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S-Matrix Formulation of Statistical Mechanics

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We have formulated the statistical mechanics in terms of the *S* matrix, which describes the scattering processes taking place in the thermodynamical system of interest. Such a formulation is necessary for studying the systems whose microscopic constituents behave according to the laws of relativistic quantum mechanics. Our result is a simple prescription for calculating the grand canonical potential of any gaseous system given the free-particle energies and *S*-matrix elements. When applied to a nonrelativistic gas, it gives a simple prescription for calculating all virial coefficients. Simplified relativistic gas models are considered as examples of application. A general form of the Levinson's Theorem for any number of particles follows immediately from our formalism. Its applications in statistical mechanics are briefly discussed.

I. INTRODUCTION

In this paper we present a formulation of statistical mechanics in terms of the *S*-matrix elements, which describes the scattering processes taking place in the thermodynamical system under consideration. The purpose of such a formulation is to be able to calculate, at least in principle, the equation of state of a relativistic system. By a relativistic system we mean a thermodynamical system whose microscopic constituents behave according to the principles of relativistic quantum mechanics. At present, the *S* matrix is the only quantity that can be obtained from the relativistic quantum mechanics. Therefore, to study the thermodynamical properties of relativistic systems, an *S*-matrix formulation of statistical mechanics is indispensable.

To our knowledge, there has been no general statistical mechanics formulated for *interacting* relativistic systems. Noninteracting systems, i.e., ideal gases, are in principle trivial to analyze. On the other hand, the statistical mechanics of interacting nonrelativistic systems has a

long history of development. Among the many formalisms and methods developed are two which have been widely applied to practical problems, and will play an important role in our subsequent analyses. The first is the method of virial expansion.[1] It was developed long ago and was found useful by chemists in calculating the equation of states of dilute gases. The second is the more recently developed method based on the field-theory formalism, sometimes referred to as the "temperature-Green's-function method."[2] With the diagrammatic technique of field theory incorporated, it is widely used in solid-state and low-temperature physics.

There is an interesting and well-known result in the virial expansion theory. That is, the second virial coefficient may be expressed in terms of two-body scattering phase shift.[1] This result is also derived by Goldberger using the more modern method of scattering theory.[3] It suggests that an S-matrix formulation via the virial expansion should be possible.

However, the (quantum-mechanical) virial expansion theory virtually ends at the second virial coefficient. As is illustrated in Ref. 1, the usual formulation in terms of W and U functions are so involved that it is not convenient even for formal discussion of virial coefficients higher than the second. There exist lengthy analyses of the third virial coefficient.[4] They are indeed elegant and elaborate pieces of work for the special problems involved but, due to the complexity of the traditional method, they can hardly be used for general discussions. Only recently have there been some attempts in developing a general theory of the virial expansion, but more modern methods in statistical physics do not seem to have been exploited.[5] As we shall show, by using the language of diagrammatics, the general discussion on virial coefficients becomes very concise.

An important feature of the nonrelativistic statistical mechanics is that the interaction Hamiltonian plays an essential role. The method of the temperature Green's function would be readily applicable to relativistic systems were it not for the absence of a meaningful interaction Hamiltonian in relativistic quantum mechanics. In quantum electrodynamics, the interaction Hamiltonian is but an intermediate formal device to calculate the S matrix. In fact, all the parameters in the theory become meaningful only after the S matrix has been put in the renormalized final form. In weak interaction, the interaction Hamiltonian is purely phenomenological, and, for strong interaction, there is no known interaction Hamiltonian.

Worse than having no interaction Hamiltonian, we have not established relativistic quantum mechanics as such. It is, thus, very difficult to develop a statistical mechanics based on relativistic-quantum-mechanical first principles, which do not exist at present. It is clear then, in order to establish mathematically a relativistic statistical mechanics, one has to make a judicious extrapolation from the nonrelativistic formalism.

What we shall do is to use the diagram technique of the temperature-Green's-function method as far as we can, assuming the existence of an interaction Hamiltonian. After getting the counting and statistics straight, we eliminate the interaction Hamiltonian by using the identities in the formal scattering theory. In the final formulas, only the S-matrix elements appear. Since the S matrix is always defined, our results can be carried over to relativistic systems upon minor modifications. Such a procedure seems to be entirely justified. The only concept in diagrammatics needed is the connectedness and disconnectedness. The interaction Hamiltonian in the intermediate stages may be viewed as a formal device to guarantee the unitarity and symmetry properties of the S matrix.

The outline of the paper is the following: In Sec. II, we discuss general aspects of the grand canonical ensemble and other qualitative features of the problem. Sections III and IV are devoted to the detailed derivation of the S-matrix expansion for mula for the grand canonical potential. The results are applied to the nonrelativistic virial expansion in Sec. V. The application to relativistic systems is discussed in Sec. VI. Simple examples of explicit calculations and further details are included in Sec. VII. In Sec. VIII, we derive a general form of Levinson's Theorem for an arbitrary number of particles. Its application is discussed. In Sec. IX, we summarize and give some concluding remarks.

This paper is self-contained. To understand this paper, no knowledge of relativistic quantum mechanics or that of temperature Green's function is required. A modest understanding of the most basic features of Feynman diagrams will be helpful. Some of the material in Secs. II and III is well known but is included for completeness. References to the original papers on this material can be found in Refs. 1 and 2.

II. GENERAL FEATURES

The basic principles of nonrelativistic statistical mechanics are well known. In this section, we show how they can be generalized to study relativistic systems.

It is the relativistic quantum mechanics, which governs the motion of the microscopic constituents of the relativistic system, that makes the relativistic statistical mechanics qualitatively different from the nonrelativistic one. The principles of statistics, the idea of the entropy, and the laws of thermodynamics are in general independent of this microscopic detail. In nonrelativistic quan-

tum mechanics, one speaks of the two-body potential which changes the motion of particles. In relativistic quantum mechanics, there is a much greater variety of phenomena such as the creation and the annihilation of particles. One must explicitly take into account the general features of the electromagnetic, the weak and the strong interactions. The gravitational interaction is purely macroscopic and will not be discussed here.

We shall first discuss the role of the conservation laws in constructing the grand canonical potential Ω. It will be followed by a discussion of how dynamical information is put in and of the notion of the virial expansion.

A. Conservation Laws and the Grand Potential

We recall from nonrelativistic statistical mechanics that the grand potential Ω is given by

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp[-\beta(H - \mu N)]. \tag{2.1}$$

The equation of state is obtained upon eliminating μ from

$$\Omega = -PV, \qquad N = -\partial\Omega/\partial\mu. \tag{2.2}$$

Recalling the derivation of the grand canonical ensemble, we notice that β and μ play the role of the Lagrange multipliers in maximizing the entropy keeping the total energy and the total number of particles fixed. β^{-1} is then interpreted as the temperature and μ, the chemical potential. Note that the total energy and the total number of particles are conserved quantities. We also recall that, if there are two species of particles 1 and 2, the grand potential has the form

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp[-\beta(H - \mu_1 N_1 - \mu_2 N_2)]. \tag{2.3}$$

Now, if the reactions

$$1 \rightleftharpoons 2 \tag{2.4}$$

are allowed to take place, we know, from the condition for chemical equilibrium, that

$$\mu_1 = \mu_2 \equiv \mu . \tag{2.5}$$

Thus,

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp\{-\beta[H - \mu(N_1 + N_2)]\}. \tag{2.6}$$

The important feature illustrated above is that, for every conserved (extensive) quantity, there is an independent Lagrange multiplier. The total energy is always conserved and there is always the multiplier β. In (2.2), N is conserved, and we have μ. In (2.6), $N_1 + N_2$ is conserved, and we have μ, but not μ_1 and μ_2 because N_1 and N_2 are not separately conserved due to the reaction (2.4). In general, given the set of conserved quantities $N_1, N_2, \ldots$, we assign a set of multipliers μ_1, $\mu_2, \ldots$. The grand potential then can be constructed as

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp[-\beta(H - \textstyle\sum_i \mu_i N_i)]. \tag{2.7}$$

The equation of state is then obtained from

$$-PV = \Omega, \qquad N_i = -\partial\Omega/\partial\mu_i . \tag{2.8}$$

These results depend only on conservation laws and are otherwise completely general.

When the energy of the particles in the system becomes relativistic, the particle numbers are no longer conserved. One, in general, has a mixture of many kinds of particles. There are conservation laws observed in decay and scattering experiments such as the conservation of the baryon number, the lepton number, and the electric charge. They can be safely assumed to hold in any thermodynamic system. When one assigns a multiplier to each of the relevant conservation laws and substitutes them in (2.7), one has the appropriate grand potential. For example, in a model where all but the strong interaction is turned off, the grand potential is given by

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp[-\beta(H - \mu_B B - \mu_S S - \mu_I I)], \tag{2.9}$$

where B, S, and I are, respectively, the baryon number, the strangeness, and the third component of the isotopic spin. There could be situations in cosmological problems where the thermal equilibrium is reached locally in less than nanoseconds so that one may use (2.9) to start with and treat the electromagnetic and weak interactions as perturbations.

B. Dynamical Information

The main task of statistical mechanics is to calculate the grand potential given the dynamical information concerning the microscopic interactions. For nonrelativistic systems, this information is in principle fully contained in the two-body potential, which is treated in various forms of perturbation theory. As was mentioned in the Introduction the most useful and now fashionable form seems to be the temperature-Green's-function method.[2] This method employs the perturbation expansion of field theory with the time variable taken as imaginary running between 0 and $-i\beta$ [so that $\exp(-itH)$ becomes $\exp(-\beta H)$]. The

Feynman-Dyson expansion can be made for $\exp(-\beta H)$, and a diagrammatic formulation can be set up. As was mentioned previously, the lack of an interaction Hamiltonian makes it difficult to apply this method to relativistic systems directly.

Dynamical information of relativistic interaction is presently obtainable only through the S-matrix elements, which describe the scattering of physical particles. Therefore, it is necessary, in order to calculate the equation of states, to write the grand potential in terms of the S matrix.

The possibility of writing Ω in terms of S-matrix elements is suggested by the fact that the second virial coefficient is expressible in terms of the two-body phase shifts.[1] We shall briefly review some of the basic features of the virial expansion for completeness. For a more detailed discussion, Ref. 1 is highly recommended.

C. Virial Expansion

To obtain the nonrelativistic virial expansion, one begins by writing the sum over the spectrum of N in the trace explicitly, i.e.,

$$\Omega = -\beta^{-1} \ln \mathrm{Tr} \exp[-\beta(H-\mu N)]$$

$$= -\beta^{-1} \ln\Big(\sum_{N=0}^{\infty} e^{\beta\mu N} \mathrm{Tr}_N e^{-\beta H} \Big), \tag{2.10}$$

where Tr_N is taken over states of N particles. When one expands the logarithm in powers of $e^{\beta\mu}$, one obtains the virial expansion

$$\Omega = -\beta^{-1} \sum_{N=1}^{\infty} A_N e^{\beta\mu N}. \tag{2.11}$$

When the system is dilute, i.e., when the occupation number per state is small,

$$e^{\beta(\mu-\epsilon_k)} \ll 1, \tag{2.12}$$

the expansion is expected to converge rapidly. The quantity ϵ_k is the single-particle energy (in the absence of interaction) of the state k. Even when (2.12) is not true, (2.11) can always be taken as a formal power series in $e^{\beta\mu} \equiv z$:

$$\sum_{N=1}^{\infty} A_N z^N. \tag{2.13}$$

This power series in z defines a function in the z plane that is analytic around the origin. By analytic continuation, it is possible to obtain Ω in the region where the power series does not converge. For example, for the free Fermi gas, we have the well-known result

$$\Omega = -\beta^{-1} \textstyle\sum_k \ln\{1+\exp[-\beta(\epsilon_k-\mu)]\}, \tag{2.14}$$

which is the analytic continuation of

$$\text{const} \times \sum_{N=1}^{\infty} (-)^{N+1} N^{-5/2} z^N, \tag{2.15}$$

with $z = e^{\beta\mu}$. As a power series, (2.15) diverges for $|z| \geq 1$, but (2.14) is always valid.

In general, the analytic continuation of (2.13) may not give the correct thermodynamics for all z. From the work of Lee and Yang,[6] one knows that Ω becomes singular on the real axis at $z=z_0$, where z_0 is the position of the first phase transition. Whether or not one can (in physically interesting situations) go into the complex plane and continue around z_0 is simply unknown. It appears that in the lattice-gas model, where Ω develops a continuous distribution of poles on the unit circle, the analytic continuation of Ω has only a limited region of validity.[6]

As will be seen later our work in this paper will be based on the expansion of Ω in powers of one or more z. Thus, our results are, in principle, applicable for any state of the system which can be reached by analytic continuation from the region around $z=0$, but do not apply to other states which may well exist in interesting cases. In practice, of course, our formulas will be useful only when the expansion in powers of z converges rapidly or when one can at least partially sum terms to all orders in z.

The quantum-mechanical calculation of the coefficients A_N is still in a primitive stage. The coefficient A_1 can easily be shown to be the ideal-gas term. A_2 may be written in terms of the two-body scattering phase shifts. The general features of higher coefficients have not been investigated. The main reasons seem to be the following: First, in the traditional theory of the virial expansion, there is no effective way of expanding the logarithm in (2.10). The method of U and W functions is so complicated that a general discussion becomes very difficult. Such difficulty never arises in the temperature-Green's-function method, which, of course, became available long after the development of the virial expansion. The second reason is that the derivation of A_2 in terms of the phase shift is very difficult to generalize when more than two particles are involved. This difficulty, as will become clear in Sec. III, is overcome when the method of formal scattering theory and diagrammatic techniques are properly generalized and utilized. General prescriptions for calculating A_N will be given.

D. S-Matrix Expansion

The physical basis for an S-matrix formulation can be seen clearly from the theory of the second virial coefficient.[1] Let us mention some of its relevant features briefly. Go back to (2.10) and consider terms up to $N=2$. Expanding the logar-

ithm, we have (ignoring bound states)

$$-\beta(\Omega-\Omega_0)=A_2 e^{-2\beta\mu}$$

$$A_2=\mathrm{Tr}_2(e^{-\beta H}-e^{-\beta H_0})$$

$$=\int dE\, e^{-\beta E}[dn/dE-(dn/dE)_0], \quad (2.16)$$

where Ω_0 is the grand potential for the ideal gas, dn/dE and $(dn/dE)_0$ are, respectively, the density of two-particle eigenstates of H and that of H_0. In other words, A_2 depends on the change of the density of two-particle states due to the interaction. Now, we notice that we are considering two particles in an infinite volume. As long as the interaction is of a finite range, the density of states can only depend on the asymptotic part of the two-particle wave functions. The details of the wave functions in the scattering region contribute only an infinitesimal part in the infinite volume limit. More precisely, the density of states is determined by the boundary condition for the wave functions at the walls of the box in which the system is quantized. When the size of the box becomes infinite, it is sufficient to consider the asymptotic form of the wave function when applying the boundary condition.

The asymptotic wave functions are completely specified by the two-body scattering phase shifts, (which may be obtained from the derivatives of the S-matrix elements with respect to the energy). Thus, we conclude that A_2 can be expressed in terms of the S-matrix elements describing two-body scattering. For further detail, see Ref. 1.

It seems clear that the above arguments apply to A_N for $N>2$ as well. A_N will depend only on the asymptotic N-body wave functions, which are completely specified by the S-matrix elements describing the scatttering of N particles, as long as N stays finite while the volume is let go to infinity.

It seems clear also that, for a liquid or a solid, where an asymptotic wave function can hardly have a precise meaning in general, it would be very difficult to have a meaningful expression of Ω in terms of S-matrix elements.

The above qualitative conclusions hold for relativistic systems as well. It remains to construct a quantitative mathematical scheme that applies to both relativistic and nonrelativistic systems.

Without any assumption, it follows from the expression (2.7) for the grand potential for a system, in general, that

$$\Omega=-\beta^{-1}\sum_{N_1N_2\cdots}A_{N_1N_2\cdots}\exp(\beta\textstyle\sum_i\mu_i N_i). \quad (2.17)$$

The sum is taken over all possible values of the quantum numbers $(N_1, N_2, \ldots)$. This may be viewed as a direct generalization of the virial series (2.11). In view of what we just discussed about the validity of virial expansion, we expect that (2.17) can describe relativistic gases only. The problem of phase transition in a relativistic system is, thus, out of the reach of our formalism, which will be largely based on (2.17).

What we shall do is to establish a prescription to calculate $A_{N_1N_2}\ldots$ in terms of the S-matrix elements between states specified by the set of quantum numbers $(N_1, N_2, \ldots)$. Such a prescription cannot be derived from first principles because, as was mentioned in Sec. I, there are no established first principles in relativistic quantum mechanics besides symmetry principles. We shall proceed with the diagrammatics familiar in the temperature-Green's-function method assuming the existence of an interaction Hamiltonian. The prescription in terms of S-matrix elements results after eliminating the interaction Hamiltonian by using identities in formal scattering theory.

III. S-MATRIX EXPANSION

Guided by the general discussion in Sec. II, we proceed to the mathematical details. For the simplicity of discussion, we assume that there is one species of particles interacting via a two-body potential. The grand potential is given by

$$\Omega=-\beta^{-1}\ln\mathrm{Tr}\exp[-\beta(H-\mu N)]$$

$$=-\beta^{-1}\ln\textstyle\sum_N e^{\beta\mu N}\mathrm{Tr}_N e^{-\beta H}. \quad (3.1)$$

It is often convenient but not essential for the discussion to consider terms with a definite N in the trace.

There are two problems. First, in the argument of the logarithm in (3.1), $\mathrm{Tr}_N e^{-\beta H}$ is of $O(V^N)$, where V is the volume of the system. There are delicate cancellations after one expands the logarithm so that the terms remaining finally are proportional to V. One must rewrite (3.1) so that these cancellations are already taken into account and only terms proportional to V appear. This is a counting problem. The second problem is to eliminate the two-body potentials so that only the S matrix appears in the final expression. Let us consider the counting problem first.

A. Counting Problem

Our approach here will be similar but not identical to that used in the temperature-Green's-function method. To simplify the notation, let us measure the single-particle energy from the chemical potential so that

$$H_0 \to H_0 - \mu N, \qquad \mathrm{Tr} e^{-\beta H} \to \sum_N \mathrm{Tr}_N e^{-\beta H}, \tag{3.2}$$

$$H = H_0 + V, \qquad V = \sum_{i<j} V_{ij}, \tag{3.3}$$

where V_{ij} is the interaction between the particles i and j. To evaluate the trace, one needs a complete set of states. We shall use the eigenstates of H_0. Let us label a single-particle state by the label k. Then the eigenstates of H_0 are labeled by the ordered set $\{\kappa\} = (k_1, k_2, \ldots, k_N), N = 1, 2, 3, \ldots$.

A diagonal element $\langle \kappa | e^{-\beta H} | \kappa \rangle$ may be interpreted as the amplitude of finding the state $|\kappa\rangle$ at the imaginary time $-i\beta$ given the state $|\kappa\rangle$ at time zero. To obtain the trace, one sums all these amplitudes. To eliminate spurious powers of volume in Ω, a diagrammatic representation of these amplitudes is most useful. Let us write $\exp(-\beta H)$ as a Feynman-Dyson expansion

$$e^{-\beta H} = \sum_{n=0}^{\infty} (-)^n \int_0^{\beta} d\tau_1 d\tau_2 \cdots d\tau_n \times [e^{-(\beta-\tau_1)H_0} V e^{-(\tau_1-\tau_2)H_0} V \cdots V e^{-\tau_n H_0}], \tag{3.4}$$

where $\beta > \tau_1 > \tau_2 > \cdots > \tau_n > 0$. The grand potential is then expanded in powers of V_{ij} when (3.4) is substituted in the expression

$$\Omega = -\beta^{-1} \ln \mathrm{Tr}\, e^{-\beta H}. \tag{3.5}$$

Every term in (3.4) has a diagrammatic representation. A diagonal element is then the sum of diagrams in which each particle returns to its initial state after a time $-i\beta$. Figure 1 shows a typical term. At this point, we must notice that we have ignored the exchange effect due to the identity of particles. In other words, terms like

$$\langle k_1 k_2, \ldots, k_N | e^{-\beta H} | k_2 k_1, \ldots, k_N \rangle$$

are, by definition, not diagonal elements and therefore, not counted in the trace. To avoid unnecessary complications, we shall proceed without these terms. Later, when the procedures of counting and transforming to the S-matrix form become familiar, these terms will be put in.

FIG. 1. A typical term in the expansion of Ω. The imaginary time runs upward. The dashed lines represent two-particle potentials. The solid line denotes free particles.

A diagram in general consists of mutually disconnected parts and the corresponding amplitude is of the form

$$[\underbrace{C_1(\kappa_1) C_1(\kappa_1') \cdots}_{m_1 \text{ factors}}][\underbrace{C_2(\kappa_2) C_2(\kappa_2' \cdots}_{m_2}] \cdots \times [\underbrace{C_n(\kappa_n) C_n(\kappa_n' \cdots}_{m_n}], \tag{3.6}$$

where the connected diagram C_i occurs m_i times. When we sum over the κ's, we get

$$(m_1! m_2! \cdots m_n!)^{-1} (\mathrm{Tr} C_1)^{m_1} (\mathrm{Tr} C_2)^{m_2} \cdots \times (\mathrm{Tr} C_n)^{m_n}. \tag{3.7}$$

The division by $(m_1! m_2! \cdots m_n!)$ is to avoid counting the same amplitude more than once. Note that we are regarding $\langle \kappa | e^{-\beta H} | \kappa \rangle$ and $\langle \kappa' | e^{-\beta H} | \kappa' \rangle$ as the same amplitude if κ and κ' differ only by a permutation of labels. This is in accord with the basic rule of statistical mechanics that each distinct configuration must be counted only once.

Summing over $m_1, m_2, \ldots, m_n$ in (3.7), and then summing over n we find

$$\mathrm{Tr} e^{-\beta H} = \exp \mathrm{Tr}(C_1 + C_2 + C_3 + \cdots). \tag{3.8}$$

Using (3.5), we have

$$\Omega = -\beta^{-1} \mathrm{Tr}(C_1 + C_2 + \cdots) \equiv -\beta^{-1} [\mathrm{Tr} \exp(-\beta H)]_c + \Omega_0. \tag{3.9}$$

The subscript c denotes that only connected diagrams with the interaction acting at least once are kept. Ω_0 is the ideal-gas part of Ω, i.e., the sum of one-particle diagrams

$$\Omega_0 = -\beta^{-1} \mathrm{Tr}_1 e^{-\beta H_0}.$$

In other words, Ω is the sum of all connected diagrams. Each connected diagram is proportional to the volume. Thus, the elimination of spurious higher powers of volume is completed.

It is straightforward to construct rules to calculate these connected diagrams. However, we are not interested in using these diagrams directly for calculation. We proceed to the next problem, i.e., how to express $[\mathrm{Tr} \exp(-\beta H)]_c$ in terms of the S matrix.

B. Transforming to S-Matrix Elements

The diagrams in imaginary time which we just discussed contain the statistical and dynamical information in a mixed form. In other words, the statistical averaging and the description of particle motions are not separated. Since the S matrix contains only dynamical information and no statis-

tical information, we must first disentangle $[\mathrm{Tr}\exp(-\beta H)]_c$ so that the statistical and dynamical information appear separately. It turns out to be very difficult to do this separation for each individual imaginary time diagram. However, for the sum of diagrams, it is straightforward.

By inspecting the diagrams, one can write down the sum of connected diagrams involving a given number of particles in terms of the form $\mathrm{Tr}(e^{-\beta H'} - e^{-\beta H_0})$ (apart from the trivial free-particle term). H' is the Hamiltonian with some interaction terms switched off. For example,

$$\text{for } N=2, \quad (\mathrm{Tr}e^{-\beta H})_c = \mathrm{Tr}(e^{-\beta H} - e^{-\beta H_0}), \tag{3.10}$$

$$\text{for } N=3, \quad (\mathrm{Tr}e^{-\beta H})_c = \mathrm{Tr}[e^{-\beta H} - e^{-\beta H_0} - \sum_{i<j} (e^{-\beta(H_0+V_{ij})} - e^{-\beta H_0})]. \tag{3.11}$$

Figure 2 shows these examples in terms of diagrams. The rule is simple. One just subtracts out the disconnected parts from the total. We notice that only the form $\mathrm{Tr}(e^{-\beta H'} - e^{-\beta H_0})$ appears with various kinds H'. For example, $H' = H$ and $H' = H_0 + V_{ij}$, respectively, in the first and third terms in (3.11).

To isolate the parameter β, we define the resolvent operator $G(E)$ of H as a function of the complex variable E, and similarly $G_0(E)$, by

$$G(E) = (E - H)^{-1}, \quad G_0(E) = (E - H_0)^{-1}, \tag{3.12}$$

$$\text{Thus,} \quad \mathrm{Tr}e^{-\beta H} = \oint \frac{dE}{2\pi i} e^{-\beta E} \mathrm{Tr}G(E), \tag{3.13}$$

where the counterclockwise contour encloses the spectrum of H. Equation (3.13) can also be written as an integral along the real axis

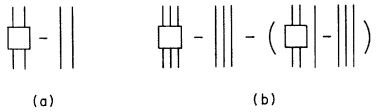
$$\mathrm{Tr}e^{-\beta H} = -\int \frac{dE}{\pi} e^{-\beta E} \mathrm{Im}\,\mathrm{Tr}G(E). \tag{3.14}$$

The argument of $G(E)$ is understood to have an imaginary part $i\eta$. The quantity η is let to approach 0^+ after the volume is let go to infinity. The range of the E integral extends over the spectrum of H.

Similarly, we define G' as

$$G'(E) = (E - H')^{-1}, \tag{3.15}$$

for any Hamiltonian H'. Of course, (3.14) holds



(a) (b)

FIG. 2. The connected diagrams expressed as differences of the sum of all diagrams (square boxes) and disconnected diagrams.

when H is replaced by any H' and G by the corresponding G'.

It is well known that the series expansion for G, i.e.,

$$G = \sum_{n=0}^{\infty} G_0(VG_0)^n \tag{3.16}$$

can be represented by diagrams. Equation (3.16) is simply the Born series in the usual perturbation theory. The diagrams are geometrically identical to the imaginary time diagrams. The sum of connected G diagrams can be written as combinations of terms of the form $(G' - G_0)$ similar to the form $(e^{-\beta H'} - e^{-\beta H_0})$ encountered previously. Corresponding to (3.10) and (3.11), for example, we have, for $N=2$

$$(\mathrm{Tr}G)_c = \mathrm{Tr}(G - G_0), \tag{3.17}$$

and for $N=3$,

$$(\mathrm{Tr}G)_c = \mathrm{Tr}[G - G_0 - \sum_{i<j} (G_{ij} - G_0)], \tag{3.18}$$

(3.17) and (3.18) are also depicted by Fig. 2. G_{ij} is, of course, $(E - H_0 - V_{ij})^{-1}$. It is clear then that

$$(\mathrm{Tr}e^{-\beta H})_c = -\int \frac{dE}{\pi} e^{-\beta E} \mathrm{Im}(\mathrm{Tr}\,G(E))_c. \tag{3.19}$$

In other words, the sum of connected imaginary time diagrams is simply an integral transform of the connected diagrams for G. This is obvious in view of the fact that the integral transform is linear and the two kinds of diagrams have identical geometric structures. $G(E)$ now contains no statistical information.

It remains to express $(\mathrm{Tr}G)_c$ in terms of the S matrix. Since $(\mathrm{Tr}\,G)_c$ is a linear combination of terms of the form $\mathrm{Tr}(G' - G_0)$ with various G''s, we shall start by analyzing $\mathrm{Tr}(G - G_0)$.

In the following, we apply techniques familiar in the formal theory of scattering to rewrite $\mathrm{Tr}(G - G_0)$ in terms of the S matrix generated by the interaction Hamiltonian $V = H - H_0$.

We define the operators T, Ω, and S, which are functions of the complex variable E, by

$$T(E) = V + VG(E)V, \quad \Omega(E) = G(E)G_0^{-1}(E),$$

$$S(E) = \Omega^{-1}(E^*)\Omega(E), \quad \text{where } V = H - H_0. \tag{3.20}$$

Note that we are using the symbol Ω here for GG_0^{-1} to conform to the notation for the wave matrix in scattering theory. We are using the same symbol to denote the grand potential since it is standard in statistical mechanics. The proper meaning of Ω should be clear from the context involved. We list some identities which can be derived easily from the definitions in (3.20).

$$G=\Omega G_0=G_0+G_0TG_0, \tag{3.21}$$

$$T=V\Omega=V+VG_0T=V+TG_0V, \tag{3.22}$$

$$\Omega=1+GV=1+G_0T, \tag{3.23}$$

$$\Omega^{-1}=1-G_0V, \tag{3.24}$$

$$G^\dagger=G^*,\quad G_0^\dagger=G_0^*,\quad T^\dagger=T^*,$$

$$\Omega\dagger=\Omega^{T*},\quad \Omega^T\equiv G_0^{-1}G. \tag{3.25}$$

The star means to take the complex conjugate of the variable E, i.e., $E\to E^*$, The dagger denotes the Hermitian conjugation. Using (3.24) and (3.22), we find that

$$S=\Omega^{*-1}\Omega=1+(G_0-G_0^\dagger)T, \tag{3.26}$$

$$S^{-1}=\Omega^{-1}\Omega^*=1-(G_0-G_0^\dagger)T^\dagger. \tag{3.27}$$

A less trivial identity is

$$T-T^\dagger=T^\dagger(G_0-G_0^\dagger)T$$

$$=T(G_0-G_0^\dagger)T^\dagger=V(G_0-G_0^\dagger)V, \tag{3.28}$$

which may be regarded as the unitarity condition or the optical theorem in operator form. When E approaches the real axis from above, $G_0-G_0^\dagger$ approaches a δ function:

$$G_0-G_0^\dagger=-2\pi i\delta(E-H_0). \tag{3.29}$$

We shall, in the following discussion, take (3.29) as the definition of $\delta(E-H_0)$. The variable E on the left-hand side of (3.29) is allowed to approach the real axis only after the infinite volume limit is taken. Thus, in a more appealing form, we have

$$S=1-2\pi i\delta(E-H_0)T,$$

$$S^{-1}=1+2\pi i\delta(E-H_0)T^\dagger. \tag{3.30}$$

Note that S^{-1} is not the same operator as $S^\dagger$. One has $\langle\kappa|S^\dagger|\kappa'\rangle=\langle\kappa|S^{-1}|\kappa'\rangle$ only when both $|\kappa\rangle$ and $|\kappa'\rangle$ are eigenstates of H_0 with the same energy.

Armed with the above identities, we now proceed to establish the important identity, i.e.,

$$-4i\,\mathrm{Im}\,\mathrm{Tr}[G(E)-G_0(E)]$$

$$=\mathrm{Tr}\left(S^{-1}\frac{\partial S}{\partial E}-\frac{\partial S^{-1}}{\partial E}S\right)\equiv\mathrm{Tr}S^{-1}\overrightarrow{\frac{\partial}{\partial E}}S. \tag{3.31}$$

We shall verify (3.31) directly via the definition of S. Substituting $S=\Omega^{*-1}\Omega$ [see (3.20)] in (3.31), we have

$$\mathrm{Tr}S^{-1}\overrightarrow{\frac{\partial}{\partial E}}S=\mathrm{Tr}\Omega^{-1}\Omega^*\overrightarrow{\frac{\partial}{\partial E}}\Omega^{*-1}\Omega$$

$$=\mathrm{Tr}\left(\Omega^{-1}\overrightarrow{\frac{\partial}{\partial E}}\Omega+\Omega^*\overrightarrow{\frac{\partial}{\partial E}}\Omega^{*-1}\right). \tag{3.32}$$

Using (3.24), (3.23), and (3.22), one has

$$\Omega^{-1}\overrightarrow{\frac{\partial}{\partial E}}\Omega=(1-G_0V)\overrightarrow{\frac{\partial}{\partial E}}\Omega=\frac{\partial}{\partial E}\Omega-G_0\overrightarrow{\frac{\partial}{\partial E}}V\Omega$$

$$=\overrightarrow{\frac{\partial}{\partial E}}G_0T-G_0\overrightarrow{\frac{\partial}{\partial E}}T=-2G_0^2T. \tag{3.33}$$

Substituting (3.33) in (3.32) and utilizing the fact that $G-G_0=G_0TG_0$, one has

$$\mathrm{Tr}S^{-1}\overrightarrow{\frac{\partial}{\partial E}}S=-4i\,\mathrm{Im}\,\mathrm{Tr}(G-G_0), \tag{3.34}$$

which is exactly (3.31). Using (3.34) and (3.14) we have

$$\mathrm{Tr}(e^{-\beta H}-e^{-\beta H_0})=\int dE e^{-\beta E}(4\pi i)^{-1}\mathrm{Tr}S^{-1}\overrightarrow{\frac{\partial}{\partial E}}S. \tag{3.35}$$

This equation and (3.34) play an essential role in all subsequent discussions.

So far, S is an operator function of E formally given by (3.30). How is S related to the S matrix describing the actual scattering processes? From scattering theory,[7] we know that the S-matrix element $S_{\kappa\kappa'}$ describing the scattering from the state $|\kappa'\rangle$ to the state $|\kappa\rangle$ is given by

$$S_{\kappa\kappa'}=\delta_{\kappa\kappa'}-2\pi i\delta(E_{\kappa'}-E_\kappa)T_{\kappa\kappa'}(E_{\kappa'}). \tag{3.36}$$

Equation (3.30) then shows that

$$S_{\kappa\kappa'}=\langle\kappa|S(E_{\kappa'})|\kappa'\rangle. \tag{3.37}$$

Those matrix elements $\langle\kappa|S(E)|\kappa'\rangle$ satisfying the condition $E=E_{\kappa'}$ will be called "on-shell" elements of S. The on-shell elements form the physical S matrix. It is more convenient to speak of the on-shell T-matrix elements appearing in (3.36). The matrix element $\langle\kappa|T(E)|\kappa'\rangle$ is on-shell if $E_\kappa=E_{\kappa'}=E$. Thus, the element $\langle\kappa|S(E)|\kappa'\rangle$ is on-shell if the corresponding T-matrix element is on-shell.

We now verify that indeed only on-shell elements appear in (3.35). Let us first express S explicitly in terms of T. By (3.30), we have

$$\mathrm{Tr}S^{-1}\overrightarrow{\frac{\partial}{\partial E}}S=-2\pi i\frac{\partial}{\partial E}\mathrm{Tr}\delta(E-H_0)(T+T^\dagger)$$

$$-(2\pi i)^2\mathrm{Tr}\delta(E-H_0)T^\dagger\overrightarrow{\frac{\partial}{\partial E}}\delta(E-H_0)T. \tag{3.38}$$

Let us label the states in such a way that the total energy, i.e., the eigenvalue of H_0, is one of the labels, and let it be written out explicitly. It follows that the S-matrix elements are always expressed in terms of $T_{EE}(E)$.

The first term of (3.38) is manifestly on-shell since the δ function picks out only the states with energy E. The second term of (3.38) is complicated by the two-way differentiation $\overleftrightarrow{\partial}/\partial E$. Consider the term with $\partial/\partial E$ acting to the right. We have

$$\sum_{E'E''} \delta(E-E')\, T^{\dagger}_{E'E''}(E)\frac{\partial}{\partial E}\,\delta(E-E'')T_{E''E'}(E). \tag{3.39}$$

The sum over labels other than the energy label is understood. The T's are in general slowly varying functions of E', E'', and E, so that E' and E'' may be treated as continuous variables like E. Using properties of the δ function, (3.39) may be written

$$\sum_{E'E''}\left(\delta(E-E')T^{\dagger}_{EE}(E)\,\frac{\partial}{\partial E}\,[\delta(E-E'')T_{EE}(E)]+R\right) \tag{3.40}$$

$$R=-\delta(E-E')\left(\frac{\partial}{\partial E''}\,T^{\dagger}_{EE''}(E)\right)\delta(E-E'')\,T_{EE}(E)$$

$$-\delta(E-E')T^{\dagger}_{EE}(E)\delta(E-E'')\frac{\partial}{\partial E'}\,T_{EE'}(E). \tag{3.41}$$

Do the same for the term with $\overleftarrow{\partial}/\partial E$ acting to the left. One obtains a term like (3.40) with $\overleftarrow{\partial}/\partial E$ instead of $\overrightarrow{\partial}/\partial E$ and a term $-R$, which cancels the R in (3.40). Therefore, only the form $T_{EE}(E)$ appears in the final expression. Our conclusion is then that, in (3.38) the operator may be replaced by the "on-shell operator"

$$S=1-2\pi i\delta(E-H_0)T_{EE}(E), \tag{3.42}$$

which is effectively the S matrix.

Use of the same symbol S should not cause any confusion. To save writing in the subsequent discussions, we introduce the new notation

$$\begin{aligned}\mathcal{T}&\equiv\mathcal{T}(E)\equiv 2\pi\delta(E-H_0)T_{EE}(E),\\ \mathcal{T}^{\dagger}&\equiv\mathcal{T}^{\dagger}(E)\equiv 2\pi\delta(E-H_0)T^{\dagger}_{EE}(E).\end{aligned} \tag{3.43}$$

Thus, we have

$$S=1-i\mathcal{T},\qquad S^{-1}=1+i\mathcal{T}^{\dagger} \tag{3.44}$$

and the result we just obtained is

$$\mathrm{Tr}S^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}S=-i\frac{\partial}{\partial E}\,\mathrm{Tr}(\mathcal{T}+\mathcal{T}^{\dagger})+\mathrm{Tr}\mathcal{T}^{\dagger}\frac{\overleftrightarrow{\partial}}{\partial E}\mathcal{T}. \tag{3.45}$$

As the reader might have noticed, after putting the S in (3.35) on-shell, the E integration covers only the spectrum of H_0 and can no longer include the bound-state spectrum of H. Indeed we have overlooked the bound states contained implicitly in (3.35) as poles of $T(E)$. These poles actually offset the δ function $\delta(E-H_0)$. A special treatment is necessary to bring out these implicit poles. In order not to complicate the discussion further at this stage, we shall leave the bound-state problem to the end of Sec. IV. Let us simply ignore bound states until then.

After going a long way in establishing (3.35) and putting S on-shell, we now use it to express the grand potential in terms of the S matrix. Since, as was illustrated before, $[\mathrm{Tr}\exp(-\beta H)]_c$ is a linear combination of terms of the form $\mathrm{Tr}(e^{-\beta H'}-e^{-\beta H_0})$ with various H', (3.35) can be applied repeatedly, each time substituting H' for H, and S' for S, where S' is the S matrix generated by $H'-H_0$. Combining all terms, one gets simply, using (3.9),

$$(\mathrm{Tr}e^{-\beta H})_c=\int dE e^{-\beta E}(4\pi i)^{-1}\left(\mathrm{Tr}S^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}S\right)_c, \tag{3.46}$$

$$(\mathrm{Tr}e^{-\beta H})_c=-\beta(\Omega-\Omega_0). \tag{3.47}$$

In (3.46), S includes matrix elements of all processes involving any number of particles. The subscript c again indicates that only the connected diagrams are kept. To see just what we mean by all these, let us look at how the terms in (3.46) involving three particles are obtained and expressed in diagram form.

Substituting (3.35) in (3.11), we have for $N=3$,

$$(\mathrm{Tr}_3e^{-\beta H})_c=\int dE\, e^{-\beta E}(4\pi i)^{-1}\times\mathrm{Tr}_3\left(S^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}S-\sum_{i<j}S_{ij}{}^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}S_{ij}\right), \tag{3.48}$$

where S is the full three-body S matrix and S_{ij} is the S matrix generated by V_{ij}. We have

$$S_{ij}=1-i\mathcal{T}_{ij}. \tag{3.49}$$

$\mathcal{T}_{ij}$ describes the scattering of particles i and j but leaves the remaining particle moving freely. The usual diagram representation for $\mathcal{T}_{ij}$ will be a ladder sum for the pair ij and a free line for the remaining particle. These are clearly disconnected diagrams.

For the full T matrix, we write

$$\mathcal{T} = \mathcal{T}_c + \sum_{i<j} \mathcal{T}_{ij}, \tag{3.50}$$

where $\mathcal{T}_c$ is the completely connected part. With the help of (3.38), (3.48) may be expressed in terms of $\mathcal{T}_c$ and $\mathcal{T}_{ij}$. We have

$$(\mathrm{Tr}_3 e^{-\beta H})_c = \int dE\,(4\pi i)^{-1}(\mathrm{Tr}_3 S^{-1}\overleftrightarrow{\frac{\partial}{\partial E}}S)_c,$$

$$(\mathrm{Tr}_3 S^{-1}\overleftrightarrow{\frac{\partial}{\partial E}}S)_c = -i\frac{\partial}{\partial E}\mathrm{Tr}_3(\mathcal{T}_c + \mathcal{T}_c^\dagger)$$

$$+\mathrm{Tr}_3\Big[\mathcal{T}_c^\dagger\overleftrightarrow{\frac{\partial}{\partial E}}\mathcal{T}_c + \sum_{i<j}\Big(\mathcal{T}_c^\dagger\overleftrightarrow{\frac{\partial}{\partial E}}\mathcal{T}_{ij} + \mathcal{T}_{ij}^\dagger\overleftrightarrow{\frac{\partial}{\partial E}}\mathcal{T}_c\Big)$$

$$+\sum_{i<j}\sum_{i'<j'}\mathcal{T}_{ij}^\dagger\overleftrightarrow{\frac{\partial}{\partial E}}\mathcal{T}_{i'j'}\Big], \quad (i,j)\neq(i',j'). \tag{3.51}$$

The first term in (3.51) can be simply represented by connected T-matrix diagrams [see Fig. 3(a)].

The second term can also be expressed diagrammatically. We use a dashed line to indicate where $\overleftrightarrow{\partial}/\partial E$ is [see Fig. 3(b)]. Let us call these diagrams "second-type" diagram and call the ordinary T-matrix diagrams the "first type". Equation (3.51) simply states that all connected diagrams of both types are to be summed. This rule is easily generalized to cases where more than three particles are involved.

To summarize, we have, for the grand potential

$$\Omega = \Omega_0 - \frac{1}{\beta}\int dE\, e^{-\beta E}(4\pi i)^{-1}(\mathrm{Tr}S^{-1}\overleftrightarrow{\frac{\partial}{\partial E}}S)_c, \tag{3.52}$$

where Ω_0 is the grand potential for the ideal gas, and

$$\Big(\mathrm{Tr}S^{-1}\overleftrightarrow{\frac{\partial}{\partial E}}S\Big)_c = \Big[\mathrm{Tr}\Big(-i\frac{\partial}{\partial E}(\mathcal{T}+\mathcal{T}^\dagger) + \mathcal{T}^\dagger\overleftrightarrow{\frac{\partial}{\partial E}}T\Big)\Big]_c \tag{3.53}$$

is the sum of all connected diagrams of the first and the second types.

What we have accomplished so far is a clean separation of the dynamical part, which is now expressed in terms of the S matrix, from the statistical part, which now appears via $e^{-\beta E}$. We first expressed Ω in terms of connected imaginary time diagrams and then transformed them into connected diagrams representing scattering processes. The whole analysis is really a counting procedure, which would be extremely difficult without the use of diagrams. We would like to emphasize that no details of diagrams even entered into our discussion except in examples. The only notion that appeared was that of connectedness. Nor is the detailed form of H_0 and V relevant. Also note that the role of the particle number N is no more than that of a label classifying diagrams. For the sake of clarity, we have not included the exchange effect due to the identity of particles. Neither have we shown how bound states are included. The final rules for calculation can be given only after we settle these questions, to which we now turn our attention.

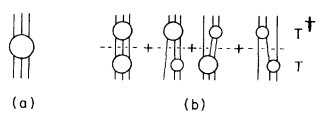


FIG. 3. Circles represent connected T-matrix diagrams. (a) Completely connected three-body T matrix. (b) Diagrams of the second type for $N=3$.

IV. EXCHANGE EFFECT AND BOUND STATES

The results of Sec. III must be properly extended to include bound states and the exchange effect due to the identity of particles. As will be seen, such an extension is particularly crucial for relativistic generalization.

A. Exchange Terms

We shall consider the case of identical fermions only. For a system of bosons or of mixed species, one simply changes the appropriate minus signs to plus signs.

Let the operator A be defined as

$$A = \sum_P \delta_P P, \tag{4.1}$$

where P is a permutation of particle labels. $\delta P = \pm 1$ depending on whether P is an even or an odd permutation. The sum is taken over all $N!$ permutations, if A operates on an N-particle state. To include the exchange effect, $\mathrm{Tr}e^{-\beta H}$ must be replaced by

$$\mathrm{Tr}Ae^{-\beta H}. \tag{4.2}$$

The counting procedure given in Sec. III B must be modified. Going back to our imaginary time diagrams, we see that, in addition to the purely diagonal terms, there are exchange diagrams [see Fig. 4(a), for example]. Note that, since A commutes with V, which is totally symmetric in labels, there is no need for modifying the Feynman-Dyson expansion (3.4) in the intermediate states.

The exchange diagrams always look connected because there are particle lines crossing each other. We can, therefore, look upon the permutation as a special kind of interaction, which we shall call the "exchange interaction." The definition of connected diagrams is now extended to include those joined by exchange interactions. Note that, for the exchange interaction to have an

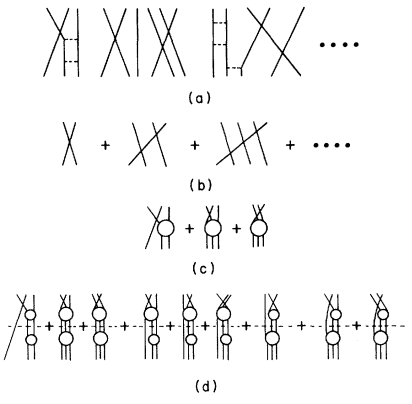


FIG. 4. (a) Typical diagram involving exchanges. (b) Connected diagrams for a free gas. (c) Three-body exchange diagrams of the first type (the T-matrix diagrams with exchange). (d) Three-body exchange diagrams of the second kind.

effect at all, there must be some overlapping between the single-particle wave functions being exchanged. This fact effectively states that the exchange interaction is of a "finite range." From this, one concludes that the contribution of connected diagrams, under the new extended definition, is always proportional to the volume.

With these modifications, the previous counting procedure goes through exactly the same way and one arrives at (3.9). To see how the exchange diagrams work, let us consider the example of $V=0$, i.e., the free Fermi gas. The exchange diagrams are shown in Fig. 4(b). For a given N, it is easy to show that there are $(N-1)!$ permutations which leave none of the elements of $(1, 2, 3, \ldots, N)$ unchanged, and that $\delta_P = (-)^{N-1}$ for all these permutations. Since

$$\mathrm{Tr}_N = \frac{1}{N!} \sum_{k_1, k_2, \ldots, k_N},$$

where $N!$ is to avoid counting the same amplitude more than once, and since only particles with the same k are affected, we have

$$(\mathrm{Tr}_N A e^{-\beta H_0})_c = (-)^{N-1} N^{-1} \sum_k e^{-\beta \epsilon_k N}. \quad (4.3)$$

By (3.9), we have

$$\Omega_{\mathrm{free}} = -\frac{1}{\beta} \sum_{N=1}^{\infty} (-)^{N-1} N^{-1} \sum_k e^{-\beta \epsilon_k N} = -\frac{1}{\beta} \sum_k \ln(1 + e^{-\beta \epsilon_k}) \equiv \Omega_0. \quad (4.4)$$

The subscript 0 now indicates the free gas with exchange effect included. Equation (4.4) is a well-known result.

To transform the imaginary time diagrams into the S-matrix form, we proceed the same way as in Sec. III B, with the exchange diagrams included. By inspecting the diagrams, one can write down the sum of connected diagrams involving a given number of particles in terms of the form $\mathrm{Tr}A'(e^{-\beta H'} - e^{-\beta H_0})$, apart from the trivial free particle terms given by (4.4). For example, for $N=3$,

$$(\mathrm{Tr}_3 A e^{-\beta H})_c = \mathrm{Tr}_3 [A(e^{-\beta H} - e^{-\beta H_0}) - \sum_{i<j} A_{ij}(e^{-\beta(H_0 + V_{ij})} - e^{-\beta H_0}) + \Big((A-1) - \sum_{i<j} (A_{ij} - 1)\Big) e^{-\beta H_0}], \quad (4.5)$$

where A_{ij} is the A operator operating on the particles i and j only. The first term in (4.5) is the full three-particle term with the free part taken out. The second term, which includes all disconnected diagrams, describes the interactions within a pair. The third term is the connected free-particle term.

In Sec. III B, the essential step was to establish (3.35), i.e., to express $\mathrm{Tr}(e^{-\beta H} - e^{-\beta H_0})$ in an S-matrix form. Similarly, our task here is to express $\mathrm{Tr}A(e^{-\beta H} - e^{-\beta H_0})$ in an S-matrix form. An important fact is that one always has

$$[A', H'] = 0. \quad (4.6)$$

For example, in (4.5) we have $[A, H] = 0$ in the first term and $[A_{ij}, H_0 + V_{ij}] = 0$ in the second term. The interaction term is always totally symmetric in any subset of N particles, and therefore, commutes with all permutations acting on that subset of particles.

We recall that, in establishing (3.35), the only property of the trace which we utilized was the invariance of products of operators under cyclic permutations. This property is not affected when the operator A is inserted because A commutes with H, H_0 and therefore with T, S, Ω, and G. Thus, one simply inserts A in the traces on both sides of (3.35) and obtains

$$\mathrm{Tr}A(e^{-\beta H} - e^{-\beta H_0}) = \int dE\, e^{-\beta E} (4\pi i)^{-1} \mathrm{Tr} A S^{-1} \frac{\overleftrightarrow{\partial}}{\partial E} S. \quad (4.7)$$

The arguments in Sec. III B putting S on-shell are not affected by the presence of A either. Going through everything in Sec. III B with A carried along, we finally arrive at

$$\Omega = \Omega_0 - \frac{1}{\beta} \int dE\, e^{-\beta E} (4\pi i)^{-1} (\mathrm{Tr} A S^{-1} \frac{\overleftrightarrow{\partial}}{\partial E} S)_c, \quad (4.8)$$

corresponding to (3.52). Ω_0 is now the free-particle grand potential with exchange effects included, and [corresponding to (3.53)]

$$(\mathrm{Tr}AS^{-1}\frac{\partial}{\partial E}S)_c$$

$$=(\mathrm{Tr}A[-i\frac{\partial}{\partial E}(\mathcal{T}+\mathcal{T}^\dagger)+\mathcal{T}^\dagger\frac{\partial}{\partial E}\mathcal{T}])_c, \quad (4.9)$$

is the sum of all connected diagrams of first and the second types, which now include exchange diagrams. Again, using $N=3$ as an example, we have diagrams shown in Figs. 4(c) and 4(d) in addition to those in Fig. 3(a) and 3(b).

B. Bound States

So far we have ignored bound states, or composite particles, which may form as a result of interactions. The bound states manifest themselves as poles of certain matrix elements of $G(E)$ and $T(E)$. These poles are not in the spectrum of H_0. As was pointed out previously, these pole terms are easily lost upon putting the operator S on-shell because of the δ function $\delta(E-H_0)$ unless one is extremely careful in various limiting processes. It is necessary to reformulate the problem in such a way that these pole terms are kept explicitly. This problem is sufficiently complicated so that we shall ignore the exchange diagrams first for simplicity and put them in later.

Let us go back to the beginning and consider the N-particle term $(\mathrm{Tr}_N e^{-\beta H})_c$. If there are bound states of N particles, the matrix elements of $G(E)=(E-H)^{-1}$ will have simple poles at $E_{B_i}(\vec{\mathrm{P}})$, where $\vec{\mathrm{P}}$ is the total momentum of the states sandwiching $G(E)$, and $E_{B_i}(\vec{\mathrm{P}})$ is the energy of the ith bound state. These poles contribute

$$-\frac{1}{\beta}\sum_{\vec{\mathrm{P}}}\sum_i e^{-\beta E_{B_i}(\vec{\mathrm{P}})} \quad (4.10)$$

to the grand potential, as is easily seen from (3.13). One can, therefore, explicitly separate these terms out from the beginning and redefine the E integrals in (3.13) and (3.14) so that the lower limit of E is above the largest of $E_{B_i}(\vec{\mathrm{P}})$ for a given $\vec{\mathrm{P}}$. Equation (4.10) may be viewed as the contribution of free composite particles labeled by i. If one adds up all such terms from $N=2, 3, 4, \ldots$, together with Ω_0, one has the grand potential of the free elementary and composite particles.

When one or more of the subsets of the N particles form bound states, one encounters scattering processes involving composite particles in the asymptotic states. There appear poles in the matrix elements of $G(E)$ and $T(E)$ to account for these processes. For example, consider the case of $N=3$. If a two-particle bound state exists, there will be processes like

(1, 2) bound + 3 free → 1 free + (2, 3) bound.

This process is reflected by the existence of poles of

$$\langle\vec{p}_1'\vec{p}_2'\vec{p}_3'\,|\,G(E)\,|\,\vec{p}_1\vec{p}_2\vec{p}_3\rangle\ .$$

For fixed $\vec{p}_1+\vec{p}_2, \vec{p}_3, \vec{p}_1'$, and $\vec{p}_2'+\vec{p}_3'$, at $E=\epsilon_B(\vec{p}_1+\vec{p}_2)+\epsilon_{p_3}$ and at $E=\epsilon_{\vec{p}_1'}+\epsilon_B(\vec{p}_2'+\vec{p}_3')$. Here $\epsilon_B(\vec{p})$ is the two-particle bound-state energy at momentum $\vec{p}$. These poles are also outside the spectrum of H_0.

To study the effect of composite-particle scattering processes, let us first classify the asymptotic states into *channels*. For example, in the three-particle case where there is one two-body bound state, there are 4 channels, i.e., 1,2 bound, 3 free; 1,3 bound, 2 free; 2,3 bound, 1 free; and 1,2,3 all free. If there exists two different two-body bound states, there will be 7 channels.

In the infinite volume limit, any two states in different channels are orthogonal, since, as can be checked easily, their scalar product vanishes at least like $O(V^{-1/2})$. This fact suggests that we extend the set of free-particle states to a larger set including the asymptotic states in all channels. In each channel, the part of the interaction Hamiltonian which is responsible for the composite particles should be included in the free Hamiltonian operating in this extended set of states. When the trace is taken over the extended set, one then should automatically pick up those pole terms we missed before, and get a formalism in which a composite particle behaves just like a different particle. We proceed to carry out this program.

We define H_α, V_α, v_α by

$$H_\alpha+V_\alpha=H,\ H_\alpha=H_0+v_\alpha,\quad V_\alpha=V-v_\alpha, \quad (4.11)$$

where α is any channel label, v_α is responsible for the composite particles in the channel α. We shall always label the all-free channel by 0. Thus $v_0=0$, $V_0=V$. Let us also define

$$G_\alpha=(E-H_\alpha)^{-1}, \quad (4.12)$$

$$\Omega_\alpha=G\,G_\alpha^{-1},\qquad \Omega_\alpha^{T}=G_\alpha^{-1}G. \quad (4.13)$$

One easily verifies that

$$\Omega_\alpha=1+G\,V_\alpha,\quad \Omega_\alpha^{-1}=1-G_\alpha V_\alpha. \quad (4.14)$$

Analogous to the definition $S=\Omega^{*-1}\Omega$ in Sec. III, we define

$$S_{\alpha\beta}=\Omega_\alpha^{*-1}\Omega_\beta. \quad (4.15)$$

Thus, by definition, $S=S_{00}$. Note that $S_{\alpha\beta}$ con-

tains pole terms describing scattering involving channels other than α and β. For example, S_{00} has poles describing composite particles, as has been discussed. What we shall do is to look at one pair of channels α,β at a time and ignore pole terms describing channels other than α and β. More precisely, we consider $\langle\alpha|S_{\alpha\beta}|\beta\rangle$, where $|\alpha\rangle, |\beta\rangle$ are any states in the channels α and β, respectively. We suppress all other labels of the states. Let us now establish the equation

$$\frac{1}{4\pi i}\sum_{\alpha\beta}\langle\beta|S^{-1}_{\alpha\beta}|\alpha\rangle\frac{\overleftrightarrow{\partial}}{\partial E}\langle\alpha|S_{\alpha\beta}|\beta\rangle = -\frac{1}{\pi}\operatorname{Im}\sum_{\beta}\langle\beta|G-G_\beta|\beta\rangle. \tag{4.16}$$

Some clarification of notation is needed before we proceed. The matrix elements of $G(E)$ have various pole terms corresponding to various channels as discussed previously. The rule is that, in $\langle\alpha|G(E)|\beta\rangle$, we ignore all but those pole terms describing the propagation from channel β to channel α. Thus, $G_\alpha|\beta\rangle = 0$ if $\alpha\neq\beta$, and $\sum_\alpha G|\alpha\rangle\langle\alpha| = G$. The sum over all other labels in (4.16) is understood. Substituting (4.15) in the left-hand side of (4.16), we obtain

$$\frac{1}{4\pi i}\sum_{\alpha\beta}\langle\beta|\Omega_\beta^{-1}\Omega^*_\alpha|\alpha\rangle\frac{\overleftrightarrow{\partial}}{\partial E}\langle\alpha|\Omega_\alpha^{*-1}\Omega_\beta|\beta\rangle = (4\pi i)^{-1}\sum_\beta[\langle\beta|\Omega_\beta^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}\Omega_\beta|\beta\rangle + \langle\beta|\Omega_\beta^{*}\frac{\overleftrightarrow{\partial}}{\partial E}\Omega_\beta^{*-1}|\beta\rangle]. \tag{4.17}$$

We have used the fact that

$$\sum_\alpha\Omega_\alpha|\alpha\rangle\langle\alpha|\Omega_\alpha^{-1} = \sum_\alpha GG_\alpha^{-1}|\alpha\rangle\langle\alpha|G_\alpha G^{-1} = \sum_\alpha G|\alpha\rangle\langle\alpha|G^{-1} = GG^{-1} = 1, \tag{4.18}$$

since G_α commutes with $|\alpha\rangle\langle\alpha|$ and $\sum_\alpha G|\alpha\rangle\langle\alpha| = G$. By (4.14), we have

$$\begin{aligned}\Omega_\beta^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}\Omega_\beta &= (1-G_\beta V_\beta)\frac{\overleftrightarrow{\partial}}{\partial E}\Omega_\beta\\ &= \frac{\partial}{\partial E}\Omega_\beta - G_\beta\frac{\overleftrightarrow{\partial}}{\partial E}V_\beta\Omega_\beta\\ &= \frac{\overleftrightarrow{\partial}}{\partial E}(1+G_\beta V_\beta\Omega_\beta) - G_\beta\frac{\overleftrightarrow{\partial}}{\partial E}V_\beta\Omega_\beta\\ &= -2G_\beta^2 V_\beta\Omega_\beta.\end{aligned} \tag{4.19}$$

Again, G_β commutes with $|\beta\rangle\langle\beta|$, and

$$G_\beta V_\beta\Omega_\beta G_\beta = G - G_\beta. \tag{4.20}$$

Substituting (4.19) in (4.17), using (4.20), we get (4.16). Equation (4.16) may be viewed as an extended version of (3.31). It remains to define a T matrix operating on the extended set of states. Substituting (4.14) in (4.15), one finds

$$S_{\alpha\beta} = (1-G_\alpha^\dagger V_\alpha)(1+GV_\beta). \tag{4.21}$$

Considering the case $\alpha=\beta$ first, we have

$$\begin{aligned}S_{\alpha\alpha} &= 1 - G_\alpha^\dagger V_\alpha\Omega_\alpha + G_\alpha\Omega_\alpha{}^T V_\alpha\\ &= 1 + (G_\alpha - G_\alpha^\dagger)T_{\alpha\alpha},\end{aligned} \tag{4.22}$$

where $\Omega_\alpha{}^T = G_\alpha^{-1}G$ and $T_{\alpha\alpha}$ is defined by

$$T_{\alpha\alpha} = V_\alpha\Omega_\alpha = \Omega_\alpha{}^T V_\alpha. \tag{4.23}$$

More explicitly,

$$S_{\alpha\alpha} = 1 - 2\pi i\,\delta(E-H_\alpha)T_{\alpha\alpha} \tag{4.24}$$

anologous to (3.30).

For $\alpha\neq\beta$, we have

$$S_{\alpha\beta} = 1 - G_\alpha^\dagger V_\alpha\Omega_\beta + G_\alpha\Omega_\alpha{}^T V_\beta. \tag{4.25}$$

We define

$$T_{\alpha\beta} = G_\alpha^{-1}GG_\beta^{-1},\quad \alpha\neq\beta. \tag{4.26}$$

From this definition

$$V_\alpha\Omega_\beta = T_{\alpha\beta} - G_\beta^{-1},\quad \Omega_\alpha{}^T V_\beta = T_{\alpha\beta} - G_\alpha^{-1}, \tag{4.27}$$

and (4.25) becomes

$$S_{\alpha\beta} = G_\alpha^\dagger G_\beta^{-1} - 2\pi i\,\delta(E-H_\alpha)T_{\alpha\beta}. \tag{4.28}$$

We are only interested in the matrix elements $\langle\alpha|S_{\alpha\beta}|\beta\rangle$, which appear in (4.16). The first term of (4.28) gives $\langle\alpha|G^\dagger{}_\alpha G_\beta{}^{-1}|\beta\rangle$. Since $|\beta\rangle$ is an eigenstate of G_β, $G^\dagger{}_\alpha$ operates on $|\beta\rangle$ directly. According to our rule under which (4.16) is established, $G_\alpha|\beta\rangle$ must be dropped for $\alpha\neq\beta$. Thus, we shall drop the first term in (4.28). Combining (4.28) and (4.24), we have, for all α, β,

$$S_{\alpha\beta} = \delta_{\alpha\beta} - 2\pi i\,\delta(E-H_\alpha)T_{\alpha\beta}, \tag{4.29}$$

with $T_{\alpha\beta}$ defined by (4.23) and (4.26). By the same arguments, we have

$$S_{\alpha\beta}^{-1} = \delta_{\alpha\beta} + 2\pi i\,\delta(E - H_\beta)T^\dagger_{\beta\alpha}. \tag{4.30}$$

The notion of connectedness of diagrams is not modified by the existence of bound states. Leaving out the disconnected diagrams on both sides of (4.16), we have, including the N-particle bound-state contribution,

$$-\frac{1}{\pi}\,\mathrm{Im}(\mathrm{Tr}_N G)_c = \sum_P \sum_i \delta(E - E_{B_i}(\vec{P}))$$
$$+ (4\pi i)^{-1}\left(\sum_{\alpha\beta}\langle\beta|S_{\alpha\beta}^{-1}|\alpha\rangle \frac{\overleftrightarrow{\partial}}{\partial E}\langle\alpha|S_{\alpha\beta}|\beta\rangle\right)_c, \tag{4.31}$$

where we have used the old notation $\mathrm{Tr}_N G$ for taking the trace over all states of N particles. Equation (4.31) is then related to $(\mathrm{Tr}e^{-\beta H})_c$, via (3.19).

The proof that the S in (4.31) may be replaced by the physical S matrix goes exactly like that given in Sec. III B [see (3.38) – (3.42)]. Of course, on-shell means now on the energy shell of the particles, elementary or composite, in the channels involved.

To summarize: We have first singled out the contribution of freely moving composite particles [see (4.10)], then we have collected the pole terms of G which describe the scatterings involving composite particles in the asymptotic state. The conclusion is then that Eq. (3.46) stays the same formally. We have now a multispecies system. Ω_0 includes the contribution from the free particles of all species. The S matrix includes elements for all possible scatterings of particles in the system.

Finally, we put in the exchange diagrams to account for the identity of particles.

There are three kinds of permutations. Those of the first kind exchange particles within a given composite particle. Because the internal wave function is properly antisymmetrized (or symmetrized), the exchange terms, together with the direct term, give a factor $N!$ if there are N particles in the composite particle. This $N!$ cancels the $(N!)^{-1}$ in the original graph counting, which forbids counting the same amplitude twice. The net result is that one can ignore the exchanges of this kind and simply treat the composite particle as an individual particle.

The permutations of the second kind exchange particles in different composite particles but always keep composite particles as units. For example, when one exchanges two hydrogen atoms, one exchanges the protons and, at the same time, exchanges the electrons [see Fig. 5(a)]. Under the permutations of this kind, the identical composite particles behave like identical elementary particles. The hydrogen atoms in the above examples behave like two elementary bosons. Our previous discussion on exchanges of elementary particles apply here, too.

Those of the third kind involve exchanging a constituent particle of a composite particle and other particles which are not constituents of that composite particle. For example, the two electrons of the two hydrogen atoms shown in Fig. 5(b) are exchanged, but not the protons. This kind of exchange diagram arises from the fact that, due to the finite size of the hydrogen atom, it is not possible to construct a field operator for the hydrogen atoms that obeys the commutation rules of a Bose field. However, these exchange diagrams are clearly part of the T matrix for H-H scattering and do not require any special consideration. For example, there is a repulsive interaction between two hydrogen atoms due to the exchange of electrons, and it is included in the H-H scattering amplitude.

We can now put our expression of the grand potential in its final form, i.e.,

$$\Omega = \Omega_0 - \frac{1}{\beta}\int dE\, e^{-\beta E}(4\pi i)^{-1}(\mathrm{Tr}AS^{-1}\frac{\overleftrightarrow{\partial}}{\partial E}S)_c. \tag{4.32}$$

Ω_0 is the free-gas term, which is the sum of the free-gas terms of all species of particles, each obeying either Bose of Fermi statistics. The second term involves the matrix elements of all scattering processes. It is the sum of all connected diagrams of the first and second types discussed in Sec. IV, including the exchange diagrams. All the particles, composite or not, are treated on the same footing.

We have thus eliminated the interaction Hamiltonian completely. The only objects appearing in (4.32) are the energies of the free particles, their statistics and quantum numbers, and the S-matrix elements. We would like to emphasize that it is crucial, in the expression for Ω for a relativistic system, to treat all particles on the same footing. This is because in relativistic quantum mechanics, there is no way to tell about

FIG. 5. The thick lines represent protons and, the thin lines, electrons. The ladders represent hydrogen atoms. The dashed lines denote the Coulomb potential responsible for the binding. (a) Exchange of two hydrogen atoms. (b) Exchange of the electrons as a term in the T matrix for the scattering of two hydrogen atoms.

the elementarity or compositness of particles. The only thing one can say along this line is through the S-matrix elements via the Levinson's Theorem, which we shall discuss later. Equation (4.32) is easily generalized and applied to relativistic systems. Before doing that, we apply it to study the virial expansion first.

V. VIRIAL EXPANSION

In this section, we put the nonrelativistic virial expansion into the S-matrix form, and, at the same time become more familiar with the details of (4.32).

For definiteness, consider a system of fermions F. Suppose there exists a set of n_2 bound states of 2 fermions F_2^i, and a set of n_3 bound states of 3 fermions F_3^i, etc.

To calculate the grand potential, we must classify and list the terms in the trace. Preferably, the terms are listed in descending order of their contributions to Ω. Let us first write the characteristics of the single particles:

$$F,\ \text{fermion},\quad N=1,\quad \text{energy}=\epsilon_p=p^2/2m, \tag{5.1}$$

$$F_2^i,\ \text{boson},\quad N=2,\quad \epsilon_p^{(2)i}=p^2/4m-B_i^{(2)},\quad i=1,\ 2,\ \ldots,n_2, \tag{5.2}$$

$$F_3^i,\ \text{fermion},\quad N=3,\quad \epsilon_p^{(3)i}=p^2/6m-B_i^{(3)},\quad i=1,\ldots n_3, \tag{5.3}$$

and so on. $B_i^{(2)}$, $B_i^{(3)}$, ... are the binding energies. Every particle carries a quantum number N, the fermion number, which is a conserved quantity. Note that in (5.1)–(5.3) we measure the single fermion energy from zero, instead of from μ as was done in Secs. III and IV, because we want to see the μ dependence explicitly.

We now list the scattering channels in the order of increasing N:

$$N=2,\quad F+F, \tag{5.4}$$

$$N=3,\quad F+F_2^i,\quad F+F+F, \tag{5.5}$$

$$N=4,\quad F+F_3^i,\quad F_2^i+F_2^j,\quad F+F+F+F,\ \text{etc.} \tag{5.6}$$

In a scattering process, the c.m. motion involves no dynamics. We should therefore separate its effect from the dynamics explicitly, and write the S matrix in the c.m. frame.

For a given N, the energy due to the c.m. motion is $P^2/2(Nm)$, where $\vec{P}$ is the total momentum of the particles involved in that channel. For a given channel, it is convenient to measure the total energy from the lowest-energy level in the c.m. frame. We define ϵ by

$$E=P^2/2(Nm)-B_{N\alpha}+\epsilon, \tag{5.7}$$

$$B_{N\alpha}=\sum_{i=1}^{n_2} m_{\alpha i}^{(2)}B_i^{(2)}+\sum_{i=1}^{n_3} m_{\alpha i}^{(3)}B_i^{(3)}+\cdots, \tag{5.8}$$

where $B_{N\alpha}$ is the total binding energy of the channel $N\alpha$. $m_{\alpha i}^{(l)}$ is the number of F_l^i's in the channel. Since the S-matrix elements are independent of $\vec{P}$, (4.32) becomes

$$-\beta(\Omega-\Omega_0)=V\sum_{N=2}^{\infty}\sum_{\alpha}A_{N\alpha}\exp(\beta\mu N-\beta B_{N\alpha})\lambda^{-3}(Nm), \tag{5.9}$$

where

$$A_{N\alpha}=\int_0^{\infty}d\epsilon\, e^{-\beta\epsilon}\left(\frac{1}{(4\pi i)^{-1}}\mathrm{Tr}_{N\alpha}AS^{-1}\frac{\overleftarrow{\partial}}{\partial\epsilon}S\right)_c, \tag{5.10}$$

and

$$\lambda^{-3}(M)=\int d^3p(2\pi)^{-3}\exp(-\beta P^2/2M)=(M/2\pi\beta)^{3/2}. \tag{5.11}$$

The trace $\mathrm{Tr}_{N\alpha}$ in (5.10) is restricted to the channel $N\alpha$ in the c.m. frame. The intermediate states between S^{-1} and S can, of course, be in channels $N\beta$ with $\beta\neq\alpha$. $A_{N\alpha}$ is a dimensionless quantity. Because of the ϵ integration, the temperature dependence of $A_{N\alpha}$ will not be exponential. The dominant temperature dependence is thus the factor

$$\exp(\beta\mu N)\exp(\beta B_{N\alpha}). \tag{5.12}$$

For a dilute gas, where the occupation number per state is much less than 1, $e^{\beta\mu}$ is roughly of the order of magnitude of the number per state. Equation (5.9) is then a power series in $e^{\beta\mu}$, i.e., the virial expansion, rapidly convergent for a dilute gas. Note that the factor $e^{\beta B_{N\alpha}}$ makes channels with large binding energy more important. The virial series will start converging when (5.12), not just $e^{\beta\mu N}$ alone, becomes small.

For example, consider a hydrogen gas at a temperature low compared to B, the binding en-

ergy of a hydrogen molecule. The term due to channels with n_1 atoms and n_2 molecules has a factor

$$\exp(\beta\mu n_1)\exp[\beta(2\mu+B)n_2]. \tag{5.13}$$

Thus, the virial expansion will not converge unless $2\mu+B$ is negative. Since βB is assumed to be large, n_1 may be set to zero and one effectively has a virial expansion for the molecular gas, i.e., an expansion in powers of $e^{\beta\mu'}$, where $\mu'=2\mu+B$.

It seems that (5.9) and (5.10) provide a simple scheme for calculating the higher virial coefficients which were never available before.

VI. RELATIVISTIC SYSTEMS

A. General Formula

As was stated in Sec. II, for any system, relativistic or nonrelativistic, the grand potential takes the form

$$\Omega=-\beta\ln\mathrm{Tr}\exp[-\beta(H-\textstyle\sum_i\mu_i N_i)], \tag{6.1}$$

where $(N_1, N_2\ldots)$ is the set of conserved quantities, and $(\mu_1, \mu_2, \ldots)$ is the set of corresponding Lagrange multipliers, or generalized chemical potentials. The result (4.32) is readily generalized upon replacing μ, N by the sets $(\mu_1\mu_2\ldots)$ and $(N_1, N_2\ldots)$. As was discussed in the Introduction, the spirit is that, since only physical particles and S-matrix elements remain in (4.32), it may be taken as valid in general even though it is established via a nonrelativistic procedure.

The classification of channels follows very much the same procedure as given in Sec. V. Before considering the quantum numbers explicitly, we shall first factor out the c.m. motion as was done in Sec. V.

Consider a channel with a given set of quantum numbers $(N_1, N_2, \ldots)\equiv\mathfrak{N}$, and labeled by an additional label α. Suppose there are n particles in the channel. The sum over states takes the form

$$\int\prod_{i=1}^{n}[d^3p_i(2\pi)^{-3}] \tag{6.2}$$

in the momentum representation. Let m_i be the mass of the ith particle and $\epsilon_i=(m_i{}^2+p_i{}^2)^{1/2}$ be its energy. To facilitate the Lorentz transformation to the c.m. frame, we change the normalization of the plane-wave state $\vec{p}_i$ from unity to ϵ_i/m_i. Then the S-matrix elements become invariant and the sum (6.2) is replaced by

$$\int\Pi_i d^3p_i(2\pi)^{-3}(m_i/\epsilon_i). \tag{6.3}$$

We now assert that

$$\Pi_i d^3p_i(2\pi)^{-3}(m_i/\epsilon_i)=[\Pi_i d^3p_i'(2\pi)^{-3}\times(m_i/\epsilon_i')]\delta(\textstyle\sum_i\vec{p}_i')\,d^3P(w/E), \tag{6.4}$$

where $(\epsilon_i', \vec{p}_i')$ is the energy momentum of the ith particle in the c.m. frame and the δ function is to secure that the total momentum in the c.m. frame vanishes. The other parameters in (6.4) are defined as

$$\vec{P}=\textstyle\sum_i\vec{p}_i,\quad w=\sum_i\epsilon_i',\quad E=(w^2+\vec{P}^2)^{1/2}. \tag{6.5}$$

Thus, $(E, \vec{P})$ is the energy momentum of the n-particle cluster and w is the mass of the cluster. Equation (6.4) can be proved by induction. The $n=2$ case may be checked by straightforward algebra. It is left as an exercise for the reader. If we write a variable E' in terms of a new variable w' by

$$E'=(\vec{P}^2+w'^2)^{1/2}. \tag{6.6}$$

Then, $(w'/E')\delta(E-E')=\delta(w-w')$ and $dE'(d/dE')=dw'(d/dw')$. In this way, one can obtain from (4.32), that

$$-\beta(\Omega-\Omega_0)=V\textstyle\sum_\nu a_\nu e^{\beta\mu\mathfrak{N}}, \tag{6.7}$$

where $\mu=(\mu_1, \mu_2, \ldots)$, $\mathfrak{N}=(N_1, N_2, \ldots)$, $\nu=(\mathfrak{N}, \alpha)$ $\times\mu\mathfrak{N}=\sum_i\mu_i N_i$, α stands for the other labels required in fixing a channel, and

$$a_\nu=\int d^3P(2\pi)^{-3}\int dw\exp[-\beta(P^2+w^2)^{1/2}]\times(4\pi i)^{-1}\left(\mathrm{Tr}_\nu AS^{-1}\frac{\overleftrightarrow{\partial}}{\partial w}S\right)_c. \tag{6.8}$$

The trace Tr_ν is taken in the c.m. frame over the channel ν. Carrying out the P integral, we have

$$a_\nu=(2\pi^2\beta)^{-1}\int_{M_\nu}^{\infty}dw\,w^2K_2(\beta w)(4\pi i)^{-1}\times\left(\mathrm{Tr}_\nu AS^{-1}\frac{\overleftrightarrow{\partial}}{\partial w}S\right)_c. \tag{6.9}$$

K_2 is a modified Bessel function. The lower limit of the w integral is the rest energy of the particles in the channel, i.e., the sum of the masses, which we denote by M_ν. When the temperature is much lower than M_ν, it is easy to see from (6.8) that (6.7) reduces to the nonrelativistic expression (5.9). Or, one can use the approximation

$$K_2(\beta w)\approx(\tfrac{1}{2}\pi\beta w)^{1/2}e^{-\beta w} \tag{6.10}$$

in (6.9) to obtain (5.9). Note that here, w and all the other energy variables all include the masses involved while only the kinetic energy is included in the ϵ of (5.9).

B. Classification of Channels

To illustrate the qualitative features of our results, let us ignore the weak and the electromag-

netic interaction, and discuss a gas of strongly interacting particles.

We denote the baryons collectively by B, their antiparticles by $\bar{B}$, and the various mesons by π. Only stable particles are included. The unstable particles show up in the resonance scattering of stable particles, as will be discussed in Sec. VIC. For simplicity, we will imagine that all the baryons have a common mass M_B and that the mesons have a common mass m_π.

The conserved quantities appearing in the general formulas (6.1) and (6.9) are $(B, I, S) = \mathfrak{N}$, i.e., the baryon number, the third component of the isotopic spin and the strangeness. Corresponding to $\mathfrak{N}$, we have the chemical potentials $(\mu_B, \mu_I, \mu_S) = \mu$. Let us first classify the channels by the baryon number. (a) $B = 0$, with π, 2π, 3π, 4π, ..., any number of π's; $B\bar{B}$, $B\bar{B}$+ any number of π's; $2(B\bar{B})$, ..., etc. In other words, all channels involving any number of π's and equal numbers of B's and $\bar{B}$'s. (b) $B = 1$; all channels in (a) with one more B. (c) $B = -1$; all channels in (a) with one more $\bar{B}$, etc. Obviously, for $B = \pm n$, one adds to (a) nB or $n\bar{B}$, n = any positive integer.

The baryon number is analogous to the fermion number N in our previous discussion on the nonrelativistic system. The qualitative difference between B and N is that N is always positive while B can be negative. More important, the appearance of arbitrary numbers of π's and $B\bar{B}$ pairs result in an infinite number of channels for each fixed B.

How do these qualitative differences diminish as one passes to the nonrelativistic limit? What is the expansion corresponding to the power series of $e^{B\mu}$ in the nonrelativistic system? The answer to these questions becomes clear when we note that the masses are the lower bounds of energies and that the nonrelativistic chemical potential μ is measured from the fermion mass. In other words, we can make the connection $\mu_B = \mu + m_B$. For a channel with n_π mesons, n_B baryons, and $n_{\bar{B}}$ antibaryons, the lower bound in energy is

$$\epsilon_{\min} = n_\pi m_\pi + n_B m_B + n_{\bar{B}} m_{\bar{B}}. \tag{6.11}$$

It is clear, from (6.8), that we can define a new energy variable ϵ' by $w = \epsilon_{\min} + \epsilon'$ and pull out a factor $\exp(-\beta\epsilon_{\min})$ from a_ν. With the factor $\exp\beta\mu_B B$, we have the factor

$$\exp(-\beta m_\pi n_\pi)\exp[-\beta(m_B - \mu_B)n_B] \times \exp[-\beta(m_B + \mu_B)n_{\bar{B}}], \tag{6.12}$$

for this channel. In the limit

$$\beta^{-1} \ll m_B, \quad m_B - \mu_B \ll m_B, \tag{6.13}$$

we see that only those channels with $n_{\bar{B}} = 0$ need to be kept. For $\beta^{-1} \ll m_\pi$, the mesons also drop out of the scene. One is left with the baryons alone. The sum (6.7) is thus a series in powers of $\exp[-\beta(m_B - \mu_B)]$, i.e., in powers of $e^{\beta\mu}$. Thus, we see that when the temperature is much lower than the masses of particles involved, we get back to the nonrelativistic virial expansion.

It is then clear that the expansion (6.7), which is the relativistic generalization of the virial expansion, is a series in powers of

$$\exp(-\beta m_\pi), \quad \exp[-\beta(m_B + \mu_B)],$$

$$\text{and} \quad \exp[-\beta(m_B - \mu_B)]. \tag{6.14}$$

The convergence of this series is unclear since the S matrix involving many particles is unknown. However, it seems clear that it must be summed formally to infinite orders if $|\mu_B| > m_B$. In other words, when the gas becomes highly degenerate, it is necessary to know the S-matrix elements involving an infinite number of particles. When $|\mu_B| < m_B$, and the temperature is not much higher than m_π, one may get a reasonable approximation by keeping only the channels involving a few particles.

Let us now look at the role of the other two quantum numbers, i.e., the isospin and the strangeness. Consider the former first. The term $-\mu_I I$ in the grand potential is formally identical to the Zeeman term in magnetic systems. In other words, μ_I plays the role of a magnetic field, and I plays the role of the magnetic moment. The moments tend to line up along the field. Thus, when μ_I is larger, one will have a larger total isotopic spin (i.e., more π^+ and protons than π^- and neutrons). When the sign of μ_I is reversed, so is the total isotopic spin. The role of μ_S and s is entirely similar and will not be discussed.

We have illustrated some of the general features of the classification of terms by considering the baryon-meson system. When the electromagnetic and weak forces are involved, new features appear. The important ones are discussed in the following.

C. Electromagnetic Interaction Alone

When only the electromagnetic force is involved, the above discussion applies with e^-, e^+, and γ playing the roles of B, $\bar{B}$, and π, respectively. The photon has no mass and one thus has to include terms involving infinitely many photons. However, since the coupling constant e is small, one can use the perturbation theory for the S-matrix element. To the order e^n, there can be no more than n particles involved in the scattering except for exchange terms, which can always be summed. Thus, (6.7) seems to be applicable and effective. Once the S-matrix elements to a given order in e are given, the grand potential can be calculated

to that order. We shall consider the lowest-order terms in Sec. VI D. Note that there is no problem in renormalization here because we only deal with physical quantities. The renormalization is carried out when one calculates the S-matrix elements. When both the strong and the electromagnetic interactions are involved, the problem becomes very difficult. This is mainly because there is no established theory of radiative corrections to the strong S matrix.

D. Weak Interaction

Neutrinos are involved in many weak processes. Due to the weakness of these processes, neutrinos will escape any system not too enormous in size, and cannot be thermalized. Thus, when neutrino emissions take place, one does not have a system in thermal equilibrium. However, they may be treated by perturbation theory to give parameters such as the rate of change of the temperature and pressure of a strongly or electromagnetically interacting system. Such a perturbation theory is yet to be formulated.

VII. EXAMPLES AND FURTHER DETAILS

We have discussed various features of the S-matrix expansion of the grand potential assuming that the S-matrix elements are given. In practice the S-matrix elements are most often unknown, unfortunately. In this section, we shall consider some examples where over-simplified S-matrix elements are used in order to illustrate more explicitly the qualitative features of the expansion formula. Further details of the general formula will also be explored.

A. Resonance Scattering

Consider a system of muons, electrons, and neutrinos with only weak interactions. That is, we neglect the electromagnetic interactions of muons and electrons. Due to the extreme feebleness of the weak interaction, one knows that the equilibrium state can be adequately described by a perfect gas, with the only real role of the interaction being to adjust the relative numbers of e's, μ's, ν_e's, and ν_μ's. The way in which this falls out of our S-matrix formalism is not quite straightforward.

The problem here is that the muon is unstable, and therefore, cannot be rigorously included in the asymptotic states which define the S matrix. In fact, one has to regard the muon as a resonance in reactions like $e+\bar{\nu}_e+\nu_\mu \to e+\bar{\nu}_e+\nu_\mu$. However, it is not hard to see how the above picture of a perfect gas emerges. We note that the amplitude for $e+\bar{\nu}_e+\nu_\mu \to e+\bar{\nu}_e+\nu_\mu$ is negligibly small except in a tiny region of phase space where the resonance reaction $e+\bar{\nu}_e+\nu_\mu \to \mu \to e+\bar{\nu}_e+\nu_\mu$ can take place. In the resonance region, the amplitude is of order unity. Evidently, the scattering amplitudes can be neglected only after the resonance poles have been removed. As the reader may have already guessed, taking account of the resonance poles simply reinstates the muon as an elementary particle which is to be treated on the same footing as e's, ν_e's, and ν_μ's. We will not explicitly show this here but rather work out a simpler case.

For a nonrelativistic system, the two-body term in the virial series (5.9) is easily shown to be

$$\sum_l \int_0^\infty d\epsilon\, e^{-\beta\epsilon} \frac{1}{\pi} \frac{d}{d\epsilon} \delta_l(\epsilon), \tag{7.1}$$

where $\delta_l(\epsilon)$ is the phase shift for angular momentum l. Now if in the partial wave l_0 there is a sharp resonance at $\epsilon = \epsilon_0$ then $\delta_{l_0}(\epsilon)$ rises rapidly from 0 to π in a narrow region around ϵ_0. The derivative of the phase shift will then be almost a δ function, i.e.,

$$\frac{1}{\pi} \frac{d}{d\epsilon} \delta_{l_0}(\epsilon) \approx \delta(\epsilon - \epsilon_0), \tag{7.2}$$

and the resonance will clearly contribute a term $e^{-\beta\epsilon_0}$ to the virial coefficient. This is, of course, identical in form to a bound state so we see that at least in this case, a sharp resonance acts just like a stable particle.

To see this in more detail, consider a fictitious system of spinless mesons π (mass m) and spinless baryons N (mass M). Suppose the scattering processes are dominated by an s-wave πN resonance N^* with a mass M^* and a half-width Γ. In other words, we consider the process

$$\pi + N \to N^* \to \pi + N \tag{7.3}$$

only, and ignore all other processes. Equation (7.3) is depicted in Fig. 6. The kinematic parameters are defined as follows:

$$\epsilon_1 = (m^2 + k^2)^{1/2}, \quad \epsilon_2 = (M^2 + k^2)^{1/2}, \quad \epsilon' = \epsilon_1 + \epsilon_2, \tag{7.4}$$

where $\vec{k}$ is the momentum of N in the c.m. frame. Let the N^* decay matrix element be g. Then the Golden Rule for the decay rate gives

$$2\Gamma = 2\pi \int d^3k\, (2\pi)^{-3} \delta(\epsilon' - M^*)(M/\epsilon_2)(2\epsilon_1)^{-1} g^2 . \tag{7.5}$$

We have normalized the meson plane wave to $2\epsilon_1$ and the baryon plane wave to ϵ_2/M. Since

$$d^3k(\epsilon_1\epsilon_2)^{-1} = (k/\epsilon')d\epsilon'\, d\Omega , \tag{7.6}$$

where $d\Omega$ is the solid angle element in the $\vec{k}$ direction, we have

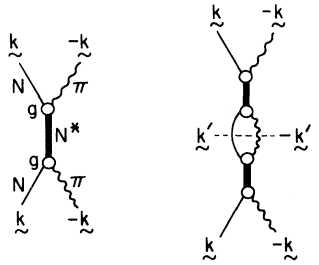


FIG. 6. $N\pi$ resonance scattering. Diagrams of the first (left) and the second (right) types.

$$\Gamma=(g^2/4\pi)(M/M^*)k. \tag{7.7}$$

The invariant T-matrix element for (7.3) is given by

$$T=g^2(\epsilon'-M^*+i\Gamma)^{-1}\ . \tag{7.8}$$

Neglecting exchange diagrams, we have, following the notation of (3.38)–(3.40),

$$\mathrm{Tr}S^{-1}\frac{\overleftrightarrow{\partial}}{\partial\epsilon}S=-i\,\mathrm{Tr}(\mathcal{T}+\mathcal{T}^\dagger)+\mathrm{Tr}\mathcal{T}^\dagger\frac{\overleftrightarrow{\partial}}{\partial\epsilon}\mathcal{T}, \tag{7.9}$$

$$\mathcal{T}=2\pi\delta(\epsilon-H_0)T. \tag{7.10}$$

Substituting (7.10) and (7.8) in (7.9) and taking (7.7) into account to eliminate g, we have

$$\frac{1}{4\pi i}\mathrm{Tr}S^{-1}\frac{\overleftrightarrow{\partial}}{\partial\epsilon}S=-\mathrm{Re}\frac{d}{d\epsilon}\frac{\Gamma}{\pi}(\epsilon-M^*+i\Gamma)^{-1}$$

$$+2\pi\,\mathrm{Im}\left(\frac{\Gamma^2}{\pi}\right)(\epsilon-M^*-i\Gamma)^{-1}\frac{\partial}{\partial\epsilon}(\epsilon-M^*+i\Gamma)^{-1}. \tag{7.11}$$

We now substitute (7.11) in (6.7). When the resonance is narrow, one easily shows that (7.11) behaves like $\delta(\epsilon-M^*)$. Thus, we have

$$-\beta(\Omega-\Omega_0)=\sum_{\vec{p}}\int d\epsilon\, e^{-\beta(P^2+\epsilon^2)}\,\delta(\epsilon-M^*)e^{-\beta\mu_B}. \tag{7.12}$$

This result says that the resonance, at least under above approximations, contributes to Ω like a free particle of mass M^* would. When (7.3) is replaced by a corresponding process with antiparticles, one gets (7.12) with μ_B replaced by $-\mu_B$ as expected.

We leave it to the reader to convince himself that a sharp resonance acts like a particle in more general situations, e.g., three-particle scattering. The remainder of this subsection is devoted to further physical examples of the role played by unstable particles. Before proceeding, however, we should give a quantitative meaning to the words sharp resonance. In the example discussed above, the resonant phase shift changes by π in a region around M^* whose length is of order the total width 2Γ of the resonance. To justify the approximation (7.12) one must suppose that the Boltzmann factor does not vary considerably over an interval of length Γ. Evidently this leads to the condition

$$\beta\Gamma\ll 1 \tag{7.13}$$

for a sharp resonance. At any reasonable temperature the muon whose width is of order 10^{-9} eV certainly satisfies this criterion.

As another example of the importance of unstable states, recall that a heated gas of hydrogen atoms with its associated radiation field is well approximated by a perfect gas built out of photons, electrons, protons, and the various states of atomic hydrogen. In the usual treatment of the problem, each atomic state is treated as a separate elementary object. In our S-matrix formalism, the ground state of hydrogen would enter as a bound state but the higher levels would show up as sharp resonances in photon-hydrogen scattering.

Finally, suppose one were concerned with a system of hadrons at temperatures such that pions and nucleons are the predominant constituents. At this sort of temperature, the π-N interaction will be dominated by the (3.3) resonance N^*. This suggests a model where the nonresonant interaction is neglected and the N^* is treated as a sharp resonance (even though its width is not small). It should not be hard for the reader to see that the result of this model would simply be a perfect gas composed of π's, N's, and N^*'s. We have not investigated the validity of such a model in detail; hence we leave the π, N, N^* gas as a suggestion worth studying rather than a theory. Questions concerning the consequences of whether the resonances are elementary particles will be mentioned in Sec. VIII.

B. Summing the Exchange Diagrams

Before we go to the next example, where we study the lowest-order (in α) correction to the free grand potential of the electron-positron-photon gas, we first give a general prescription for summing the exchange diagrams.

Consider the diagram shown in Fig. 7(a) where one of the final particles, originally labeled by 2, gets exchanged with two other particles 3 and 4. We use the vertical dotted lines to connect the same labels explicitly. Let us stay in the lab frame and assume the particles are fermions. In the momentum representation, the contribution of Fig. 7(a) to $\mathrm{Tr}\,A\mathcal{T}$ is

$$(-)^2\sum_{p_1p_2}2\pi\delta(E-2\epsilon_2-\epsilon_1-\epsilon_2)\tfrac{1}{2}T. \tag{7.14}$$

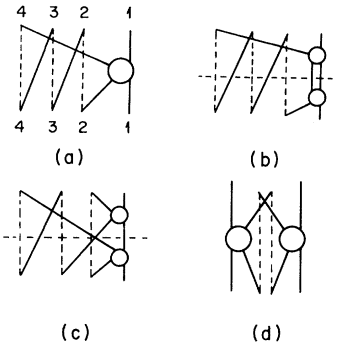


FIG. 7. Exchange diagrams. The vertical dashed lines are only to keep track of which particles are exchanged with which. (a)–(c) Exchange diagrams treated as corrections to the two-body term. (d) Typical diagram of an (originally disconnected) T matrix connected via exchange.

Again, the single-particle energy is measured from the chemical potential. T is the on-shell T-matrix element for the two-body forward scattering $(p_1,p_2)\to(p_1,p_2)$. Note that $p_3=p_4=p_2$. The factor $(-)^2$ comes from the fact that the permutation $(234)\to(342)$ is even. The factor $\frac{1}{2}$ comes from the fact that 1 and 2 are identical particles. If we make the variable change $E-2\epsilon_2\to E$ to remove the extra $2\epsilon_2$ in (7.13), we must also change the $e^{-\beta E}$ factor to be integrated over later to

$$(-)^2 e^{-\beta E} e^{-2\beta\epsilon_2}. \tag{7.15}$$

We have also pulled out the $(-)^2$ factor in (7.13) so that the remaining part of (7.13) is exactly the two-body scattering term without exchanging with any other particle. It is easy to verify that, if n, instead of two, particles are exchanged with the particle 2 in Fig. 7(a), (7.15) becomes

$$(-)^n e^{-\beta E} e^{-n\beta\epsilon_2}. \tag{7.16}$$

Summing over n, using the fact that

$$1+\sum_{n=1}^{\infty} e^{-n\beta\epsilon_2}(-)^n=(1+e^{-\beta\epsilon_2})^{-1}, \tag{7.17}$$

we effectively replace the two-body scattering term by

$$\sum_{p_1 p_2} (1+e^{-\beta\epsilon_2})^{-1} 2\pi\delta(\epsilon-\epsilon_1-\epsilon_2)\,T. \tag{7.18}$$

This is for the exchange correction to one of the particles, i.e., particle 2. The same arguments apply to particle 1 and the diagrams like Fig. 7(b). In fact, one simply inserts a factor $(1+e^{-\beta\epsilon_p})^{-1}$ for every single fermion state that is summed in the trace. For the type 2 diagrams, additional exchange diagrams like Fig. 7(c) occur. Thus, in the sum over the free particle states connecting $\mathcal{T}\dagger$ and $\mathcal{T}$, one also inserts $(1+e^{-\beta\epsilon_p})^{-1}$ for every single fermion state. For bosons, we use $(1-e^{-\beta\epsilon_p})^{-1}$ instead.

We now go to the c.m. frame as we did before. Let

$$\vec{v}=\vec{P}/E \tag{7.19}$$

be the velocity of the center of mass [see (6.5) for notation]. Also, let the Lorentz factor $(1-v^2)^{-1/2}$ be denoted by γ. Thus, we have, writing out the chemical potential explicitly

$$\epsilon_p-\mu=\gamma(\epsilon_{p'}+\vec{v}\cdot\vec{p}')-\mu, \tag{7.20}$$

where $\vec{p}'$ is the momentum in the c.m. frame. The correction factor $(1\pm e^{-\beta\epsilon_p})^{-1}$ discussed above must be written

$$\{1\pm\exp-\beta[\gamma(\epsilon_{p'}+\vec{v}\cdot\vec{p}')-\mu]\}^{-1} \tag{7.21}$$

in the c.m. frame.

Notice that we have only summed the free-particle lines joined to a T matrix via exchange but we have not considered separate pieces of T matrices joined by exchange, for example, see Fig. 7(d). We have not obtained a simple prescription to sum this type of diagram.

C. Electromagnetic System

When only the electromagnetic interaction is involved, we may take advantage of the fact that, to $O(e^n)$, the connected S matrix has only elements involving at most n particles. As a second example of application of the S-matrix expansion formula, let us calculate Ω to the second order in e.

To secure charge neutrality, the total number of e^+ must be equal to that of e^- in the system. The difference of the electron number and positron number is a conserved quantity and to it there corresponds a chemical potential μ. The charge neutrality condition implies that $\mu=0$.

The second-order processes are:

$$\begin{aligned}&\text{(a)}\quad e^+ + e^- \rightleftharpoons e^+ + e^-,\\ &\text{(b)}\quad e^+ + e^- \rightleftharpoons 2\gamma,\\ &\text{(c)}\quad e^\pm + \gamma \rightleftharpoons e^\pm + \gamma,\\ &\text{(d)}\quad 2e^\pm \rightleftharpoons 2e^\pm.\end{aligned} \tag{7.22}$$

To the second order, there is no diagram of type 2, i.e., it is sufficient to consider the term

$$-i\frac{\partial}{\partial\epsilon}\,\mathrm{Tr}A(\mathcal{T}+\mathcal{T}^\dagger), \tag{7.23}$$

since the terms in $\mathcal{T}\dagger(\overleftarrow{\partial}/\partial\epsilon)\mathcal{T}$ are of the fourth

order or higher. The process (b) above will not contribute to (7.23) and can therefore be ignored.

The diagrams for the T-matrix elements are shown in Fig. 8. The charge neutrality implies also that ($a1$), ($d1$), and ($d3$) cancel exactly. Since the exchanged photons in these diagrams have exactly zero energy and momentum due to the fact that we are calculating only the forward T matrix, each of these diagrams would be infinite. This is the electrostatic energy of the system, which does not exist for a system with no net charge.

The diagrams have all been analyzed in text books.[8] We simply write down the T-matrix elements following the rules of electrodynamics. The evaluation of the trace involves the sum over the spinor space and then over the momentum space. Consider the former first. The contribution of Fig. 8(a2) is

$$T_a = e^2 \operatorname{tr} \Lambda_+(p_1)\gamma_\mu \Lambda_-(p_2)\gamma^\mu (p_1+p_2)^{-2}. \quad (7.24)$$

We follow the notation of Ref. 8. The trace symbol tr denotes the trace over the spinor space. Equation (7.24) is easily evaluated to give

$$T_a = -e^2[m^{-2} + 2(p_1+p_2)^{-2}]. \quad (7.25)$$

Figure 8(d2) gives

$$\tfrac{1}{2} T_d = \tfrac{1}{2} e^2 \operatorname{tr} \Lambda_+(p_1)\gamma_\mu \Lambda_+(p_2)\gamma^\mu (p_1-p_2)^{-2}$$

$$= e^2[\tfrac{1}{2} m^{-2} + (p_1-p_2)^{-2}]. \quad (7.26)$$

Figure 8(d4) gives the same contribution as (7.24). Figure 8(c1) gives

$$\tfrac{1}{2} T_c = e^2 \sum_\epsilon \operatorname{tr} \Lambda_+(p) \not{\epsilon}$$

$$\times [S_F(p+k) + S_F(p-k)] \not{\epsilon} = e^2/m, \quad (7.27)$$

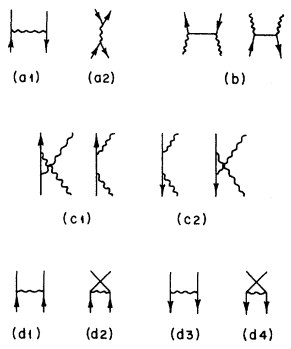


FIG. 8. Second-order scattering diagrams in electrodynamics. (a) e^+e^- scattering. (b) Pair creation and annihilation. (c) Compton scattering. (d) e^-e^- and e^+e^+ scatterings.

where ϵ denotes the photon polarization vector. Figure 8(c2) gives the same contribution as (c1). Since there is no advantage in this simple example to use the c. m. frame, we shall use the lab frame. The formula for the grand potential reduces to

$$-\beta(\Omega - \Omega_0) = -\int dE\, e^{-\beta E} (2\pi)^{-1} \operatorname{Re}(d/dE) \operatorname{Tr} A\mathcal{T} + O(e^4) \quad (7.28)$$

as was already mentioned. Collecting (7.24)–(7.27) we have

$$\operatorname{tr} \mathcal{T} = 2\pi\delta(E - \epsilon_{p_1} - \epsilon_{p_2})(T_a + T_d) + 2\pi\delta(E - \epsilon_p - k)\, T_c, \quad (7.29)$$

where $\epsilon_p = (p^2+m^2)^{1/2}$. Putting in the exchange corrections via the prescription given in Sec. VII B, we have finally

$$\Omega - \Omega_0 = V \int \frac{d^3p_1 d^3p_2 (2\pi)^{-6} (m/\epsilon_{p_1})(m/\epsilon_{p_2})}{(e^{\beta\epsilon_{p_1}}+1)(e^{\beta\epsilon_{p_2}}+1)} \times 2e^2[(p_1-p_2)^{-2} + (p_1+p_2)^{-2} + m^{-2}] + V \int \frac{d^3p\, d^3k (2\pi)^{-6} (m/\epsilon_p)(2k)^{-1} 2e^2/m}{(e^{\beta\epsilon_p}+1)(e^{\beta k}-1)}. \quad (7.30)$$

In the nonrelativistic limit, the term $(p_1-p_2)^{-2}$ dominates since

$$(p_1-p_2)^{-2} = [2m^2 - 2(\epsilon_{p_1}\epsilon_{p_2} - \vec{p}_1\cdot\vec{p}_2)]^{-1} \approx -(\vec{p}_1 - \vec{p}_2)^{-2}, \quad (7.31)$$

and the other terms are of $O(m^{-2})$ or $O(m^{-1})$.

We have not investigated higher-order terms. On physical grounds, we expect terms involving $\alpha^n(\ln\alpha)^m$ as well as powers of α. When positronium states are involved, the S-matrix elements will almost certainly contain $\ln\alpha$. One also expects the plasma oscillation to play a role. The nonrelativistic electron-gas theory suggests that an $\alpha^2\ln\alpha$ term will appear.

D. Apparent Divergences in Certain Diagrams

In using the momentum eigenstates, i. e., the plane waves, as the basis states, one encounters forward scattering matrix elements that diverge.

This unpleasant feature already occurs in the three-body terms. For example, Fig. 9(a), which is a special term in the connected 3-particle T matrix, gives a contribution to $\mathrm{Tr}(\mathcal{T}+\mathcal{T}^\dagger)$ proportional to

$$\mathrm{Re}\sum_{p_1p_2p_3}\delta(E-\epsilon_{p_1}-\epsilon_{p_2}-\epsilon_{p_3})\,T_{12}\times(E-\epsilon_{p_1}-\epsilon_{p_2}-\epsilon_{p_3}+i\eta)^{-1}\,T_{23}\,. \tag{7.32}$$

The intermediate-state energy is forced to be the same by momentum conservation. Thus, the energy denominator blows up as (7.32) shows. Similarly, Figs. 9(b)–9(d) are all divergent due to the occurrence of the forms $\delta(x)\,(x\pm i\eta)^{-1}$, $\delta(x)\delta(x)$, or $(x+i\eta)^{-1}(x-i\eta)^{-1}$. In diagrams involving four or more particles, worse divergences occur for the same reason. See Fig. 9(e), for example.

These divergences are spurious. It can be shown by straightforward but rather lengthy algebra that these divergent terms cancel one another when they are combined.

Physically, these divergent terms may be attributed to the infinite extension of the plane waves. For example, Fig. 9(a) describes the scattering of 2 and 3 after 2 interacts with 1. However, particle 2 is under the influence of 1 all the time since the plane wave of 1 is infinitely extended. Thus particle 1 behaves like a background medium. The effect of a medium includes shifting the energy of the particle propagating in it and giving it a width as well. Such an effect is incompatible with the physical picture of a sequence of two scattering events implied by Fig. 9(a). It is not surprising that, if one expands a propagator or a δ function with an energy shift in powers of that energy shift, one will have very singular terms. The over-all δ function multiplying the T matrix is not intended for such singular terms.

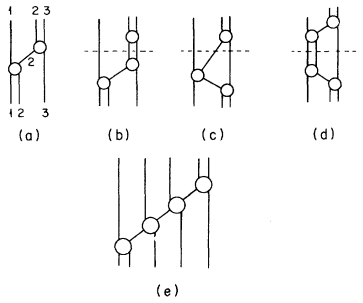


FIG. 9. Terms with singular denominators in the T matrix. (a) Three-body forward T-matrix term which has a singular denominator for the intermediate states in the momentum representation. (b)–(d) Singular terms of the second type owing to the appearance of the term (a) in the T matrix. (e) Singular five-body term in the forward T matrix.

It seems clear that these apparently divergent terms will be manifestly absent if one removes the infinite extension of the wave functions. If one uses wave-packet states, the sequence of scatterings can always be defined with no ambiguity. However, wave-packet states are not eigenstates of H_0 and are, therefore, inconvenient in practice. A reasonable choice seems to be the set of angular momentum eigenstates. For example,[9] in the three-particle case, we can use eigenstates of the angular momentum (l, m) of the pair (1, 2) in its center of mass, its c. m. energy ν, the total angular momentum (J, M) in the c. m. frame of the three-body system, and the total c. m. energy ϵ'. This way, the intermediate states of Fig. 9(a) will be summed over, and no divergence occurs, since the integration over ϵ' smears up the energy denominator. Explicitly, in the c. m. frame, (7.32) becomes

$$\mathrm{Re}\sum_{J,M,l'm'l''m''}\int d\epsilon'd\nu'd\epsilon''d\nu''\,\delta(\epsilon-\epsilon')\times\langle JMl'm'\epsilon'\nu'|T_{12}|JMl''m''\epsilon''\nu'\rangle\times(\epsilon-\epsilon''+i\eta)^{-1}\langle JMl''m''\epsilon''\nu''|T_{23}|JMl'm'\epsilon'\nu'\rangle\,. \tag{7.33}$$

The sum over the total momentum is suppressed. Although the angular momentum basis may seem to be inconvenient for formal discussion, it is convenient, and in fact most often used, for more detailed analysis and actual calculations.[9,10]

We have thus shown that, by properly choosing the basis states, the diagrams in Fig. 8 are well behaved. However, we would like to emphasize that scattering processes described by these diagrams do form a special class in contrast to those which do not give trouble in the momentum representation. These will play an important role in multiparticle scattering because, as Figs. 8(a) and 8(d) indicate, a particle can travel, between two scattering events, over a distance long compared to the range of the force, and therefore effectively provides an interaction of a much longer range. In other words, two clusters of particles can interact by exchanging a real particle. This long-range interaction is important because the probability for all the particles to cluster within the range of force is very small. It seems that these processes have not received extensive study so far, mainly because of the scattering theory involving multiparticle initial and final states is not extensively developed yet and also the detailed analyses on three-body scattering so far have employed the angular momentum basis.

The assertion that one can use the on-shell T matrix in the angular momentum representation, in spite of the fact it is undefined in the momentum

representation, may seem questionable. How does one know that the limit $\eta \to 0$ can be taken before the summation over the angular momenta? This limit is supposed to be taken last.

The answer seems clear if we note that the total angular momentum is a conserved quantity just like the baryon number. We can project out the subspace of a definite angular momentum from the beginning, when we consider the imaginary time diagrams, where no $\eta \to 0$ singularity occurs. Then one transforms the formula to the S-matrix form as before for each angular momentum subspace. Thus, the question of the $\eta \to 0$ limit never occurs.

Finally, let us verify explicitly in the following example that it is completely valid to use the on-shell T matrix in the angular momentum representation.

Consider the three-body term (7.32) in the c.m. frame. For simplicity we let the two-body potential $V(\vec{r})$ be the contact potential $g\delta(\vec{r})$ and consider only the term proportional to g^2.

The quantity of interest in the momentum representation is

$$a = \int d^3p_1 d^3p_2 d^3p_3\, \delta(\vec{p}_1+\vec{p}_2+\vec{p}_3) \int d\epsilon\, e^{-\beta\epsilon} \times \frac{\partial}{\partial\epsilon} \langle \vec{p} | \frac{1}{2\pi i}(G_0^\dagger - G_0)\tfrac{1}{2}g^2(G_0+G_0^\dagger)|\vec{p}\rangle = \beta^{-1}\int d^3p_1 d^3p_3 \int d\epsilon\, e^{-\beta\epsilon} \times [-\tfrac{1}{2}g^2\delta'(\epsilon-\epsilon_1-\epsilon_2-\epsilon_3)], \quad (7.34)$$

where $(G_0^\dagger - G_0)/2\pi i$ is the expression for $\delta(E-H_0)$ before η tends to zero. The symbol $|\vec{p}\rangle$ stands for $|\vec{p}_1, \vec{p}_2, \vec{p}_3\rangle$. The δ' function comes from the fact that

$$\langle \vec{p}|(G_0 - G_0^\dagger)(G_0+G_0^\dagger)|\vec{p}\rangle = -\frac{d}{d\epsilon}\langle \vec{p}\,|G_0 - G_0^\dagger|\vec{p}\rangle = 2\pi i\delta'(\epsilon-\epsilon_1-\epsilon_2-\epsilon_3). \quad (7.35)$$

The limit $\eta \to 0$ is taken in the last step. For simplicity, let the mass of a particle be $\frac{1}{2}$, so that $\epsilon_i = \vec{p}_i{}^2$. Thus, (7.34) becomes

$$a = \beta^{-1}\tfrac{1}{8}(2\pi)^2 g^2 \int_0^\infty d\epsilon_1 d\epsilon_3\, e^{-2\beta(\epsilon_1+\epsilon_3)} \times \{\exp[-2\beta(\epsilon_1\epsilon_3)^{1/2}] - \exp[2\beta(\epsilon_1\epsilon_3)^{1/2}]\}. \quad (7.36)$$

We have taken into account that

$$\epsilon_2 = (-\vec{p}_1 - \vec{p}_3)^2 = \epsilon_1+\epsilon_3+2(\epsilon_1\epsilon_3)^{1/2}\hat{p}_1\cdot\hat{p}_3, \quad (7.37)$$

and have integrated over $\hat{p}_1\cdot\hat{p}_3$.

Now, we calculate the quantity a using the angular-momentum-basis states

$$\Psi_{JMM_z\epsilon}(R) = [8^{-1}\pi^{-2}(2J+1)]^{1/2}\mathfrak{D}_{MM_z}^{J}(R), \quad (7.38)$$

where the energies $\epsilon_1, \epsilon_2, \epsilon_3$ are assumed fixed, and R is the set of Eulerian angles specifying the orientation of the triangle formed by the three momenta. These basis states have been discussed by Omnes.[11]

In terms of this new basis set, we have

$$a = \tfrac{1}{8}\sum_{JMM_z}\int d\epsilon_1 d\epsilon_2 d\epsilon_3 \times \int d\epsilon\, e^{-\beta\epsilon}\frac{\partial}{\partial\epsilon}\delta(\epsilon-\epsilon_1-\epsilon_2-\epsilon_3) \times \langle JMM_z\epsilon\,|\tfrac{1}{2}(T+T^\dagger)|JMM_z\epsilon\rangle = \tfrac{1}{8}\beta^{-1}\sum_J(2J+1)\int d\epsilon_1 d\epsilon_2 d\epsilon_3 \times 2\pi\int_{-1}^{1}dx\int_0^{2\pi}d\phi P_J(x)\,\mathrm{Re}T(\vec{p},\vec{p}'), \quad (7.39)$$

where we have chosen the z axis along $\vec{p}_1$, and $\vec{p}_2$, $\vec{p}_3$ lying in the xz plane. By definitions,

$$\epsilon_i = \vec{p}_1{}^2 = \vec{p}_1{}'^2, \quad \hat{p}_1\cdot\hat{p}_1' = x, \quad \hat{p}_1\cdot\hat{p}_3 = \lambda,$$

$$\mathrm{Re}T(\vec{p},\vec{p}') = g^2 P(\epsilon_2-\epsilon_1-\epsilon_3-2\vec{p}_1'\cdot\vec{p}_3)^{-1}. \quad (7.40)$$

Note that T is on-shell. Using (7.40), (7.39) becomes

$$a = \tfrac{1}{8}\beta^{-1}\sum_J(2J+1)(2\pi)^2 g^2 \times \int_0^\infty d\epsilon_1 d\epsilon_3 \exp[-2\beta(\epsilon_1+\epsilon_3)]\int_0^1 d\lambda \times \{\exp[-2\beta\lambda(\epsilon_1\epsilon_3)^{1/2}] - \exp[2\beta\lambda(\epsilon_1\epsilon_3)^{1/2}]\} \times \int_{-1}^{2\lambda^2-1}dx\,\frac{P_J(x)}{[(1-x)(2\lambda^2-1-x)]^{1/2}}. \quad (7.41)$$

The integrals are well defined for each J.

As long as we stay away from the point $\lambda = 1$, the sum over J gives zero because, if we sum over J,

$$\sum_J(2J+1)P_J(x) = 2\delta(x-1), \quad (7.42)$$

which vanishes for $x \neq 1$. Therefore, it is only necessary to integrate over λ from $1-\delta$ to 1, where δ is very small. To extract the contribu-

tion from $\lambda = 1$, we let the path of the x integral go from -1 to 1 and then from 1 to -1 but under the cut extending from $-\infty$ to $2\lambda^2 - 1$. Then we divide the integral by 2. The result, after integrating over λ, is

$$a = \tfrac{1}{8}\ \beta^{-1}\sum_J (2J+1)(2\pi)^2 g^2 \times \int d\epsilon_1 d\epsilon_3 \exp[-2\beta(\epsilon_1+\epsilon_3)] \times \{\exp[-2\beta(\epsilon_1\epsilon_3)^{1/2}] - \exp[2\beta(\epsilon_1\epsilon_3)^{1/2}]\} \times \tfrac{1}{2}\int_{-1}^{1} dx P_J(x)\ , \qquad (7.43)$$

which is the same as (7.36). We have thus illustrated that it is perfectly legitimate to use the on-shell T matrix in the angular momentum representation at least in a simple but nontrivial case.

VIII. LEVINSON'S THEOREM

We shall establish a general version of the Levinson's Theorem, which gives much physical insight into the S-matrix formula for the grand potential.

In the theory of two-body potential scattering, the Levinson's Theorem states that

$$n_{Bl} + \frac{1}{\pi}[\delta_l(\infty) - \delta_l(0)] = n_{Bl} + \frac{1}{\pi}\int_0^\infty d\epsilon \frac{d}{d\epsilon}\delta_l(\epsilon) = 0, \qquad (8.1)$$

where $\delta_l(\epsilon)$ is the lth phase shift at the c.m. energy ϵ, and n_{Bl} is the number of bound states with spin l. The generalization of (8.1) to three-body scattering has been done by Wright.[9]

The Levinson's Theorem simply states that the total number of states is not altered by the presence of the interaction. This will become clear later, if not clear already.

Consider the two-body term of a given angular momentum l in the virial series (5.9). We have

$$\sum_B e^{-\beta E_{Bl}} + \int_0^\infty d\epsilon\, e^{-\beta\epsilon}\frac{1}{\pi}\frac{d}{d\epsilon}\delta_l(\epsilon), \qquad (8.2)$$

where $-E_{Bl}$ is the binding energy of the bound state B. We have used the relation $\langle l\epsilon|\, S\,|l\epsilon\rangle = \exp[2i\delta_l(\epsilon)]$. At temperatures $\beta^{-1} \gg \epsilon_{\max}$, where $d\delta_l(\epsilon)/d\epsilon = 0$ for $\epsilon > \epsilon_{\max}$, $\epsilon^{-\beta\epsilon}$, and $\exp(-\beta E_{Bl})$ may be replaced by unity in (8.2), which then vanishes by (8.1). The physical interpretation of this result is clear. Equation (8.2) is a correction term to the free-particle grand potential due due to the interaction, which shifts the energy levels below a certain upper bound $\epsilon_{\max}$. When the temperature is much higher than $\epsilon_{\max}$, the sum over states weighted by the Boltzmann factor, which is 1, over these levels simply gives the phase-space volume occupied by these levels. The phase-space volume cannot be changed by the interaction. Therefore, (8.2) must vanish. The free-particle term already includes this phase-space volume. The composite particle plays no part. This result should hold when more than two particles are involved.

We proceed to generalize the Levinson's Theorem to the scattering involving an arbitrary number of particles. With our formalism, this can be done very simply

Let us go back to the formula (4.31), which is

$$-\frac{1}{\pi}\mathrm{Im}(\mathrm{Tr}_N G)_c = (4\pi i)^{-1}(\mathrm{Tr}_N S^{-1}\overleftrightarrow{\frac{\partial}{\partial E}} S)_c + \sum_i \sum_{\vec{P}} \delta(E - E_{B_i}(\vec{P}))\,, \qquad (8.3)$$

where we have suppressed the channel labels of (4.31).

Recall that $(\mathrm{Tr}_N G)_c$ is a linear combination of terms of the form

$$\mathrm{Tr}_N(G' - G_0), \qquad (8.4)$$

where $G' = (E - H')^{-1}$, with various H's. For examples, see (3.17) and (3.18). The total number of states in the phase space is

$$\oint \frac{dE}{2\pi i}\mathrm{Tr}\frac{1}{E-H'} = -\int \frac{dE}{\pi}\mathrm{Im}\,\mathrm{Tr}G'(E) \qquad (8.5)$$

for any relevant H', since the total phase-space volume is independent of the interaction. In view of (8.4), we must have

$$-\frac{1}{\pi}\int dE\,\mathrm{Im}[\mathrm{Tr}_N G(E)]_c = 0. \qquad (8.6)$$

Restricting to a given total momentum and a given set of conserved quantum numbers λ, (8.6) and (8.3) give

$$n_{B\lambda} + \int_0^\infty d\epsilon\,(4\pi i)^{-1}\left(\mathrm{Tr}_\lambda A S^{-1}\frac{\partial}{\partial\epsilon}S\right)_c = 0, \qquad (8.7)$$

where ϵ is the c.m. kinetic energy and Tr_λ is taken over the states labeled by λ, including channels involving composite particles as in (4.31). We have included the antisymmetrization or symmetrization operator A to denote that exchange connected scattering diagrams are to be included as described before. Eq. (8.7) is a general form of the Levinson's Theorem in nonrelativistic quantum mechanics. Using (8.7), one easily shows that (5.9), the virial series, gives simply

$$\Omega = \Omega_{0\,\mathrm{elem}} \qquad (8.8)$$

in the infinte temperature limit, where $\Omega_{0\,\mathrm{elem}}$ is the grand potential of the gas of free elementary particles.

The relativistic generalization of Levinson's Theorem may be written

$$n_{d\lambda} - n_{e\lambda} + \int_{M_\lambda}^{\infty} dw \frac{1}{4\pi i} \left(\mathrm{Tr}_\lambda A S^{-1} \frac{\partial}{\partial w} S \right)_c = 0, \quad (8.9)$$

where w is the c. m. energy and M_λ is the minimum of the sum of masses of the particles in the scattering states over which the trace is taken. $n_{d\lambda}$ is the number of discrete levels, and $n_{e\lambda}$ the number of elementary particles labeled by λ. These elementary particles are supposed to stay even if there were no scattering. They can be stable or unstable. Of course, (8.9) is not derived and cannot be derived from the present-day relativistic quantum mechanics. It is simply a guess based on the nonrelativistic Levinson's Theorem. It has the correct nonrelativistic limit and contains only physical quantities well defined relativistically and is, therefore, probably valid in general.

Under certain approximations and further plausible assumptions, the Levinson's Theorem can tell us a great deal of qualitative information. For example, consider the baryon-meson gas. The atomic nuclei are very much composite particles and that part of interaction which is responsible for them should only be responsible for scatterings at energies comparable to the binding energies of nuclei. We thus expect that, by the Levinson's Theorem, when the temperature is much higher than the nuclear binding energy, the contribution to the grand potential due to the nuclei vanishes. One only has to deal with the scatterings of nucleons and mesons at higher energies.

The conclusion (8.8) should also hold for a relativistic gas at infinite temperatures. Note that what a large temperature does is to make the Boltzmann factor a constant over the range of the energy integral so that the Levinson's Theorem can be applied. To some extent, an extremely high-fermion degeneracy can do qualitatively the same thing. For example, consider the baryon-meson system with $\mu_B \to \infty$. As a result of summing the exchange diagrams, the Boltzmann factors $\exp[-\beta(\epsilon_p - \mu_B)]$ are effectively replaced by the Fermi factors $[\exp\beta(\epsilon_p - \mu_B) + 1]^{-1}$. The Fermi factor is unity for ϵ_p ranging from zero to near μ_B and damps out beyond μ_B. Thus, the energy integrals encountered in the S-matrix formula for Ω have a unity weighting factor up to near μ_B; the Levinson's Theorem again says that composite particles and their scatterings can give no contribution except near and above the Fermi level μ_B. In other words, one simply has a free Fermi gas of elementary particles if the phenomena pertinent to the particles near and above the Fermi level are ignored. This is what one would expect intuitively. The grand potential of an extremely degenerate free Fermi gas of elementary particles depends essentially on the phase space volume bounded by the Fermi level. This volume is unchanged when the interaction is turned on. Of course, we know from the nonrelativisitc theory of degenerate Fermi gases that almost all of the interesting phenomena occurs near the Fermi level. Our qualitative conclusion here is simply that the same is expected for the relativistic case.

The above examples are meant only to be rough estimates based on the Levinson's Theorem. Quantitative applications of this theorem are yet to be studied and are expected to be very fruitful in statistical mechanical problems.

IX. SUMMARY AND DISCUSSION

We have developed a simple and general prescription for calculating the grand potential given the free-particle energies and the S-matrix elements. This prescription seems to be the only one existing that makes sense within the framework of the present-day relativistic quantum mechanics. In its nonrelativistic limit, it provides a tractable prescription for calculating the higher virial coefficients. Our analysis has been based on the diagrammatics combined with the formal scattering theory. The main step was simply the transformation of the imaginary time diagrams into diagrams for the scattering matrix elements. The set of conserved quantum numbers provides a natural scheme for classifying the free-particle states and the S-matrix elements between them. We have worked out simple examples to illustrate the qualitative features of the general formula. The Levinson's Theorem comes as a bonus result of our formalism.

As we have pointed out before, for this S-matrix formulation to be useful for practical calculations, one needs an effective way of obtaining multiparticle S-matrix elements. Of course, one does not, at present, know much about the multiparticle S-matrix elements. Only recently has there been some work done on nonrelativistic three-body scattering calculation. We expect that the third virial coefficients of simple gases can be computed using the prescription given here in the near future. It seems that the multiparticle scattering problem is by itself a very interesting and important problem and it should deserve more attention.

Although the S-matrix formula for the grand potential is completely general, the physical picture behind it is clearly that of a dilute gas with scattering events occurring here and there. When the density becomes higher, we expect from our knowledge about nonrelativistic systems, that in general the collective motions will become

significant. Then the dilute-gas picture is no longer a convenient one. Special techniques must be developed to make partial sums over infinite number of S-matrix elements. Since no such technique is feasible within the scope of relativistic quantum mechanics, we feel that the sensible thing to do is to study the S-matrix formula in more detail in the low-density region and then make extrapolations to higher densities.

We have analyzed only the grand potential, from which all thermodynamic properties can be derived. To formulate the hydrodynamics, one often needs transport coefficients in addition to thermodynamic parameters. The transport coefficients, such as the electrical conductivity and the viscosity, are related to the statistical averages of the product of current operators via the Kubo formulas. In other words, they are related to the current correlation functions, usually at the long wavelength and low-frequency limit. The nonrelativistic formulation of the current correlation functions is well known. We have not attempted its relativistic generalization.

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