find

$$\delta \bar{\partial} = \bar{\partial} \beta \int d^3 R \langle \mathbf{M} \rangle(\mathbf{R}) \cdot \delta \mathbf{B}_0(\mathbf{R}), \quad (3.26e)$$

where $\langle \mathbf{M} \rangle(\mathbf{R})$ is the statistical mean

$$\langle \mathbf{M} \rangle(\mathbf{R}) \equiv \bar{\partial}^{-1} \sum_N \frac{1}{N!} e^{\beta \mu N} \text{Tr}[e^{-\beta H^N} \mathbf{M}(\mathbf{R})]. \quad (3.26f)$$

If $\mathbf{B}_0(\mathbf{R})$ were an arbitrary vector field, we could conclude from Eq. (3.26e) that $\langle \mathbf{M} \rangle(\mathbf{R})$ can be obtained by functional differentiation of $\bar{\partial}$

$$\langle \mathbf{M} \rangle(\mathbf{R}) = \Theta \delta \ln \bar{\partial} / \delta \mathbf{B}_0(\mathbf{R}). \quad (3.26g)$$

However, the condition $\nabla \cdot \mathbf{B}_0 = 0$ precludes this. Therefore, in the evaluation of $\bar{\partial}$, we shall consider $\mathbf{B}_0(\mathbf{R})$ always to be an *arbitrary* vector field, and shall never assume $\nabla \cdot \mathbf{B}_0 = 0$. Then the relation (3.26g) is valid. (To be sure, we have already used $\nabla \cdot \mathbf{B}_0 = 0$ to allow for the gauge transformation, but that was a transformation of the Hamiltonian *prior* to the evaluation of $\bar{\partial}$.)

In the diagrammatic evaluation of the F 's [see Eq. (3.10)], we may classify each diagram according to the power (r) of \mathbf{B}_0 in its value. Correspondingly we write

$$F(N_1, N_2) \equiv \sum_{r=0}^{\infty} F^{(r)}(N_1, N_2). \quad (3.27)$$

The terms $F^{(0)}$ have already been evaluated for the equation of state in the absence of \mathbf{B}_0 . The terms $F^{(1)}$ lead [see (3.26g)] to a magnetization independent of \mathbf{B}_0 ; for a gas, this vanishes except possibly in the neighborhood of the walls (where there is a preferred direction), and hence will be ignored. The terms $F^{(2)}$ lead to a linear relation between $\langle \mathbf{M} \rangle(\mathbf{R})$ and $\mathbf{B}_0(\mathbf{R})$, and will be evaluated in the next section. The result will be an integral equation for $\langle \mathbf{M} \rangle$ of the following form:

$$\begin{aligned} \langle \mathbf{M} \rangle(\mathbf{R}) &= \xi(n, \Theta) \\ &\times \left[\mathbf{B}_0(\mathbf{R}) - \int' d^3 R' \mathbf{\Lambda}(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle(\mathbf{R}') \right], \end{aligned} \quad (3.28)$$

where the prime on the integral sign denotes the exclusion of an infinitesimal sphere about \mathbf{R} , and where $\xi(n, \Theta)$ is a virial expansion

$$\xi(n, \Theta) = n \alpha_1(\Theta) + n^2 \alpha_2(\Theta) + O(n^3). \quad (3.29)$$

The expressions for the α 's will be stated in Sec. IV.

It remains to relate \mathbf{B}_0 to the macroscopic total field \mathbf{B} . In analogy to the definition of macroscopic electric field,¹² we define

$$\mathbf{B}(\mathbf{R}) \equiv \nabla \times \mathbf{A}(\mathbf{R}), \quad (3.30)$$

¹² W. F. Brown, Jr., in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XVII. It is fully discussed by A. N. Kaufman, *Am. J. Phys.* **29**, 626 (1961).

where $\mathbf{A}(\mathbf{R})$, the macroscopic vector potential, is in turn defined as

$$\mathbf{A}(\mathbf{R}) \equiv \mathbf{A}_0(\mathbf{R}) + \int d^3R' |\mathbf{R} - \mathbf{R}'|^{-1} \nabla' \times \langle \mathbf{M} \rangle(\mathbf{R}'). \quad (3.31)$$

Because of the singularity of the integrand at $\mathbf{R}' = \mathbf{R}$, we exclude an infinitesimal sphere from the integration, without changing the value of the integral. Substituting into (3.30), we obtain

$$\mathbf{B}(\mathbf{R}) = \mathbf{B}_0(\mathbf{R}) - \int d^3R' \mathbf{A}(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle(\mathbf{R}') + \frac{8\pi}{3} \langle \mathbf{M} \rangle(\mathbf{R}). \quad (3.32)$$

The \mathbf{H} field is then

$$\mathbf{H}(\mathbf{R}) \equiv \mathbf{B}(\mathbf{R}) - 4\pi \langle \mathbf{M} \rangle(\mathbf{R}) \quad (3.33a)$$

$$= \mathbf{B}_0(\mathbf{R}) - \int d^3R' \mathbf{A}(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle(\mathbf{R}') - \frac{4\pi}{3} \langle \mathbf{M} \rangle(\mathbf{R}). \quad (3.33b)$$

Thus Eq. (3.28) reads

$$\langle \mathbf{M} \rangle(\mathbf{R}) = \xi(n, \Theta) [\mathbf{H}(\mathbf{R}) + \frac{4}{3}\pi \langle \mathbf{M} \rangle(\mathbf{R})], \quad (3.34a)$$

or

$$\langle \mathbf{M} \rangle(\mathbf{R}) = \chi(n, \Theta) \mathbf{H}(\mathbf{R}), \quad (3.34b)$$

where the magnetic susceptibility χ is

$$\chi \equiv \xi(1 - \frac{4}{3}\pi\xi)^{-1}. \quad (3.35)$$

Now we eliminate $\langle \mathbf{M} \rangle$ from (3.34b) by (3.33a), and obtain

$$\mathbf{B}(\mathbf{R}) = \mu(n, \Theta) \mathbf{H}(\mathbf{R}), \quad (3.36)$$

where the magnetic permeability μ is related to ξ by

$$\frac{\mu - 1}{\mu + 2} = \frac{4\pi}{3} \xi. \quad (3.37)$$

Finally, substitution of (3.29) into (3.37) yields the Clausius-Mossotti expansion (1.2).

IV. MAGNETIZATION

In the present section, we calculate the linear magnetic response. From Eqs. (3.26g), (3.10a), and (3.27), this is

$$\langle \mathbf{M} \rangle(\mathbf{R}) = \Theta \delta \sum_{N_1, N_2} F^{(2)}(N_1, N_2) / \delta \mathbf{B}_0(\mathbf{R}). \quad (4.1)$$

The quantity $F^{(2)}(N_1, N_2)$ is given by (3.10b), with $L_{N'}$ replaced by $L_{N'}^{(2)}$, which selects linked graphs of N' quasimolecules of second order in \mathbf{B}_0 . The Hamiltonian $H(N_1, N_2)$ to be used in (3.10b) has the form of Eq. (1.3).

The single quasimolecule Hamiltonian H_a is given by Eq. (2.14), with

$$\mathbf{P}_i \equiv \mathbf{p}_i + \frac{1}{2}(q_i/c) \mathbf{s}_i \times \mathbf{B}_0(\mathbf{R}_a) \quad (4.2)$$

from (2.10) and (3.25a), and M_{ij} defined in (2.4). We recall that the \mathbf{v} 's of M_{ij} may be replaced by \mathbf{P}/m 's. Now we substitute (4.2) into (2.14), and expand H_a in powers of \mathbf{B}_0

$$H_a \equiv H_a^{(0)} + H_a^{(1)} + H_a^{(2)}. \quad (4.3)$$

The terms independent of \mathbf{B}_0 are

$$H_a^{(0)} = \sum_i^a \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i < j}^a \left[\frac{q_i q_j}{r_{ij}} - \frac{q_i q_j \mathbf{p}_i \cdot \mathbf{p}_j}{m_i m_j c^2} \right] : \mathbf{T}_{ij}. \quad (4.4a)$$

If a is a free molecule, the magnetic interaction terms of (4.4a) are relatively unimportant, but if a is a pair, they represent the strong magnetic interaction of two magnetized molecules in contact. In $H_a^{(1)}$ and $H_a^{(2)}$, we may neglect the contributions of the M_{ij} terms, as they are of relative order $r_0/a_0 \sim (137)^{-2}$. We find

$$H_a^{(1)} = -\mathbf{u}_a^p \cdot \mathbf{B}_0(\mathbf{R}_a), \quad (4.4b)$$

and

$$H_a^{(2)} = -\frac{1}{2} \alpha_a^d [\mathbf{B}_0(\mathbf{R}_a)]^2. \quad (4.4c)$$

Here \mathbf{u}_a^p is the paramagnetic dipole moment (operator) of quasimolecule a

$$\mathbf{u}_a^p \equiv \frac{1}{2} c^{-1} \sum_i^a (q_i/m_i) \mathbf{s}_i \times \mathbf{p}_i, \quad (4.5)$$

while α_a^d is its diamagnetic polarizability (operator)

$$\alpha_a^d \equiv -\frac{1}{4} c^{-2} \sum_i^a (q_i^2/m_i) (\mathbf{s}_{i\perp})^2, \quad (4.6)$$

$\mathbf{s}_{i\perp}$ being the projection of \mathbf{s}_i on the plane transverse to $\mathbf{B}_0(\mathbf{R}_a)$.

The interaction H_{ab} between two quasimolecules is taken to be

$$H_{ab} = \mathbf{u}_a \mathbf{u}_b : \mathbf{A}_{ab} + \psi(R_{ab}); \quad (4.7)$$

in accordance with our discussion in Sec. II, we postpone until the following section the treatment of the other interaction terms. In \mathbf{u}_a , defined by (2.22e), we again replace \mathbf{v}_i by \mathbf{P}_i/m_i and use (4.2), obtaining

$$H_{ab} = H_{ab}^{(0)} + H_{ab}^{(1)} + H_{ab}^{(2)}, \quad (4.8)$$

with

$$H_{ab}^{(0)} \equiv \mathbf{u}_a^p \mathbf{u}_b^p : \mathbf{A}_{ab} + \psi(R_{ab}). \quad (4.9)$$

The terms $H_{ab}^{(1)}$ and $H_{ab}^{(2)}$ involve the diamagnetic moments of the quasimolecules. For every graph containing $H_{ab}^{(1)}$ or $H_{ab}^{(2)}$, one can find a graph of lower order in r_0/a_0 . Hence for consistency of our approximation, we use only $H_{ab}^{(0)}$.

Our discussion of the evaluation of $\langle \mathbf{M} \rangle(\mathbf{R})$ will be schematic, and illustrated by the appropriate diagrams, since we do not wish to repeat here the detailed formalism fully discussed in KW.

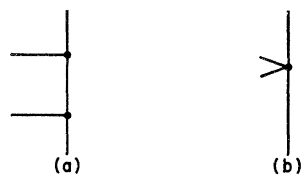


FIG. 1. Single-quasimolecule graphs. In (a), the quasimolecule (vertical line) has two paramagnetic ($H_a^{(1)}$) interactions with the external field. In (b), it has a single diamagnetic ($H_a^{(2)}$) interaction.

We begin with graphs for a *single* quasimolecule (either a free molecule or a pair), shown in Fig. 1. Correspondingly, one evaluates $F^{(2)}(1,0)$ and $F^{(2)}(0,1)$. The contributions to $\langle \mathbf{M} \rangle$ are, respectively,

$$\langle \mathbf{M} \rangle_{(1,0)}(\mathbf{R}) = z\alpha_f \cdot \mathbf{B}_0(\mathbf{R}) \quad (4.10)$$

and

$$\langle \mathbf{M} \rangle_{(0,1)}(\mathbf{R}) = z^2\alpha_p \cdot \mathbf{B}_0(\mathbf{R}). \quad (4.11)$$

The polarizabilities are defined as

$$\alpha_f \equiv -\gamma^{-1} \text{Tr}(2\pi i)^{-1} \int dw e^{-\beta w} (w - H_f^{(0)})^{-1} \times [\mathbf{u}_f^p (w - H_f^{(0)})^{-1} \mathbf{u}_f^p - \alpha_f^d \mathbf{I}], \quad (4.12)$$

and

$$\alpha_p \equiv -(2\gamma^2)^{-1} \int_{R_p < R_0} d^3 R_p \text{Tr}(2\pi i)^{-1} \times [\mathbf{u}_p^p (w - H_p^{(0)})^{-1} \mathbf{u}_p^p - \alpha_p^d \mathbf{I}]. \quad (4.13)$$

Formula (4.12) for the free-molecule polarizability α_f is analogous to Eq. (4.10) of KW. The operators $H_f^{(0)}$, \mathbf{u}_f^p , α_f^d have been defined previously [(4.4a), (4.5), (4.6)] for an arbitrary quasimolecule a ; now the subscript f indicates that the quasimolecule is a free mole-

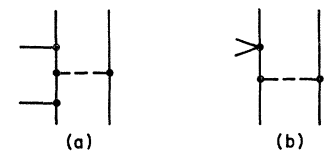


FIG. 2. Type I two-quasimolecule graphs, obtained from Fig. 1 by adding a ψ interaction (dashed line) with a second quasimolecule.

cule. The (provisional) pair polarizability α_p (4.13) is formally analogous to (4.12). We note, however, that now the operators $H_p^{(0)}$, \mathbf{u}_p^p , α_p^d are functions of the pair separation \mathbf{R}_p , which is to be integrated over. The w integration is, as in KW, over a contour enclosing the real axis in the positive sense. In KW Sec. IV, it was shown that the paramagnetic part of α_f would reduce, for a "polar" molecule, to $\frac{1}{3}\beta\langle(\mu_f^p)^2\rangle\mathbf{I}$; the diamagnetic part is evidently just $\langle\alpha_f^d\rangle$.

There are several types of two-quasimolecule graphs. First consider the type (I) shown in Fig. 2. It can be generated as indicated in the caption, but there is another suggestive approach. Let the quasimolecule of Fig. 1 be a pair; now separate the pair, letting only one member interact externally. Then let the members interact via ψ , yielding Fig. 2. This approach suggests that the contribution of this type of graph to $F^{(2)}(2,0)$ is expressible in terms of previously defined quantities.

In fact, evaluation yields

$$\langle \mathbf{M} \rangle_{(2,0)}(\mathbf{R}) = -z^2 V_0 \alpha_f \cdot \mathbf{B}_0(\mathbf{R}). \quad (4.14)$$

It is useful to add this two-free-molecule contribution to the one-pair contribution (4.11)

$$\langle \mathbf{M} \rangle_{(0,1)+(2,0)}(\mathbf{R}) = z^2 \alpha_2' \cdot \mathbf{B}_0(\mathbf{R}). \quad (4.15)$$

The two-molecule polarizability

$$\alpha_2' \equiv \alpha_p - V_0 \alpha_f \quad (4.16)$$

is completely analogous to formula (6.36) of KW. When either of the quasimolecules in a type I graph is a pair, the contribution to $\langle \mathbf{M} \rangle$ is of order z^3 , and therefore not of interest.

A second type (II) of graph is illustrated in Fig. 3. This graph is the case $N' = 2$ of a simple chain of para-

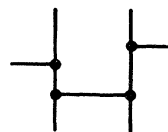


FIG. 3. In a type II two-quasimolecule graph, the quasimolecules interact paramagnetically with each other (solid horizontal line) and once each with the external field.

magnetic interactions, and will be discussed for general N' below.

A third type (III), illustrated in Fig. 4, vanishes upon evaluation. Consider, e.g., graph (a): The left-hand quasimolecule (label it 1) has three paramagnetic interactions. Hence its contribution to F involves the direct product $\mathbf{u}_1^p \mathbf{u}_1^p \mathbf{u}_1^p$ of three axial vectors of 1. Now reduce this third-rank tensor to a sum of irreducible tensors. Evidently none of the latter is a scalar. But upon taking the trace (primed), only a *scalar* yields a nonvanishing result. (This follows from the invariance of the single quasimolecule Hamiltonian under rotation and inversion.) It follows that (a) vanishes. One sees likewise that (b) and (c) vanish, while the graphs of Figs. 1 through 3 do not.

A type IV graph, shown in Fig. 5, has both paramagnetic and hard-sphere interactions between the quasimolecules. For $R_{ab} < R_0$, ψ dominates, and Fig. 5 reduces to Fig. 4(c); for $R_{ab} > R_0$, ψ vanishes, and Fig. 5 reduces to Fig. 3. Hence this type of graph yields nothing new.

Finally, a ladder graph (type V), shown in Fig. 6, has more than one (l , say) paramagnetic interaction be-

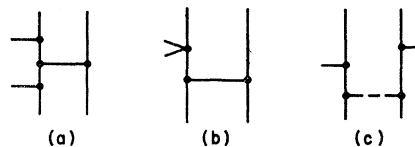
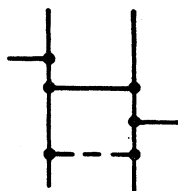


FIG. 4. In a type III graph, at least one of the molecules has interactions whose molecular operators are such that their product, when reduced, has no scalar component.

FIG. 5. The type IV graph evolves from type II by adding a ψ interaction.



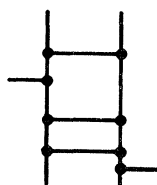
tween the quasimolecules. The dependence on R_{ab} is then R_{ab}^{-3l} . The resultant contribution, relative to Fig. 3, is of order $(\alpha_f/V_0)^{l-1}$. Recalling that $R_0 \gg a_0$, while α_f is ordinarily much less than a_0^3 , we see that ladder graphs make a negligible contribution.

Having discussed the case $N'=2$ rather thoroughly, we proceed to study the *simple chain* for arbitrary N' , shown in Fig. 7. Here the quasimolecules have only paramagnetic interactions. To insure $R_{ab} > R_0$ for each interaction, we add a ψ interaction to each link of the chain, as in Fig. 5. First suppose that each quasimolecule is a *free* molecule. The analogous analysis of KW Sec.V then applies, and we find, summing over all $N' \geq 1$,

$$\langle \mathbf{M} \rangle_{scf}(\mathbf{R}) = z\alpha_f^p \cdot \left[\mathbf{B}_0(\mathbf{R}) - \int' d^3R' \Lambda(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle_{scf}(\mathbf{R}') \right]. \quad (4.17)$$

The subscript scf means "simple chain of free molecules," α_f^p is the paramagnetic part of α_f (4.12), and

FIG. 6. A type V, or ladder, graph has several paramagnetic interactions between quasimolecules.



the prime on the integral indicates that the sphere $|\mathbf{R}-\mathbf{R}'| < R_0$ is to be excluded. Letting the exclusion sphere become infinitesimal [as in (3.32)] introduces an additional term of relative order $(R_0/L)^2$, which we assume negligible.¹³

Next we consider all simple chains in which each quasimolecule may be either a free molecule or a pair. The effect is to replace $z\alpha_f^p$ in (4.17) by $z\alpha_f^p + z^2\alpha_p^p$ where α_p^p is the paramagnetic part of α_p (4.13). Finally we break up each pair, letting the interactions act on only one member, and connect the other member to its partner with ψ . The result is then

$$\langle \mathbf{M} \rangle_{sc}(\mathbf{R}) = (z\alpha_f^p + z^2\alpha_2'^p) \cdot \left[\mathbf{B}_0(\mathbf{R}) - \int' d^3R' \Lambda(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle_{sc}(\mathbf{R}') \right]. \quad (4.18)$$

¹³ A preliminary discussion of nonlocal effects arising from this term is presented in KW for the dielectric problem; a complete discussion is given by L. Klauder, thesis, University of California (to be published).

To this we add the diamagnetic contributions of Figs. 1(b) and 2(b)

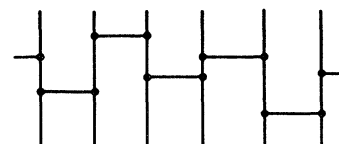
$$\langle \mathbf{M} \rangle^d(\mathbf{R}) = (z\alpha_f^d + z^2\alpha_2'^d) \cdot \mathbf{B}_0(\mathbf{R}). \quad (4.19)$$

The sum of (4.18) and (4.19) can be written as

$$\langle \mathbf{M} \rangle(\mathbf{R}) = (z\alpha_f + z^2\alpha_2') \cdot \left[\mathbf{B}_0(\mathbf{R}') - \int' d^3R' \Lambda(\mathbf{R}, \mathbf{R}') \cdot \langle \mathbf{M} \rangle(\mathbf{R}') \right], \quad (4.20)$$

if one adds negligible terms of relative order r_0/a_0 . By arguments similar to those used in the discussion of quasimolecule graphs (cf. also KW Sec. VI), one can show that all graphs other than those considered make negligible contributions.

FIG. 7. A simple chain for $N'=6$.



Since the polarizabilities are scalar tensors $\alpha_f \equiv \alpha_f \mathbf{I}$, etc., the equation (4.20) for the magnetization has the form (3.28), with

$$\xi \equiv z\alpha_f + z^2\alpha_2' \quad (4.21)$$

to $O(z^2)$. We eliminate the activity in favor of the density by Eq. (3.20), obtaining Eq. (3.29), with

$$\alpha_1 \equiv \alpha_f, \quad (4.22a)$$

and

$$\alpha_2 \equiv \alpha_2' + 2\alpha_f b(\Theta). \quad (4.22b)$$

Using the definitions (4.16), (4.12), and (3.21) for α_2' , α_f , and $b(\Theta)$, we can express $\alpha_2 \equiv \alpha_2 \mathbf{I}$ as

$$\alpha_2(\Theta) = \int d^3R e^{-\beta\phi(R, \Theta)} \left[\frac{1}{2} \alpha_2(\mathbf{R}) - \alpha_1 \right], \quad (4.23)$$

where $\alpha_2(\mathbf{R})$ is the true polarizability for a pair with fixed separation \mathbf{R} . Its formula can be obtained from that for α_f (4.12) by replacing *each* free molecule operator (including that in the definition of γ) by the corresponding operator for a pair with fixed \mathbf{R} . (See KW Sec. VI for details.)

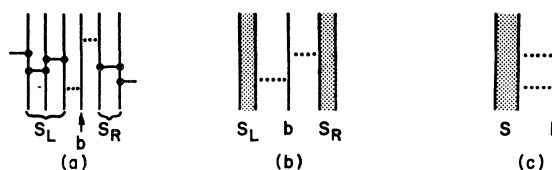


FIG. 8. A modified simple chain, in which quasimolecule b interacts, via $M^{\mu\pi}$, with S , the rest of the system appearing in the graph. Three different representations of the same graph are shown. The dotted line represents $M^{\mu\pi}$.

Thus $\alpha_2(\Theta)$, the coefficient of the imperfect gas correction to the Clausius-Mossotti formula, is expressed in terms of one- and two-molecule magnetic polarizabilities.

V. GAUGE TRANSFORMATION

We must now show that the effects of the interaction terms ignored in the preceding section are negligibly small, even though these terms themselves are not negligible in magnitude. The terms ignored are of two types, those coupling magnetic dipole moments to other moments, and those coupling moments other than magnetic dipole.

We begin with the former type, namely $M^{\mu\pi}$ (2.23b) and $M^{\mu Q}$ (2.26c). Comparing these two expressions, one sees that they are rather similar in form. The methods for treating them are correspondingly similar; hence we shall discuss here the elimination of only the simpler term $M^{\mu\pi}$:

$$-M_{ab}^{\mu\pi} = -[c^{-1}\dot{\pi}_b \cdot \mathbf{A}_a^b + (a \leftrightarrow b)] \quad (5.1a)$$

$$= c^{-1}\dot{\pi}_b \cdot \mathbf{u}_a \times \nabla_b R_{ab}^{-1} + (a \leftrightarrow b). \quad (5.1b)$$

If \mathbf{A}_a^b were a c number, the interaction $M_{ab}^{\mu\pi}$ could be eliminated (i.e., transformed to higher order) by a conventional gauge transformation. However, it is an operator, being proportional to \mathbf{u}_a , and thus its elimination requires more effort, as we shall see.

Let us consider a modified simple chain, shown in Fig. 8(a), in which quasimolecule b interacts (through its $\dot{\pi}_b$) with the rest of the system, by means of two $M^{\mu\pi}$ interactions. We note that this type of graph is the only one which need be considered, for the following reasons. In the preceding section, we have indicated that the only diamagnetic graphs of importance are single-quasimolecule graphs. Hence the graph studied here must interact with the external field by means of paramagnetic dipole moments. By the argument made in connection with the type III graph (Fig. 4), a succession of paramagnetic interactions must then occur [see S_L in Fig. 8(a)]. A different topology, i.e., multiple interactions rather than a chain, is eliminated by the argument given in connection with the type V graph (Fig. 6). By using these arguments, one is led to Fig. 8(a) as the only topology of interest involving $M^{\mu\pi}$ no more than twice. In Fig. 8(b), the graph is represented more abstractly, and now $M^{\mu\pi}$ interactions and others may appear hidden in the subsystems S_L and S_R , which interact with b from the left and right. A still more abstract representation, adequate for our purposes, is Fig. 8(c).

The effective Hamiltonian for Fig. 8(c) is

$$H = H_S + H_b + H_{Sb}, \quad (5.2)$$

in obvious notation. The interaction H_{Sb} is taken to be

$$H_{Sb} = -(1/c)\dot{\pi}_b \cdot \mathbf{A}^b, \quad (5.3a)$$

where

$$\mathbf{A}^b \equiv -\sum_a \mathbf{u}_a \times \nabla_b R_{ab}^{-1}, \quad (5.3b)$$

the sum being over all quasimolecules satisfying $R_{ab} \ll \lambda$, as discussed in Sec. II. The contribution of the graph to the partition function is proportional to

$$\sum |\langle \Xi | H_{Sb} | \Xi' \rangle|^2 (E - E')^{-1} (e^{-\beta E} - e^{-\beta E'}), \quad (5.4)$$

where $|\Xi\rangle$ and E are the eigenstates and eigenvalues of $(H_S + H_b)$, and the sum is over Ξ, Ξ' . (For brevity we omit the multiplicative factors β, γ , etc.)

We write (5.3a) as

$$H_{Sb} = -\frac{1}{c} \frac{d}{dt} (\boldsymbol{\pi}_b \cdot \mathbf{A}^b) + \frac{1}{c} \boldsymbol{\pi}_b \cdot \frac{d}{dt} \mathbf{A}^b, \quad (5.5)$$

and note that the time differentiation is equivalent to commutation with $H_S + H_b$, to the order of perturbation theory represented by the graph. We substitute (at first) just the *first* term of (5.5) in one matrix element factor of (5.4), and (5.3a) in the other factor, obtaining

$$(i\hbar c^2)^{-1} \sum \langle \Xi | \boldsymbol{\pi}_b \cdot \mathbf{A}^b | \Xi' \rangle \langle \Xi' | \dot{\pi}_b \cdot \mathbf{A}^b | \Xi \rangle (e^{-\beta E} - e^{-\beta E'}) \\ = (i\hbar c^2)^{-1} \text{Tr} \{ [\boldsymbol{\pi}_b \cdot \mathbf{A}^b, \dot{\pi}_b \cdot \mathbf{A}^b] e^{-\beta(H_S + H_b)} \}. \quad (5.6)$$

Since

$$[\boldsymbol{\pi}_b, \dot{\pi}_b] = i\hbar \mathbf{I} \sum_i q_i^2 / m_i,$$

expression (5.6) becomes

$$\text{Tr} \{ (\mathbf{A}^b)^2 e^{-\beta(H_S + H_b)} \sum_i q_i^2 / m_i c^2 \},$$

which represents the diamagnetic polarization of b by the other molecules. Since such terms were discarded in Sec. IV, they may also be neglected here.

Now we use the *second* term of (5.5) in the first matrix element factor of (5.4) and (again at first) the first term of (5.5) in the other factor, obtaining

$$(i\hbar c^2)^{-1} \sum \langle \Xi | \boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b | \Xi' \rangle \langle \Xi' | \boldsymbol{\pi}_b \cdot \mathbf{A}^b | \Xi \rangle (e^{-\beta E} - e^{-\beta E'}) \\ = \text{Tr} \{ [\boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b, \boldsymbol{\pi}_b \cdot \mathbf{A}^b] e^{-\beta(H_S + H_b)} \}. \quad (5.7)$$

Referring to Fig. 8(b), we see that the operators $\dot{\mathbf{A}}^b$ and \mathbf{A}^b of (5.7) refer to S_L and S_R , respectively; therefore they commute, and (5.7) vanishes.

Finally we use the second term of (5.5) in *both* matrix element factors of (5.4)

$$c^{-2} \sum |\langle \Xi | \boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b | \Xi' \rangle|^2 (E - E')^{-1} (e^{-\beta E} - e^{-\beta E'}). \quad (5.8)$$

We perform a partial sum \sum'' , for fixed E, E' , over the magnetic quantum numbers:

$$\sum'' |\langle \Xi | \boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b | \Xi' \rangle|^2 \sim \text{Tr}'' \{ \boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b \boldsymbol{\pi}_b \cdot \dot{\mathbf{A}}^b \}. \quad (5.9)$$

Again we utilize the fact that the two $\dot{\mathbf{A}}^b$'s refer to S_L and S_R , so that (5.9) becomes

$$\{\text{Tr}_{S_L}''\dot{\mathbf{A}}^b\} \cdot \{\text{Tr}_b''\pi_b\pi_b\} \cdot \{\text{Tr}_{S_R}''\dot{\mathbf{A}}^b\}. \quad (5.10)$$

This vanishes, since the trace of a dotted operator vanishes.

Thus the effect of the $M^{\mu\pi}$ interactions vanishes, and an analogous argument eliminates the $M^{\mu Q}$ interactions. There remain only the terms of type (c) [see the classification in the paragraph following Eq. (2.27f)] to consider. By an argument similar to that used in eliminating a type III graph (Fig. 4), we can show that a graph containing a type (c) term and an external magnetic interaction must vanish. Let d denote a quasimolecule which couples to its (graphical) neighbors by its magnetic moment \mathbf{u}_d on one side, and by a type (c) term on the other. The operators of d appearing in F would then be (allowing only R^{-3} dependence or lower order) $\mathbf{u}_d\pi_d$, $\mathbf{u}_d\pi_d\pi_d\pi_d$, $\mathbf{u}_d\mathbf{Q}_d$, $\mathbf{u}_d\mathbf{Q}_d\pi_d$, $\mathbf{u}_d\mathbf{R}_d$, $\mathbf{u}_d\mathbf{V}_d$, $\mathbf{u}_d\mathbf{L}_d$, or $\mathbf{u}_d\mathbf{\Gamma}_d$ (see Sec. II for definitions and tensor character of these quantities). Upon reduction of these direct products to irreducible tensors, no scalar appears. Therefore the trace vanishes, and such a graph makes no contribution to the magnetization.

VI. SUMMARY

In this section we wish to summarize the ideas and to motivate the methods of this paper. We have concerned ourselves with the linear response of a dilute quantum system in thermal equilibrium to an external magnetostatic field. The formalism of statistical mechanics forces us to a Hamiltonian, rather than Lagrangian, approach. Now in contrast to the *electrostatic* interactions between charged particles, where both the interaction Lagrangian and Hamiltonian are a sum of two-particle terms, the *magnetostatic* interactions have a Lagrangian which is a sum of two-body terms [Eq. (2.1)], but a Hamiltonian which is a sum of many-body terms [Eqs. (2.12) and (2.11)]. In Sec. II the many-body terms were eliminated by invoking the limited range of validity of the magnetostatic (Darwin) approximation to the near zone $r_{ij} \ll \lambda$. That the many-body terms are negligible is a result of the smallness of λ (so that the number of particles in the near zone of a given particle is not overwhelmingly large). The smallness of λ is in turn due to the high frequency of the quantum fluctuations of the electrons bound in molecules. If, on the other hand, the electrons of the system were free, as in a metal, the radiative wavelength characterizing their motion [$\lambda \sim (\Delta x)(c/v)$] would be considerably greater, and the many-body interactions could be important in studying magnetostatic correlations. On the other hand, the magnitude of the quantum fluctuations of internal vector potential is smaller in the latter

case and it might be possible to transform the many-body terms away.

Having obtained a Hamiltonian including only two-body interactions, we next developed a multipole expansion for the interaction between two molecules, valid if their separation is large compared to their size. In addition to the desirable magnetic dipole-dipole interaction ($\sim R_{lm}^{-3}$), there were found to be many other terms of the same and *lower* order in R_{lm}^{-1} . On physical grounds, it was felt that these terms could be transformed away, since they represented (to some extent) the internal vector potential, rather than the internal magnetic field. The transformation, accomplished in Sec. V, depends essentially on the fact that the molecules interact with the external field only through their magnetic dipole moments. Hence the magnetic field had to appear explicitly in the Hamiltonian, and this was possible only by means of the gauge transformation of Sec. III. But in this gauge transformation, a different gauge function had to be used for each (localized) set of particles among which electron exchange was possible. Thus we were led to the quasimolecule concept. The appearance of quasimolecules, rather than molecules, as the basic entities of the system, now required that the multipole expansion refer to the interaction between quasimolecules. Further, the introduction of quasimolecules into the Hamiltonian, rather than into the partition function (as conventional clusters), required the assumption of low density, so that quasimolecules could be defined for each configuration of importance. (The conventional cluster expansion, utilized by KW for the electrostatic problem, and valid at intermediate densities, was originally tried here and simply did not work.)

In the paragraph above we have indicated the line of reasoning which led us to the somewhat unconventional approach used in the present problem. The final result is an expression for the effect of short-range molecular interactions (imperfect gas effect) on the magnetic susceptibility. The coefficients of the virial expansion, α_1 and α_2 , were calculated explicitly for spinless electrons. The inclusion of spin is trivial, namely, in the equation (4.5) for the paramagnetic moment of a quasimolecule, one need only add in the spin magnetic moments.

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