ω at which $S(\omega, \vec{k})$ takes on its maximum value. This number can be computed directly from Eq. (15) as a function of k, and is presented in Fig. 1 along with the values measured by Cowley and Woods and reported by Sears.[15] Our estimate of ω_m is everywhere slightly less than what is observed experimentally, but the trend of this quantity as a function of k is faithfully reproduced. It is pertinent to note that a Gaussian expression for $S(\omega, \vec{k})$ like Eq. (14) would equate ω_m with $E_F(\vec{k})$ and thus generally overestimate it in the k region shown in Fig. 1. Equation (15) is therefore a qualitative improvement on the simplest possible approximation. The fact that Eq. (15) slightly overcompensates for the inadequacy of Eq. (14) is in fact typical of what occurs in a convergent term-by-term series approximation.

To get some idea of how well Eq. (15) reproduces the measured $S(\omega, \vec{k})$ aside from the shift in ω_m, we have plotted in Fig. 2 the dynamic structure factor computed from the cross-section data of Cowley and Woods[9] at 5.1 Å^{-1} along with our estimate of $S(\omega, \vec{k})$ at that wave number. The data and the curve are shown as functions of $(\omega - \omega_m)$ so as to separate the estimate of ω_m from a test of the shape of the theoretical $S(\omega, \vec{k})$. Equation (13) appears to follow the measured dynamic structure factor reasonably well, even to the extent of reproducing some of the asymmetry in the wings. From this successful comparison we conclude that our hypothesis on $S(\omega, \vec{k})$ at the lower end of the region of large momentum transfers is fundamentally sound, especially in view of the fact that reasonable agreement with experiment has been achieved without recourse to *ad hoc* parameters. The physical information to be gained from our hypothesis is limited however, since the only quantities of importance in the theoretical $S(\omega, \vec{k})$ are $\langle K \rangle$ and $\langle \Delta V \rangle$, which can be computed by other means.

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S-Matrix Formulation of Statistical Mechanics*

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Some comments on a recent paper of Dashen, Ma, and Bernstein on an *S*-matrix formulation of statistical mechanics are made and, in particular, an alternate form of one of their main results (which was obtained by Watson in 1956) is discussed.

In a recent paper by Dashen, Ma, and Bernstein[1] (DMB) a virial-expansion formulation of equilibrium statistical mechanics was given in terms of formal scattering theory. If certain limiting procedures exist (to be discussed below), then they have obtained an expression for the N-particle partition function (or what is equivalent, the Nth virial coefficient) in terms of an S matrix. In this paper one of their main results, DMB Eq. (3.35), is put in a form first obtained in 1956 by K. M. Watson[2] (W)

and additional comments are made.

A primary quantity of interest in both DMB and W is the quantum-mechanical trace

$$Z_N \equiv \mathrm{Tr}\ e^{-\beta H}, \tag{1}$$

where the Hamiltonian H of the system of N particles in a volume Σ is assumed to be of the form

$$H = H_0 + V, \tag{2}$$

with the eigenstates and eignevalues of H_0 known:

$$H_0 |k\rangle = E_k |k\rangle . \tag{3}$$

The label k stands for the complete set of quantum numbers. The trace is taken in the representation furnished by H_0:

$$Z_N = \sum_k \langle k| e^{-\beta H} |k\rangle . \tag{4}$$

Watson obtains for these diagonal elements the expression [W Eq. (20)]

$$\langle k| e^{-\beta H} |k\rangle = \sum_{\lambda_b} e^{-\beta E_{\lambda b}} |\langle \lambda_b |k\rangle|^2 + e^{-\beta E_k} + \frac{1}{2\pi i}\int_0^\infty \left(\frac{T_k(E-i\eta)}{(E-i\eta-E_k)^2} - \frac{T_k(E+i\eta)}{(E+i\eta-E_k)^2} \right) e^{-\beta E} dE, \tag{5}$$

where the first term on the right is the bound-states contribution, the second term is the free-particle contribution, and the last term is expressed in terms of the diagonal elements T_k of the N-body T matrix. η is a small positive real number. In order to compare with DMB we will focus on the last term, which can be written as

$$Z_N' \equiv \frac{-1}{\pi} \sum_k \int_0^\infty \mathrm{Im} \left(\frac{T_k(E+i\eta)}{(E+i\eta-E_k)^2} \right) e^{-\beta E} dE, \tag{6}$$

where Im implies taking the imaginary part.

The T matrix is defined by

$$T(E+i\eta) = V + VG(E+i\eta)\ V, \tag{7}$$

with G, the resolvent, given by

$$G(E+i\eta) = (E+i\eta-H)^{-1}, \tag{8}$$

$$G_0(E+i\eta) = (E+i\eta-H_0)^{-1}. \tag{9}$$

The wave matrix Ω is introduced by

$$\Omega = GG_0^{-1} = 1 + GV = 1 + G_0 T, \tag{10}$$

$$\Omega^{-1} = 1 - G_0 V, \tag{11}$$

and the scattering matrix S by

$$S(E+i\eta) = \Omega^{-1}(E-i\eta)\ \Omega(E+i\eta) . \tag{12}$$

In DMB it is shown that [see DMB Eqs. (3.32) and (3.33)]

$$\mathrm{Tr} \left(S^{-1} \frac{\partial S}{\partial E} - \frac{\partial S^{-1}}{\partial E} S \right) = -4i\mathrm{Im}\ [\mathrm{Tr}(G_0^2 T)], \tag{13}$$

which follows at once from the above definitions and the cyclic property of the trace. Combining Eq. (6) with Eq. (13) yields

$$Z_N' = \frac{1}{4\pi i}\int_0^\infty \mathrm{Tr} \left(S^{-1} \frac{\partial S}{\partial E} - \frac{\partial S^{-1}}{\partial E} S \right) e^{-\beta E} dE, \tag{14}$$

which combined with Eq. (5) gives DMB Eq. (3.35). [Note that DMB treat the bound states in a latter section and therefore the bound-states contribution does not show up explicitly in their Eq. (3.35).]

The equivalence of Watson's result with that of DMB is clear. The question is whether one form is more useful than the other in performing calculations. In principle, if one "knows" the S matrix, one "knows" the T matrix and conversely, so there is no apparent preference. However, there are some significant differences which are worth pointing out.

In the expression for the virial coefficients there are two limits to be taken: first the volume to infinity and then η to zero. This order is of extreme importance. Strictly speaking one does not have the usual S matrix of scattering theory in Eq. (14) until one carefully investigates these limits. This will have to be done with each individual calculation since it is not proven in general that the limit of the product in Eq. (14) is equal to the product of the limits. Crudely speaking, one must investigate whether

$$\lim_{\eta\to 0^+} \lim_{\Sigma\to\infty} \left(S^{-1} \frac{\partial S}{\partial E} \right) = \left(\lim_{\eta\to 0^+} \lim_{\Sigma\to\infty} S^{-1} \right) \left(\lim_{\eta\to 0^+} \lim_{\Sigma\to\infty} \frac{\partial S}{\partial E} \right), \tag{15}$$

which would be required in order to have S stand for the traditional S matrix. This must be interpreted as being schematic since one knows that the large volume limit does not exist until the "connected" part of Eq. (14) is taken (see DMB Sec. III A). However, this introduces a new difficulty in analyzing the limits since in general the limits of the connected part of the product is not equal to the product of the limits of the connected part of each factor. This has been discussed by Résibois[3] and others.

The reason for emphasizing the need for a careful investigation of the limits is that one of the main results of DMB, namely that only the "on-shell" matrix elements of the S-matrix enter, rests on the implicit assumption that Eq. (15) or the equivalent statement for the connected parts is valid.

One possible advantage of Watson's form is that

an analysis of the two limits may be easier for Eq. (6) than for Eq. (14). Another is that only the diagonal elements of the T matrix enter in Eq. (6) whereas off-diagonal elements of S are required in Eq. (14). However, off-shell matrix elements of T occur in Eq. (6) with only on-shell elements of S appearing in Eq. (14) (with above reservations).

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Classical-Path Calculation of the Impact-Broadening Operator for the Stark Broadening of H_α

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The impact-broadening operator Φ for the hydrogen line H_α is calculated by solving numerically for the S matrices using the straight-line classical-path approximation. All contributing multipoles in the perturber- (free-electron–) atom interaction [$V(t)$] are included; time ordering of the operators in the S matrices is retained. The matrix elements are compared with previous approximations based on the same model; the effects on the H_α line profile are considered.

In a previous paper[1] we numerically calculated the S matrices used to compute the impact-broadening operator $\Phi_{nn'}$ for the Stark broadening of the hydrogen-line Lyman α using the classical-path approximation. All contributing multipoles in the free-electron–atom interaction were included and time ordering of the operators in the S matrices was retained.

In this report we apply the same techniques to the hydrogen line H_α and compare the results with previous calculations using the same approximation. (Details may be found in Ref. 2.) For ease of comparison, the $\Phi_{nn'}$ matrix elements are expressed in the form (note the different sign convention as compared with Ref. 1)

$$\mathrm{Re}\Phi_{nn'} = C[E_1(y_{\min}) - K]\,\mathcal{R}\ , \quad \mathrm{Im}\Phi_{nn'} = C\,\mathcal{S}\ , \qquad (1)$$

where

$$C = \frac{-\lambda_0^2\hbar^2 N^{1/3}(2m/kT)^{1/2}}{2.61e\,\mathrm{cm}^2}$$

and

$$\mathcal{R} = [\vec{r}_n\cdot\vec{r}_n + \vec{r}_{n'}\cdot\vec{r}_{n'} - 2\vec{r}_{n'}\cdot\vec{r}_n]\ ,$$

$$E_1(y_{\min}) = -0.577 - \ln y_{\min} - \sum_{n=1}^{\infty}\frac{(-1)^n y_{\min}^n}{n\,n!}\ ,$$

$$y_{\min} = (4\pi N/3m)(e\hbar n^2/kT)^2\ .$$

With this definition of $\Phi_{nn'}$, the line profile in reduced units $\alpha(\alpha = -\Delta\lambda/F_0)$ is given by (see, for example, Ref. 3)

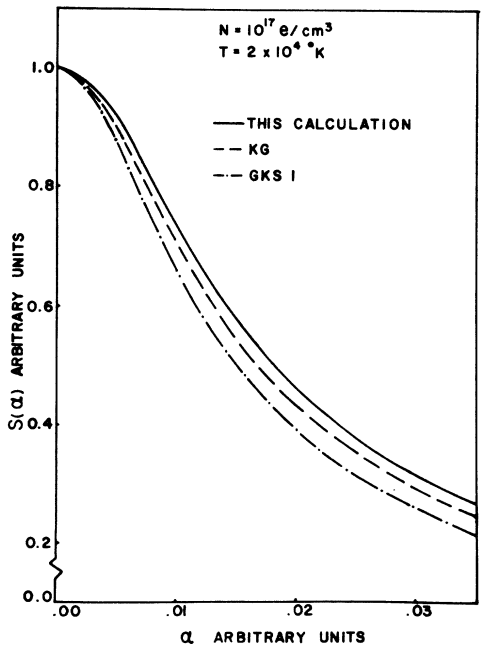

FIG. 1. Comparison of H_α profiles. The SC and BE curves are not shown. The SC curve lies almost exactly on top of the KG curve and the BE(GKSII) curve is slightly narrower than the KG curve.