PHYSICAL REVIEW A VOLUME 26, NUMBER 1 JULY 1982

Dressed-cluster and hydrodynamic expansions for line broadening in simple fluids

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(Received 6 August 1981)

We develop and compare four expansions for line broadening in simple fluids. The dressed-cluster expansions (DCE) express the line broadening in terms of the dynamics of small clusters (absorber and p perturbers, $p=1,2\ldots$) and at the same time incorporate properly the static $p+1$ particle distribution functions of the fluid; i.e., the effects of "initial correlations." The hydrodynamic expansions (HE) are perturbative in the line-broadening interaction and express the broadening in terms of dynamical correlation functions of the fluid. Each expansion involves also a renormalization procedure (partial resummation in the appropriate expansion parameter). We use two types of resummation, in the time and frequency domain, denoted POP (partial time ordering prescription) and COP (chronological time ordering prescription), respectively. All four expansions (DCE-POP, DCE-COP, HE-POP, and HE-COP) when truncated at the qth order yield the correct first q moments of the line shape and allow us to use well-known fluid correlation functions in the calculation of collisionally broadened line shapes.

I. INTRODUCTION

The broadening of absorption spectral lines is one of the most sensitive probes for dynamical interactions in a variety of systems such as low-pressure gases, liquids, and solids.[1-9] The line broadening of a two-level impurity in a fluid (foreign broadening) or of a two-level fluid (self-broadening) are usually treated using simple cluster expansions[6] which at low pressures reduce to the binary collision approximation (BCA).[1-6] In this limit the relevant microscopic information for the line broadening is finally expressed in terms of two-body dynamics (absorber and a single perturber). The BCA was extensively used in the literature not only for low-pressure gases but even for liquids.

The dynamics of fluids is usually treated using the hydrodynamic equations of motion which may be used to evaluate various correlation functions such as the dynamic structure factor $S(k,\omega)$.[10,11] The phenomena of light scattering from fluids (Rayleigh-Brillouin) are usually treated using the hydrodynamic macroscopic equations. There is therefore a difference in the traditional theoretical approaches towards the treatment of the line shapes in line broadening and light-scattering experiments. The reason is that for ordinary line broadening the absorption is a single molecule property and the fluid is just causing the broadening. On the other hand, for light scattering the phenomenon itself is caused by macroscopic density fluctuations in the fluid. This is why the microscopic BCA approach is traditionally used for the former and the macroscopic hydrodynamic approach is used for the latter. In this paper we wish to formulate the absorption line broadening in fluids in a form which will allow us to express the relevant information in terms of well-known correlation functions of the fluid. We shall develop two types of expansions. The DCE still uses the few-body dynamics of small clusters but incorporates the exact *static* density correlation functions of the fluid. The hydrodynamic expansion HE is perturbative in the interaction responsible for the line broadening but allows us to use exact *dynamical correlation functions* of the fluid which may be obtained from hydrodynamics. The role of the static distribution function of the fluid (sometimes referred to as "initial correlations") in line broadening experiments was recently given serious theoretical attention.[12,13] Burnett, Cooper, and coworkers[12] have developed a formalism which is based on the reduced equation of motion for the density matrix aimed at treating specifically these effects. Ben-Reuven[13] had treated strong field phenomena using similar methods. The present approach is based on standard many-body techniques and uses a systematic resummed expansion for the line shape. In addition to the considerable simplicity of the present approach, it has the advantage of expressing the line broadening in terms of standard correlation functions of the fluid. Consequently we get an insight regarding the microscopic information content of the line broadening and we are able to exploit the considerable progress made recently in the hydrodynamic evaluation of these correlation functions[10,11,14] and use them in a convenient way. We also make a simple connection to the macroscopic approach commonly used in light scattering. Finally, the present theory is directly applicable to the problem of ordinary line broadening in liquids near critical points, where we may use the known universal behavior of static and dynamical correlation functions[14] to predict the line broadening. At the moment there is some experimental evidence for a significant increase in the linewidth under these circumstances.[15,16]

In Sec. II we present the basic model Hamiltonian for line broadening in a fluid. In Sec. III we develop the DCE whereas in Sec. IV we develop the HE. Section V presents the analysis of the moments of the line shape and shows that a q-order DCE or HE reproduce exactly the first q moments of the line shape. Section VI gives the limiting case of the Markovian limit for both expansions whereas Sec. VII presents the static limit. Finally in Sec. VIII we give explicit expressions for both expansions to lowest order and discuss previous works.

II. THE MODEL

We consider a fluid with $N+1$ atoms contained in a volume Ω. Each atom has two states $|a\rangle$ and $|b\rangle$. We shall assume that one atom denoted s interacts with an external radiation field whereas the other N atoms are bath perturbers which interact with s and with each other. This model allows us to treat foreign broadening. Self-broadening is a special case when the s atom is identical with the other bath atoms. The two relevant internal states of the fluid are therefore

$$|a\rangle \equiv |a_s\rangle \prod_{\alpha=1}^{N} |a_\alpha\rangle \tag{1a}$$

and

$$|b\rangle \equiv |b_s\rangle \prod_{\alpha=1}^{N} |a_\alpha\rangle \;. \tag{1b}$$

The total Hamiltonian of the system is

$$H = |a\rangle H_a \langle a| + |b\rangle(\omega_{ba} + H_b)\langle b| \;, \tag{2}$$

where

$$H_a = T_s + \sum_\alpha T_\alpha + \sum_\alpha V_a^{s\alpha} + \sum_{\alpha>\gamma} V_a^{\alpha\gamma} \tag{2'}$$

and

$$H_b = T_s + \sum_\alpha T_\alpha + \sum_\alpha V_b^{s\alpha} + \sum_{\alpha>\gamma} V_a^{\alpha\gamma} \;. \tag{2''}$$

Here T_s and T_α are the kinetic energy terms of the s and α particles. $V_a^{s\alpha}(Q_\alpha - Q_s)$ and $V_a^{\alpha\gamma}(Q_\alpha - Q_\gamma)$ are the interaction energies of the s and α, and the α and γ particles, respectively, all in the $|a\rangle$ state, whereas $V_b^{s\alpha}$ is the interaction potential of an s atom in the $|b\rangle$ state with an α atom in the $|a\rangle$ state. Q_i are the Cartesian coordinates of i so that

$$T_i = -\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial Q_i^2} \;, \quad i = s, \alpha \;. \tag{3}$$

ω_{ba} is the energy difference of $|a_s\rangle$ and $|b_s\rangle$. The interaction with the radiation field is via the dipole operator D,

$$D = \sum_\alpha \mu(Q_{s\alpha})(|a\rangle\langle b| + |b\rangle\langle a|) \;. \tag{4}$$

The absorption line shape $I(\Delta)$ is given by[7]

$$\hat{I}(\Delta) = -\frac{1}{\pi}\,\mathrm{Im} I(\Delta) \;, \tag{5}$$

where

$$I(\Delta) = -i \int_0^\infty d\tau \exp(i\Delta\tau) I(\tau) \tag{6}$$

and

$$I(\tau) = \theta(\tau)\langle D(\tau) D(0)\rangle \;. \tag{7}$$

Here Δ is the detuning of the photon frequency ω from the two-level frequency ω_{ba},

$$\Delta = \omega - \omega_{ba} \;, \tag{8a}$$

$$D(\tau) = \exp(iH\tau) D \exp(-iH\tau) \;, \tag{8b}$$

and

$$\langle D(\tau) D(0)\rangle \equiv \mathrm{Tr}[D(\tau) D(0) \rho_a] \;, \tag{8c}$$

$$\rho_a = \frac{1}{Z} |a\rangle \exp(-\beta H_a) \langle a| \;, \tag{8d}$$

$$Z = \mathrm{Tr} \exp(-\beta H_a) \;, \tag{8e}$$

$\beta = (kT)^{-1}$ is the inverse temperature, and $\theta(\tau)$ is the Heaviside step function ($\theta = 1$ for $\tau > 0$, $\theta = 0$ for $\tau < 0$). For the sake of simplicity we shall hereafter take $\mu(Q_{s\alpha}) = 1$, i.e., it will be taken to be independent on Q_s. The inclusion of the Q dependence of μ is straightforward. We then have

$$I(\tau)=\mathrm{Tr}[\exp(iH_a\tau)\exp(-iH_b\tau)\rho_a] \; . \tag{9}$$

The formulations developed in Secs. III and IV for $I(\tau)$ are based on some expansion parameter. For the DCE this is the fluid density (n) and for the HE this is the line-broadening interaction strength (λ). It is always advantageous in the calculation of correlation functions to use some resummation techniques which are based on an ansatz regarding its functional dependence on the expansion parameter. This is done by expressing $I(\tau)$ or $I(\Delta)$ as a function of some quantity and expanding the latter. We shall adopt in this paper two approaches.[17] The POP approach uses the ansatz

$$I(\tau)=\exp[-F(\tau)] \; , \tag{10}$$

whereas the COP approach uses the ansatz

$$I(\Delta)=\frac{1}{\Delta-\widetilde{F}(\Delta)} \; . \tag{11}$$

It is clear that a low-order expansion of either $F(\tau)$ or $\widetilde{F}(\Delta)$ in some parameter will yield an approximation for $I(\Delta)$ which will contain terms to infinite order in that parameter. The POP and COP forms are based on the exact reduced equations of motion which any correlation function obeys[17–20]:

$$\frac{dI(t)}{dt}=-\dot{F}(t)I(t) \tag{12}$$

for the POP and

$$\frac{dI(t)}{dt}=-\int_0^t d\tau\,\widetilde{F}(t-\tau)I(\tau) \tag{13}$$

for the COP, where

$$\widetilde{F}(\Delta)=-i\int_0^\infty d\tau\exp(i\Delta\tau)\widetilde{F}(\tau) \; . \tag{13'}$$

The names COP and POP signify that the diagrammatic expansion of $\widetilde{F}(\Delta)$ involves only time-ordered products of operators, whereas the diagrams of $F(\tau)$ are not completely time ordered.[17,21] We shall thus obtain four different expansions (DCE-POP, DCE-COP, HE-POP, and HE-COP). We should emphasize that $F(\tau)$ and $\widetilde{F}(\tau)$ are obviously not the same and the relation between them is straightforward but not simple.

III. THE DRESSED-CLUSTER EXPANSIONS

The purpose of the DCE is to express the line shape in terms of the dynamics of small clusters of atoms (one perturber, two perturbers, etc.[1–6,22] but at the same time retain exact static information about the fluid, i.e., n-particle static correlation functions. The effects of the initial correlations[12,13] are included in the present expansion in a natural and obvious way. The advantages of such an expansion are clear: It is easier to obtain static information regarding fluids than to calculate the dynamical correlation functions. In the mode-coupling approach to fluid dynamics[14] one uses static information to get dynamics near critical points. The detailed derivation of the DCE is given in the Appendix. We shall present here the final results.

We define $I_p(\tau)$ as the dressed p-perturber spectrum. It is calculated for a system consisting of the absorber atom and p perturbers in a volume Ω. The "dressing" is reflected in the fact that for the distribution function we use the reduced $p+1$ particle distribution function of the fluid[23]

$$\phi_{p+1}(X_s,X_1,X_2\dots X_p)\equiv\mathrm{Tr}_{p+1,\dots,N}\,\rho_a(X_s,X_1,\dots,X_N) \; , \tag{14}$$

where

$$X_\alpha\equiv(Q_\alpha,P_\alpha) \; . \tag{15}$$

Equation (14) is valid both classically where Q_α,P_α are classical coordinates, and quantum mechanically where Q_α,P_α are operators. ϕ_{p+1} should be distinguished from the bare cluster distribution function ϕ_{p+1}^0 defined for a system with an absorber and p perturbers which is commonly used in the ordinary cluster expansions of line broadening[6]:

$$\phi_{p+1}^0(X_s,X_1,\dots,X_p)\equiv\exp[-\beta H_a^{(p+1)}(X_s,X_1,\dots,X_p)]/Z^{(p+1)} \; , \tag{16a}$$

where

$$Z^{(p+1)}\equiv\mathrm{Tr}\exp[-\beta H_a^{(p+1)}(X_s,X_1,\dots,X_p)] \; . \tag{16b}$$

Here the superscript $(p+1)$ denotes that the system contains only $p+1$ particles.

We thus define

$$I_p(\tau)\equiv\mathrm{Tr}[\exp(iH_a^{(p+1)}\tau)\exp(-iH_b^{(p+1)}\tau)\phi_{p+1}] \; . \tag{17}$$

It is easy to see that I_p has the form[6] (see the Appendix)

$$I_p(\tau)=1+\sum_{q=1}^{p}\left[\begin{matrix}p\\q\end{matrix}\right]\frac{1}{\Omega^q}\chi_q(\tau) \; , \tag{18}$$

the qth contribution is of the $\binom{p}{q}$ clusters of q perturbers. We thus have

$$I_1 = 1 + \frac{1}{\Omega}\mathcal{X}_1 ,$$
$$I_2 = 1 + \frac{2}{\Omega}\mathcal{X}_1 + \frac{1}{\Omega^2}\mathcal{X}_2 , \tag{19}$$

etc. Equations (19) may be inverted to yield

$$\mathcal{X}_1 = \Omega(I_1 - 1) ,$$
$$\mathcal{X}_2 = \Omega^2[I_2 - 2I_1 + 1) , \tag{20}$$
$$\mathcal{X}_p = \Omega^p \left[I_p - \binom{p}{1} I_{p-1} + \binom{p}{2} I_{p-2} - \cdots \right] .$$

In the thermodynamic limit we consider N perturbers, where $N \to \infty$, $\Omega \to \infty$, and N/Ω is finite. We then have

$$\binom{N}{q}\frac{1}{\Omega^q} \to \frac{n^q}{q!} , \tag{21}$$

where

$$n \equiv \frac{N}{\Omega} . \tag{22}$$

Upon substitution of Eq. (21) in Eq. (18) we get in the thermodynamic limit:

$$I(\tau) = 1 + \sum_{q=1}^{\infty} \frac{n^q}{q!}\mathcal{X}_q(\tau) . \tag{23}$$

Equation (23) is an important intermediate stage for the DCE expansions and is the starting point for the POP and COP partial resummations.

Using the POP [Eq. (10)] we introduce the ansatz

$$I(\tau) = \exp[-F(\tau)]$$
$$\equiv \exp\left[\sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(\tau) \right] . \tag{24}$$

J_q may be obtained by equating the expansions (23) and (24) term by term, i.e.,

$$\sum_{q=1}^{\infty} \frac{n^q}{q!} J_q(\tau) = \ln\left[1 + \sum_{q=1}^{\infty} \frac{n^q}{q!}\mathcal{X}_q(\tau) \right] . \tag{25}$$

Using (25), J_q will be expressed in terms of $\mathcal{X}_{q'}$, where $q' \le q$, i.e.,

$$J_1(\tau) = \mathcal{X}_1 , \tag{26a}$$

$$J_2(\tau) = \mathcal{X}_2 - \mathcal{X}_1^2 , \tag{26b}$$

$$J_3(\tau) = \mathcal{X}_3 - 3\mathcal{X}_2\mathcal{X}_1 + 2\mathcal{X}_1^3 , \tag{26c}$$

etc. Turning now to the COP scheme (11) we write

$$I(\Delta) = \frac{1}{\Delta - \tilde{F}(\Delta)} \equiv \frac{1}{\Delta + \sum_{q=1}^{\infty} (n^q/q!)\tilde{J}_q(\Delta)} . \tag{27}$$

$\tilde{J}_q(\Delta)$ will now be obtained by comparing Eqs. (23) and (27) and using Eq. (6). We thus have

$$\frac{1}{\Delta}\sum_{k=0}^{\infty}\left[-\sum_{q=1}^{\infty} \frac{n^q}{\Delta q!}\tilde{J}_q(\Delta) \right]^k$$
$$= -i\int_0^{\infty} d\tau \exp(i\Delta\tau)\left[1 + \sum_{q=1}^{\infty} \frac{n^q}{q!}\mathcal{X}_q(\tau) \right] . \tag{28}$$

In Eq. (28) all Δ should be understood $\Delta + i\epsilon$ where $\epsilon \to 0$. This guarantees convergence of all the necessary integrations. Similar to the POP, we see from Eq. (18) that $\tilde{J}_q$ will depend on $\mathcal{X}_{q'}$ where $q' \le q$. We then have

$$\tilde{J}_1(\Delta) = -i\int_0^{\infty} d\tau \exp(i\Delta\tau)\ddot{\mathcal{X}}_1(\tau) , \tag{29a}$$

$$\tilde{J}_2(\Delta) = -i\int_0^{\infty} d\tau \exp(i\Delta\tau)\ddot{\mathcal{X}}_2(\tau) + 2\tilde{J}_1^2(\Delta)/\Delta , \tag{29b}$$

$$\tilde{J}_3(\Delta) = -i\int_0^{\infty} d\tau \exp(i\Delta\tau)\ddot{\mathcal{X}}_3(\tau) + 6\tilde{J}_1(\Delta)\tilde{J}_2(\Delta)/\Delta - 6\tilde{J}_1^3(\Delta)/\Delta^2 , \tag{29c}$$

etc. In concluding this section we note the following:

(1) Equation (24) with (26) is our final result for the DCE-POP expansion, whereas Eq. (27) together with (29) is our final result for the DCE-COP expansion.

(2) J_p and $\tilde{J}_p$ are given in terms of the p-perturbers spectrum I_p. The pth order DCE are obtained by keeping the sums in Eqs. (24) and (27) to pth order. This should be done in practice by calculating the spectrum of our absorber and p perturbers Eq. (17) using the static distribution functions (14). We then get $\mathcal{X}_1 \cdots \mathcal{X}_p$. $J_1 \cdots J_p$ and $\tilde{J}_1 \cdots \tilde{J}_p$ are obtained from $\mathcal{X}_1 \cdots \mathcal{X}_p$ using Eqs. (26) and (29).

(3) As is clear from Eqs. (26) and (29), J_p and $\tilde{J}_p$ are expressed as different combinations of $\mathcal{X}_1 \cdots \mathcal{X}_q$ $q \le p$. The usefulness of the POP and COP expansions will depend on the statistical properties of our system which will determine which expansion will converge more rapidly. The exactly solvable Anderson-Talman[2] model is defined by taking $V_a^{\alpha\gamma} = 0$ in Eqs. (2), i.e., we assume that the bath atoms do not interact with each other

but only interact with the absorber. For this model it is easy to show that $J_q(\tau)$ with $q \geq 2$ vanish identically and we have the *exact* result:

$$I(\tau)^{(AT)} = \exp[nJ_1(\tau)] \ . \tag{30}$$

The COP expansion in this case is much more complicated and includes terms to all powers in density.[3]

IV. THE HYDRODYNAMIC EXPANSIONS

We shall now develop an alternative expansion for $I(\tau)$, this time in terms of *dynamical correlation functions* of the fluid. The latter may then be evaluated using hydrodynamic techniques.[10,11,14] These techniques usually apply for long wavelength phenomena but it was shown in several cases that they may be useful even for microscopic properties.[24] Let us define the perturbation responsible for the line broadening:

$$\lambda U \equiv H_b - H_a = \sum_{\alpha} U^{s\alpha} \ , \tag{31}$$

where

$$U^{s\alpha} = V_b^{s\alpha} - V_a^{s\alpha} \ . \tag{32}$$

We may then write

$$\exp(-iH_b\tau) = \exp(-iH_a\tau) \times \exp_+ \left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1) \right] , \tag{33}$$

where

$$U(\tau) = \exp(iH_a\tau) U \exp(-iH_a\tau) \ , \tag{34}$$

and where

$$\exp_+ \left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1) \right] \equiv 1 - i\lambda \int_0^\tau d\tau_1 U(\tau_1) + (-i\lambda)^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 U(\tau_1) U(\tau_2) + \cdots \ . \tag{35}$$

Upon substituting Eq. (33) in Eq. (9) we get

$$I(\tau) = \left\langle \exp_+ \left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1) \right] \rho_a \right\rangle . \tag{36}$$

For the subsequent manipulations let us introduce the following moments:

$$m_p(\tau_1, \ldots, \tau_p) \equiv \langle U(\tau_1) U(\tau_2) \cdots U(\tau_p) \rangle \equiv \mathrm{Tr}[U(\tau_1) U(\tau_2) \cdots U(\tau_p) \phi_{p+1}(X_s, X_1, \ldots, X_p)] \ . \tag{37}$$

We note that since U is a sum of single perturber terms [Eq. (31)], the product $U(\tau_1) \cdots U(\tau_p)$ may depend on $p+1$ particles at most ($s+p$ perturbers). This is why we may write ϕ_{p+1} instead of ρ_a in the definition of m_p. Alternatively if we introduce the Fourier transform

$$U(Q) = \sum_k \exp(ikQ) U_k \ , \tag{38}$$

we have

$$m_p(\tau_1, \tau_2, \ldots, \tau_p) \quad \sum_{\substack{k_1 k_2 \cdots k_p \\ \alpha_1 \alpha_2 \cdots \alpha_p}} U_{k_1} U_{k_2} \cdots U_{k_p} \langle \exp\{ik_1[Q_s(\tau_1) - Q_{\alpha_1}(\tau_1)]\} \exp\{ik_2[Q_s(\tau_2) - Q_{\alpha_2}(\tau_2)]\} \times \cdots \exp\{ik_p[Q_s(\tau_p) - Q_{\alpha_p}(\tau_p)]\} \rangle \tag{39}$$

or, equivalently,

$$m_p(\tau_1, \tau_2 \ldots, \tau_p) = \sum_{\alpha_1 \cdots \alpha_p} \int \cdots \int dr_1 \cdots dr_p U(r_1) U(r_2) \cdots U(r_p) \times \langle \delta[Q_s(\tau_1) - Q_{\alpha_1}(\tau_1) - r_1] \delta[Q_s(\tau_2) - Q_{\alpha_2}(\tau_2) - r_2] \times \cdots \delta[Q_s(\tau_p) - Q_{\alpha_p}(\tau_p) - r_p] \rangle \ . \tag{40}$$

We note that $m_1 = \langle U \rangle$ is time independent. Without loss of generality, we may include $\langle U \rangle$ in ω_{ba}, i.e., use the transformation

$$\omega_{ba} \rightarrow \omega_{ba} + \langle U \rangle \ , \tag{41a}$$

$$U \rightarrow U - \langle U \rangle \, , \tag{41b}$$

so that

$$m_1 = 0 \, . \tag{41c}$$

Using Eqs. (36), (37), and (41) we get

$$I(\tau) = 1 + (-i\lambda)^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 m_2(\tau_1,\tau_2) + (-i\lambda)^3 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 m_3(\tau_1,\tau_2,\tau_3) + \cdots \, . \tag{42}$$

Equation (42) is the starting point for the POP and COP resummations. Using the POP ansatz

$$I(\tau) = \exp\left[\sum_{q=1}^{\infty} (-i\lambda)^q K_q(\tau)\right] \tag{43}$$

we get, upon comparing (42) and (43) term by term,

$$K_1 = 0 \, , \tag{44a}$$

$$K_2 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 m_2(\tau_1,\tau_2) \, , \tag{44b}$$

$$K_3 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \, m_3(\tau_1,\tau_2,\tau_3) \, , \tag{44c}$$

$$\begin{aligned} K_4 = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 [& m_4(\tau_1,\tau_2,\tau_3,\tau_4) - m_2(\tau_1,\tau_2) m_2(\tau_3,\tau_4) \\ & - m_2(\tau_1,\tau_3) m_2(\tau_2,\tau_4) - m_2(\tau_1,\tau_4) m_2(\tau_2,\tau_3)] \, , \end{aligned} \tag{44d}$$

etc., whereas when using the COP ansatz

$$I(\Delta) = \frac{1}{\Delta + \sum_{q=1}^{\infty} (-i\lambda)^q \widetilde{K}_q(\Delta)} \tag{45}$$

we get

$$\widetilde{K}_q(\Delta) = -i \int_0^\infty d\tau \exp(i\Delta\tau) \widetilde{K}_q(\tau) \, , \tag{46}$$

$$\widetilde{K}_1(\tau) = 0 \, , \tag{47a}$$

$$\widetilde{k}_2(\tau) = m_2(\tau,0) \, , \tag{47b}$$

$$\widetilde{K}_3(\tau) = \int_0^\tau d\tau_1 m_3(\tau,\tau_1,0) \, , \tag{47c}$$

$$\widetilde{K}_4(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 [m_4(\tau,\tau_1,\tau_2,0) - m_2(\tau,\tau_1) m_2(\tau_2,0)] \, , \tag{47d}$$

etc. The various terms in the expansions of K_q and $\widetilde{K}_q$ are given by the closed expressions which may be obtained from the corresponding reduced equations of motion, Eqs. (12) and (13),[17]

$$\sum_{q=1}^{\infty} (-i\lambda)^q K_q(\tau) \equiv \ln\left\{1 + \left\langle \exp_+ \left[-i\lambda \int_0^\tau d\tau_1 U(\tau_1)\right] - 1 \right\rangle\right\} , \tag{48}$$

$$\sum_{q=2}^{\infty} (-i\lambda)^q \widetilde{K}_q(\tau) \equiv (-i\lambda)^2 \left\langle U(\tau) \exp_+ \left[-i\lambda \int_0^\tau d\tau_1 Q U(\tau_1)\right] U(0) \right\rangle , \tag{49}$$

where we introduce a projection operator Q by its action on an arbitrary operator A,

$$QA \equiv A - \mathrm{Tr}(A\rho_a) \, . \tag{50}$$

Equation (43) with (44) is our final result for the HE-POP expansion, whereas Eq. (45) with (46) and (47) is our final result for the HE-COP expansion. In both expansions we are able to express the relevant information for the line broadening in terms of m_p [Eqs. (37), (39), and (40)]. The latter may be expressed as standard correlation functions which appear in fluid dynamics.[10,11,14] Therefore, one may use, e.g., hydrodynamic (small k) approximations for their evaluation.

V. THE MOMENT ANALYSIS

The spectral moments of the line-shape function $\hat{I}(\Delta)$ provide a convenient means for evaluating the accuracy of various approximations and are widely used in comparing experimental and theoretical results.[25,26] In this section we shall analyze the significance of the DCE and the HE using the moments of the line shape. We shall start with the POP expressions. Both expansions (24) and (43) may be written in the form

$$\hat{I}(\Delta)=\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \exp(i\Delta\tau)\exp[-F(\tau)]\ , \tag{51}$$

where

$$-F(\tau)=\sum_{q=1}^{\infty}\frac{n^q}{q!}J_q(\tau) \tag{52a}$$

for the DCE, and

$$-F(\tau)=\sum_{q=1}^{\infty}(-i\lambda)^q K_q(\tau) \tag{52b}$$

for the HE. For the sake of convenience let us use the identity

$$F(\tau)=F(0)+\dot{F}(0)\tau+\int_0^\tau d\tau_1(\tau-\tau_1)\ddot{F}(\tau_1)\ , \tag{53}$$

where $\dot{F}$, $\ddot{F}$, etc., denote time derivatives. Since $F(0)=0$ we have using Eqs. (51) and (53)

$$\hat{I}(\Delta)=\frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \exp(i\Delta\tau)\exp\left[-\int_0^\tau d\tau_1(\tau-\tau_1)F(\tau_1)\right]\ , \tag{54}$$

where we have included $\dot{F}(0)$ in Δ, i.e., we modify it slightly,

$$\Delta\to\Delta-i\dot{F}(0)\ , \tag{55}$$

and where

$$\dot{F}(0)=-\sum_{q=1}^{\infty}\frac{n^q}{q!}\dot{J}_q(0) \tag{56a}$$

for the DCE, or

$$\dot{F}(0)=-\sum_{q=1}^{\infty}(-i\lambda)^q\dot{K}_q(0) \tag{56b}$$

for the HE. Note that $i\dot{F}(0)$ is real so that the transformation (55) is merely a static shift of the line. We now introduce the moments of the line shape:

$$M_k=\int_{-\infty}^{\infty}d\Delta\,\hat{I}(\Delta)\Delta^k\ ,\quad k=0,1,\ldots\ . \tag{57}$$

Using the properties of Fourier transforms we have

$$M_k=(-i)^k\frac{d^k}{d\tau^k}\times\exp\left[-\int_0^\tau d\tau_1(\tau-\tau_1)\ddot{F}(\tau_1)\right]\Bigg|_{\tau=0}\ . \tag{58}$$

Using Eq. (58) we get

$$M_0=\int d\Delta\,\hat{I}(\Delta)=1\ , \tag{59a}$$

$$M_1=\int d\Delta\,\hat{I}(\Delta)\Delta=0 \tag{59b}$$

[the reason for the transformation (54) and (55) was to make $M_1=0$],

$$M_2=\frac{d^2F(0)}{d\tau^2}\ , \tag{59c}$$

$$M_3=i\frac{d^3F(0)}{d\tau^3}\ , \tag{59d}$$

$$M_4=-\frac{d^4F(0)}{d\tau^4}+\frac{1}{2}\frac{d^2F(0)}{d\tau^2}\ . \tag{59e}$$

It is clear that M_p depends only on the first p derivatives of $F(\tau)$ at $\tau=0$. An important property of the functions J_q and K_q is that their first $q-1$ derivatives at $\tau=0$ vanish. For K_q this is obvious from Eqs. (44), since K_q involves q integrations in time. For J_q this is shown in the Appendix. We thus have

$$\frac{dJ_q(0)}{d\tau}=\frac{d^2J_q(0)}{d\tau^2}=\cdots=\frac{d^{q-1}J_q(0)}{d\tau^{q-1}}=0\ , \tag{60a}$$

$$\frac{dK_q(0)}{d\tau}=\frac{d^2K_q(0)}{d\tau^2}=\cdots=\frac{d^{q-1}K_q(0)}{d\tau^{q-1}}=0\ . \tag{60b}$$

Equations (60) guarantee that both expansions (24) and (43) when truncated at the qth order reproduce exactly the first q moments of the line shape. This arises since, by virtue of Eqs. (58) and (60), $J_{q'}$ and $K_{q'}$ with $q'>q$ cannot contribute to the first q moments.

Turning now to the COP expansion we should bear in mind that by construction the q-order COP or POP expansions reproduce $I(\tau)$ exactly up to q order in the expansion parameter. That is both q-

order COP and POP expansions reproduce the DCE expression [Eq. (23)] up to the term $O(n^q)$ and differ only in the subsequent terms $O(n^{q+1})$. Similarly for the HE they both reproduce Eq. (42) up to $O(\lambda^q)$ and differ only by $O(\lambda^{q+1})$. Equations (60) show that terms $O(n^{q+1})$ or $O(\lambda^{q+1})$ do not contribute to the first q moments of the line shape. We have thus obtained the very important result that *all four expansions, DCE-POP [Eq. (24)], DCE-COP [Eq. (27)], HE-POP [Eq. (43)] and HE-COP [Eq. (45)] when truncated at qth order reproduce exactly the first q moments of the line shape.*

We shall now write explicit expressions for the various moments. Using Eq. (59) we have

$$M_0=1\ , \tag{61a}$$

$$M_1=0\ , \tag{61b}$$

and

$$M_p=\langle U^p\rangle,\ \ p\geq 2\ . \tag{61c}$$

[The easiest way to get (61) is to use the HE-POP expansion, but Eqs. (61) hold for all the four expansions.] In order to express Eqs. (61) in terms of well-known functions of the fluid let us introduce the following static correlation functions[23]:

$$n_2(r_1,r_2)=N\langle \delta(r_1-Q_\alpha)\delta(r_2-Q_s)\rangle\ , \tag{62}$$

$$n_{p+1}(r_1,\ldots,r_{p+1})=\frac{N!}{(N-p)!}\langle \delta(r_1-Q_\alpha)\delta(r_2-Q_\beta)\cdots\delta(r_{p+1}-Q_s)\rangle\ ,$$

$$g_{p+1}(r_1,r_2,\ldots,r_p)=\Omega\frac{n_{p+1}(r_1,r_2,\ldots,r_p,0)}{n^p}\ . \tag{63}$$

Note that g_{p+1} are dimensionless.

We now separate each M_p according to the number of different perturbers,

$$\begin{aligned}M_2=\langle U^2\rangle&=\sum_{\alpha\beta}\langle U(Q_s-Q_\alpha)U(Q_s-Q_\beta)\rangle=\sum_{\alpha}\langle U^2(Q_s-Q_\alpha)\rangle+\sum_{\alpha\neq\beta}\langle U(Q_s-Q_\alpha)U(Q_s-Q_\beta)\rangle\\&=N\int dr_1dr_2U^2(r_1-r_2)\langle\delta(Q_s-r_1)\delta(Q_\alpha-r_2)\rangle\\&\quad+N(N-1)\int dr_1dr_2dr_3U(r_1-r_3)U(r_2-r_3)\langle\delta(Q_s-r_3)\delta(Q_\alpha-r_1)\delta(Q_\beta-r_2)\rangle\ .\end{aligned}\tag{64}$$

Making use of the definitions (62) and (63) we have

$$M_2=n\int d\vec{r}\,U^2(\vec{r})g_2(\vec{r})+n^2\int d\vec{r}_1d\vec{r}_2U(\vec{r}_1)U(\vec{r}_2)g_3(\vec{r}_1,\vec{r}_2)\ . \tag{65a}$$

Similarly we have for the higher moments

$$\begin{aligned}M_3=n\int d\vec{r}\,U^3(\vec{r})g_2(\vec{r})&+n^2\int d\vec{r}_1d\vec{r}_2[U^2(\vec{r}_1)U(\vec{r}_2)+U^2(\vec{r}_2)U(\vec{r}_1)]g_3(\vec{r}_1,\vec{r}_2)\\&+n^3\int d\vec{r}_1d\vec{r}_2d\vec{r}_3U(\vec{r}_1)U(\vec{r}_2)U(\vec{r}_3)g_4(\vec{r}_1,\vec{r}_2,\vec{r}_3)\ ,\end{aligned}\tag{65b}$$

$$M_p=n\int U^p(\vec{r})g_2(\vec{r})d\vec{r}+\cdots+n^p\int d\vec{r}_1d\vec{r}_2\cdots d\vec{r}_p[U(\vec{r}_1)U(\vec{r}_2)\cdots U(\vec{r}_p)]g_{p+1}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_p)\ . \tag{65c}$$

In general, M_p will depend on all the q-body static correlation functions g_q with $q\leq p+1$ (p perturbers and the absorber atom).

VI. THE MARKOVIAN LIMIT

The Markovian limit is the important case when all the relevant correlation functions of the perturbers vanish much faster than the observed broadening.[7] In this limit the line shape assumes a simple almost Lorentzian form. We shall derive here the expressions for the line shape in this limit using our four expansions.

A. The POP line shapes

Within the POP formalism the Markovian limit is obtained whenever the typical time scale of $\ddot{F}(\tau)$,

τ_c, is much shorter than the observed broadening Γ, i.e.,

$$\Gamma\tau_c << 1 \ . \tag{66}$$

This implies that the short-time behavior of $\ddot{F}(\tau)$ is irrelevant for our line shape. For times $\tau >> \tau_c$ we then have

$$\begin{aligned}\int_0^\tau d\tau_1(\tau-\tau_1)\ddot{F}(\tau_1)\\ &\simeq \tau\int_0^\infty d\tau_1\ddot{F}(\tau_1)-\int_0^\infty d\tau_1\tau_1\ddot{F}(\tau_1)\\ &\equiv(i\Delta'+\Gamma)\tau+\eta \ .\end{aligned} \tag{67}$$

Here,

$$i\Delta'+\Gamma\equiv\int_0^\infty d\tau\ddot{F}(\tau) \tag{68a}$$

and

$$\eta\equiv\eta'+i\eta''\equiv\int_0^\infty d\tau\tau\ddot{F}(\tau) \ . \tag{68b}$$

We then have

$$\hat{I}(\Delta)=\frac{\exp(-\eta')}{\pi}\left[\frac{\Gamma}{(\Delta-\Delta')^2+\Gamma^2}\cos\eta'' + \frac{\Delta-\Delta'}{(\Delta-\Delta')^2+\Gamma^2}\sin\eta''\right] \ . \tag{69}$$

Typically, η is quite small so that the line shape (69) is basically a Lorentzian with a slight asymmetry caused by the dispersive term (the second term in the brackets).[27] In the extreme case when $|\eta|\to 0$ we have

$$\hat{I}(\Delta)=\frac{1}{\pi}\frac{\Gamma}{(\Delta-\Delta')^2+\Gamma^2} \ . \tag{70}$$

To summarize, in the Markovian limit the line shape is given by the three parameters Γ, Δ', and η'' which are given in terms of $F(\tau)$ [Eqs. (68a) and (68b)], where

$$\ddot{F}(\tau)=-\sum_{q=1}^{\infty}\frac{n^q}{q!}\ddot{J}_q(\tau) \tag{71a}$$

for the DCE, and

$$\ddot{F}(\tau)=-\sum_{q=1}^{\infty}(-i\lambda)^q\ddot{K}_q(\tau) \tag{71b}$$

for the HE.

B. The COP line shapes

Within the COP formulation we obtain the Markovian limit by ignoring the frequency dependence of $\tilde{F}(\Delta)$ in (11), i.e., by set

$$\tilde{F}(\Delta)\cong\tilde{F}(0)=\tilde{\Delta}'-i\tilde{\Gamma} \ . \tag{72}$$

We then have

$$\tilde{I}(\Delta)=\frac{1}{\pi}\frac{\tilde{\Gamma}}{(\Delta-\tilde{\Delta}')^2+\tilde{\Gamma}^2} \ , \tag{73}$$

where

$$-\tilde{\Delta}'+i\tilde{\Gamma}=\sum_{q=1}^{\infty}\frac{n^q}{q!}\tilde{J}_q(0) \tag{74a}$$

for the DCE, and

$$-\tilde{\Delta}'+i\tilde{\Gamma}\equiv\sum_{q=2}^{\infty}(-i\lambda)^q\tilde{K}_q(0) \tag{74b}$$

for the HE.

Upon comparing Eqs. (68) and (71) with (74) we note that to lowest order [$O(n)$ for the DCE and $O(\lambda^2)$ for the HE] then $\Gamma=\tilde{\Gamma}$ and $\Delta'=\tilde{\Delta}'$. In the Markovian limit, therefore, the COP and POP formulations yield the same result for the width and shift of the line. There is, however, still one difference: the η factor which appears in the POP and not in the COP and which is responsible for slight asymmetry of the line, even in the Markovian limit.[6,26,27]

VII. THE STATIC LIMIT

The static limit holds when the motions in the fluid are much slower than the observed line broadening. This is the reverse of the Markovian limit and requires $\Gamma\tau_c < 1$. Formally we get this limit by neglecting the kinetic energy of the Hamiltonian H_a and H_b in Eq. (9). We then have

$$\begin{aligned}I(\tau)&=\langle\exp(i\lambda U\tau)\rho_a\rangle\\ &=\left\langle\prod_{\alpha=1}^{N}[1+f_{s\alpha}(\tau)]\rho_a\right\rangle ,\end{aligned} \tag{75}$$

where

$$f_{s\alpha}(\tau)\equiv\exp(iU^{s\alpha}\tau)-1 \ . \tag{76}$$

Equation (75) may be expanded according to the number of perturbers:

$$\begin{aligned}I(\tau)=1+\sum_{p=1}^{N}\frac{1}{p!}\langle((f_{s1}f_{s2}\cdots f_{sp})\\ \times n_{p+1}(r_1,r_2\cdots r_p,r_s))\rangle \ .\end{aligned} \tag{77}$$

Upon introducing the ansatz

$$I(\tau)=\exp\left[\sum_{p=1}^{\infty}\frac{n^p}{p!}J_p(\tau)\right] \qquad (78)$$

and comparing term by term with (77) we get[23,28]

$$J_p(\tau)=\int dr_1 \cdots dr_p f_{s1}\cdots f_{sp}\mathscr{F}_p(r_1\cdots r_p,r_s)\ , \qquad (79)$$

where $\mathscr{F}_p$ are the Ursell distribution functions[23]

$$\mathscr{F}_1=n_1(r_1)\ , \qquad (80a)$$

$$\mathscr{F}_2=n_2(r_1,r_2)-n_1(r_1)n_1(r_2)\ , \qquad (80b)$$

and

$$\mathscr{F}_k=n_k-\sum_{t=1}^{k-1}\begin{bmatrix}k-1\\ t\end{bmatrix}n_t(r_1\cdots r_t)\mathscr{F}_{k-t}(r_{t+1}\cdots r_k)\ . \qquad (80c)$$

VIII. EXPLICIT EXPRESSIONS FOR THE DCE AND HE TO LOWEST ORDER

We shall now evaluate the lowest-order approximation for the line shape using the four expansions developed in the previous sections. Starting with the DCE to lowest-order COP or POP we need only $\chi_1(\tau)$. The DCE-POP line shape becomes

$$I^{(\mathrm{POP})}(\Delta)=-i\int_0^{\infty}d\tau\exp[i\Delta\tau+n\chi_1(\tau)]\ , \qquad (81a)$$

whereas the DCE-COP line shape assumes the form

$$I(\Delta)^{(\mathrm{COP})}=\frac{1}{\Delta-in\int_0^{\infty}d\tau\exp(i\Delta\tau)\ddot{\chi}_1(\tau)}\ , \qquad (81b)$$

where

$$\chi_1(\tau)=\Omega\,\mathrm{Tr}[\exp(iH_a^{(2)}\tau)\exp(-iH_b^{(2)}\tau)\phi_2-1]\ . \qquad (82)$$

Here $H_a^{(2)}$ and $H_b^{(2)}$ include one perturber and the system atom. Denoting the eigenstates of H_a and H_b by $|\alpha\rangle$ and $|\beta\rangle$, respectively (not to be confused with the notation of Sec. II where Greek letters denoted the various perturbers) we have

$$\chi_1(\tau)=\Omega\sum_{\alpha\beta}\langle\alpha|\beta\rangle\langle\beta|\alpha'\rangle(\phi_2)_{\alpha'\alpha}\times[\exp(i\omega_{\alpha\beta}\tau)-1]\ . \qquad (83)$$

To lowest order in density (ordinary cluster expansion)[6]

$$(\phi_2)_{\alpha\alpha'}\rightarrow(\phi_2^0)_{\alpha\alpha'}=P(\alpha)\delta_{\alpha\alpha'} \qquad (84)$$

and we get[6]

$$\chi_1(\tau)=\Omega\sum_{\alpha\beta}P(\alpha)|\langle\alpha|\beta\rangle|^2[\exp(i\omega_{\alpha\beta}\tau)-1]\ . \qquad (85)$$

If we wish to evaluate (82) using classical mechanics we first rewrite it as

$$\chi_1(\tau)=\Omega\left[\mathrm{Tr}\exp_+\left[-i\int_0^{\tau}d\tau_1U(\tau_1)\right]\phi_2-1\right]\ . \qquad (86)$$

Classically we set

$$U(\tau)=U(Q(\tau)\,|\,Q_0,P_0)\ , \qquad (87)$$

which is obtained by solving Hamilton's equations using H_a and where Q_0 and P_0 are the initial values of the relative coordinates and momenta of the perturber and absorber. Also,

$$\mathrm{Tr}\rightarrow\int dQ_0dP_0\ . \qquad (88)$$

We then have

$$\chi_1(\tau)=n\int dQ_0dP_0\left[\exp\left[-i\int_0^{\tau}d\tau_1U^{s1}(\tau_1)\right]-1\right]g_2(Q_0)\Gamma(P_0)\ , \qquad (89)$$

where $\Gamma(p_0)$ is the Maxwell distribution of momenta:

$$\Gamma(P_0)=4\pi^{-1/2}(2mkT)^{-3/2}\exp(-P_0^2/2mkT)\ . \qquad (90)$$

In the static limit we have

$$\chi_1^{\mathrm{stat}}(\tau)=n\int dQ\{\exp[iU\tau]-1\}g_2(Q)\ . \qquad (91)$$

In the Markovian limit the line shape is given by Eq. (69) where the parameters are given by

$$\Delta+i\Gamma=n\int_0^{\infty}d\tau\,\ddot{\chi}_1(\tau)\ , \qquad (92a)$$

$$\eta''=n\int_0^{\infty}d\tau\,\tau\chi_1(\tau)\ , \qquad (92b)$$

where quantum mechanically

$$\ddot{\chi}_1(\tau)=\sum_{\substack{\alpha\beta\\ \alpha'}} \langle \alpha \mid \beta \rangle \langle \beta \mid \alpha' \rangle (\phi_2)_{\alpha'\alpha} \omega_{\alpha\beta}^2 \exp(i\omega_{\alpha\beta}\tau) , \tag{93a}$$

or classically

$$\ddot{\chi}_1(\tau)=-n \int dQ_0 dP_0 [(U^{sl}(\tau))^2+i\dot{U}^{s1}(\tau)] \exp \left[-i \int_0^\tau d\tau_1 U^{s1}(\tau_1) \right] g_2(Q_0)\Gamma(P_0) . \tag{93b}$$

We note again that the only difference between the POP and COP Markovian perturbative results is the presence of η in the former. For the COP $\eta=0$ and Δ and Γ are the same as for the POP. Equations (81) were recently analyzed and compared for simple model systems, both quantum mechanically (using Eq. 85) and classically (using Eq. 86).[29]

We shall now turn to the HE. To second order in λ (and setting $\lambda=1$), the HE-POP line shape is

$$I^{(\mathrm{POP})}(\Delta)=-i \int_0^\infty d\tau \exp(i\Delta\tau) \exp \left[-\int_0^\tau d\tau_1 (\tau-\tau_1) \langle U(\tau_1) U(0) \rangle \right] , \tag{94a}$$

whereas the DCE-COP line is

$$I(\Delta)^{(\mathrm{COP})}=\frac{1}{\Delta+i \int_0^\infty d\tau \exp(i\Delta\tau) \langle U(\tau) U(0) \rangle} , \tag{94b}$$

where

$$\begin{aligned}\langle U(\tau) U(0) \rangle = m_2(\tau,0) = n\Omega \sum_{kk'} U_k U_{k'} \langle \exp[ikQ_\alpha(\tau)] \exp[-ikQ_s(\tau)] \exp(ik'Q_\alpha) \exp(-ik'Q_s) \rangle \\ + n^2\Omega^2 \sum_{kk'} U_k U_{k'} \langle \exp[ikQ_\alpha(\tau)] \exp[-ikQ_s(\tau)] \exp(ik'Q_\beta) \exp(-ik'Q_s) \rangle .\end{aligned} \tag{95}$$

We thus see that $\langle U(\tau)U(0) \rangle$ includes two- and three-particle correlation functions. There is one limit in which $\langle U(\tau)U(0) \rangle$ may be further simplified. This is the *Brownian particle limit* in which s is much heavier than α so that we may ignore the time evolution of Q_s in (95) and set $Q_s(\tau)=Q_s(0)$. In this case we have

$$\langle U(\tau) U(0) \rangle = \sum_{\alpha,\beta} \sum_{kk'} U_k U_{k'} \langle \exp[ikQ_\alpha(\tau)] \exp(ik'Q_\beta) \rangle . \tag{96}$$

Using the definition of the dynamic structure factor[10,11]

$$\frac{1}{2\pi} \int_{-\infty}^\infty d\tau \exp(-i\omega\tau) \sum_{\alpha,\beta} \exp[ikQ_\alpha(\tau)] \exp(-ik'Q_\beta) \rangle \equiv S(k,\omega) \delta_{k,k'} \tag{97}$$

we have

$$\langle U(\tau) U(0) \rangle = \int_{-\infty}^\infty d\omega \sum_k \mid U_k \mid^2 S(k,\omega) \exp(i\omega\tau) . \tag{98}$$

Equation (98) when substituted in Eqs. (94) results in our lowest-order HE approximations for the line shape. The relevant information which enters Eq. (98) is the interaction potential U_k, and $S(k,\omega)$ which is well known from other experiments (neutron scattering, light scattering, etc.[10,11,14]).

In the Markovian limit the line shape assumes the form (69), where

$$\begin{aligned}\Gamma+i\Delta' &\equiv \int_0^\infty d\tau \langle U(\tau) U(0) \rangle \\ &= \int_0^\infty d\tau \int_{-\infty}^\infty d\omega \sum_k \mid U_k \mid^2 S(k,\omega) \exp(i\omega\tau) = i \int_{-\infty}^\infty d\omega \sum_k \mid U_k \mid^2 S(k,\omega) \frac{1}{\omega+i\epsilon}\end{aligned} \tag{99}$$

so that

$$\Gamma = \pi \lim_{\omega\to 0} \sum_k \mid U_k \mid^2 S(k,\omega) , \tag{100a}$$

and

$$\Delta' = PP \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{S(k,\omega)}{\omega} \,. \tag{100b}$$

Also,

$$\eta' + i\eta'' = \int_0^{\infty} d\tau \tau \langle U(\tau)U(0)\rangle = i\int_0^{\infty} d\tau \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{\partial S(k,\omega)}{\partial\omega} \exp(i\omega\tau)$$

$$= -\int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{\partial S(k,\omega)}{\partial\omega} \frac{1}{\omega + i\epsilon} \,, \tag{101}$$

so that

$$\eta' = PP \int_{-\infty}^{\infty} d\omega \sum_k |U_k|^2 \frac{\partial S(k,\omega)}{\partial\omega} \frac{1}{\omega} \,, \tag{102a}$$

and

$$\eta'' = \pi \lim_{\omega\to 0} \sum_k |U_k|^2 \frac{\partial S(k,\omega)}{\partial\omega} \,. \tag{102b}$$

As already noted in Sec. VI, the only difference between the POP and COP in this limit is that $\eta' = \eta'' = 0$ for the latter. Γ and Δ' are the same. Equation (100a) was recently derived by Madden and Hills[16] who treated line broadening in liquids near the critical point. Our present result is a generalization of their result. In concluding this section we note the following:

(1) Equation (98) when substituted in Eqs. (94) gives us two expressions for the line shapes which are not limited to the Markovian limit.

(2) The POP expression predicts a certain asymmetry of the line even in the Markovian limit [Eq. (69)]. This asymmetry was found experimentally in dilute gases.[27] We have derived here Eqs. (102) which give that asymmetry (due to η'') in terms of $S(k,\omega)$.

(3) The formulation of Sec. IV may be used to derive higher-order corrections to Eqs. (81) and (94) which will involve higher-order density correlations of the fluid.

(4) The simple result (98) is limited to the Brownian limit (heavy absorber and light perturbers). Therefore it cannot be used as it stands to treat self-broadening. Consequently, the analysis of Madden and Hills[16] who used Eq. (98) to treat the self-broadening of O_2 and N_2 near critical points if fraught with some difficulties and the more elaborate correlation function (95) should be used instead of (96).

(5) Equation (98) provides a simple connection between light-scattering and line-broadening experiments. In the former, one directly probes $S(k,\omega)$ since the density fluctuations are responsible for the light scattering. Here we get that in the limit of weak coupling (second-order HE) then the line broadening of a *heavy two-level impurity* in a fluid is basically monitoring the same function $S(k,\omega)$. We should note that for the sake of clarity in the presentation, space degeneracy was not introduced explicitly in this paper. It may be easily included at the final equations by considering $|a\rangle$ and $|b\rangle$ to be manifolds of degenerate levels and adding appropriate summations over these levels. When this is done different tensorial components of $S(k,\omega)$ may contribute to the line-broadening and light-scattering spectra. In the Markovian limit the line is not sensitive to the details of $S(k,\omega)$ as only the $\omega = 0$ component contributes to Γ and η''in Eqs. (100) and (102).

ACKNOWLEDGMENTS

I wish to thank A. Baram, A. Ben-Reuven, D. Grimbert, and J. Jortner for useful discussions. The support of the Israeli Academy of Sciences and the Alfred P. Sloan Foundation is gratefully acknowledged.

APPENDIX: THE DRESSED-CLUSTER EXPANSION

We shall now expand our line-shape function [Eq. (9)] in dressed clusters. To that end we shall first partition the Hamiltonian (2) as follows:

$$H_a \equiv H_0 + \tilde{V} \,, \tag{A1a}$$

$$H_b \equiv H_0 + V \,, \tag{A1b}$$

where

$$H_0 \equiv T_s + \sum_\alpha T_\alpha \,, \tag{A2}$$

$$\tilde{V} \equiv \sum_\alpha V_a^{s\alpha} + \sum_{\alpha > \gamma} V_a^{\alpha\gamma} \,, \tag{A3a}$$

and

$$\widetilde{V} \equiv \sum_{\alpha} V_b^s + \sum_{\alpha > \gamma} V_a^{\alpha\gamma} . \tag{A3b}$$

Let us introduce the positive and negative time-ordered exponentials as follows:

$$\exp(-iH_b\tau) = \exp(-iH_0\tau) \times \exp_+ \left[-i \int_0^\tau d\tau_1 V(\tau_1) \right] , \tag{A4a}$$

$$\exp(iH_a\tau) = \exp_- \left[i \int_0^\tau d\tau_1 \widetilde{V}(\tau_1) \right] \exp(iH_0\tau) , \tag{A4b}$$

where

$$A(\tau) \equiv \exp(iH_0\tau) A \exp(-iH_0\tau), \quad A = V, \widetilde{V} \tag{A5}$$

$$\exp_+ \left[-i \int_0^\tau d\tau_1 V(\tau_1) \right] \equiv 1 - i \int_0^\tau d\tau_1 V(\tau_1) + (-i)^2 \times \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 V(\tau_1) V(\tau_2) + \cdots , \tag{A6a}$$

$$\exp_- \left[i \int_0^\tau d\tau_1 \widetilde{V}(\tau_1) \right] \equiv 1 + i \int_0^\tau d\tau_1 V(\tau_1) + i^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 V(\tau_2) V(\tau_1) + \cdots . \tag{A6b}$$

To simplify our further manipulations let us define the time-ordering operators T_+ and $\widetilde{T}_-$ as follows: T_+ ($\widetilde{T}_-$) when operating on a product of V's ($\widetilde{V}$) at different times orders them in order of decreasing (increasing) times from left to right,

$$T_+ V(\tau_1') V(\tau_2') \cdots V(\tau_k') = V(\tau_1) V(\tau_2) \cdots V(\tau_k) , \tag{A7a}$$

$$\widetilde{T}_- \widetilde{V}(\tau_1') \widetilde{V}(\tau_2') \cdots \widetilde{V}(\tau_k') = \widetilde{V}(\tau_k) \widetilde{V}(\tau_{k-1}) \cdots \widetilde{V}(\tau_1) , \quad \tau_1 > \tau_2 \cdots > \tau_k . \tag{A7b}$$

$\tau_1 \cdots \tau_k$ is a permutation of $\tau_1' \cdots \tau_k'$. We thus have

$$\exp(iH_a\tau)\exp(-iH_b\tau) \equiv T_+ \widetilde{T}_- \exp \left[i \int_0^\tau d\tau_1 \widetilde{V}(\tau_1) \right] \times \exp \left[-i \int_0^\tau d\tau_1 V(\tau_1) \right] . \tag{A8}$$

To proceed further we shall now introduce the functions:

$$f_{jk}(\tau) \equiv \exp \left[i \int_0^\tau d\tau_1 \widetilde{V}^{jk}(\tau_1) \right] \times \exp \left[-i \int_0^\tau d\tau_1 V^{jk}(\tau_1) \right] - 1 , \tag{A10}$$

where j and k run over the absorber as well as the perturbers $j,k = s, 1 \cdots N$. In addition let us introduce a third ordering operator T^*. When T^* operates on a product of V and $\widetilde{V}$ terms rearranges them such that all $\widetilde{V}$ are to the left and all V to the right. We can now define:

$$\hat{T} \equiv \widetilde{T}_- T_+ T^* \tag{A9}$$

so that

$$\exp(iH_a\tau)\exp(-iH_b\tau) = \hat{T} \prod_{j,k=1}^{N+1} [1 + f_{jk}(\tau)] . \tag{A11}$$

Using these definitions we may rewrite Eq. (17) in the form

$$I_p(\tau) = \mathrm{Tr} \left[\hat{T} \prod_{j,k=1}^{p+1} [1 + f_{jk}(\tau)] \rho_a \right] . \tag{A12}$$

Equation (A12) is our starting point for the cluster expansion. To proceed further we shall consider the series of p perturber spectra I_p,

$$I_0 = 1 , \tag{A13a}$$

$$I_1 = I + \langle f_{s1} \phi_2(X_s, X_1) \rangle \equiv 1 + \frac{1}{\Omega} \chi_1 , \tag{A13b}$$

$$\begin{aligned} I_2 = 1 &+ [\langle f_{s1}\phi_2(X_s,X_1)\rangle + \langle f_{s2}\phi_2(X_s,X_2)\rangle] \\ &+ [\langle f_{s1} f_{s2} \phi_3(X_s,X_1,X_2)\rangle + \langle f_{s1} f_{12} \phi_3(X_s,X_1,X_2)\rangle + \langle f_{s2} f_{12} \phi_3(X_s,X_1,X_2)\rangle + \langle f_{s1} f_{s2} f_{12} \phi_3(X_s,X_1,X_2)\rangle] \\ &\equiv 1 + \frac{2}{\Omega}\chi_1 + \frac{1}{\Omega^2}\chi_2 . \end{aligned} \tag{A13c}$$

Here Ω is the volume and $\phi_{p+1}(X_s, X_1, \ldots, X_p)$ is is the reduced $P+1$ particle distribution function [Eq. (14)],

$$\langle f_{ij} f_{kl} \cdots \phi_{P+1}))\rangle \equiv \hat{T}\,\mathrm{Tr}_{s,1\cdots P}(f_{ij} f_{kl} \cdots \phi_{P+1}) . \qquad \text{(A14)}$$

In Eq. (14) each term containing k different atoms requires them to be close and is thus $O(1/\Omega^k)$. It is easy to see that the general term I_p will be given by

$$I_p = 1 + \sum_{k=1}^{p} \frac{1}{\Omega^k} \left[\begin{matrix} p \\ k \end{matrix}\right] \chi_k . \qquad \text{(A15)}$$

Equation (18) is identical with (A15).

Since each χ_k involves a product of at least k factors f and since $f(0)=0$ it is clear the the first k derivatives of χ_k at $\tau=0$ vanish. This property is used in the moment expansion (Sec. V).

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