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# Dynamical theory of binary ionic mixtures

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Following the Golden-Kalman one-component-plasma nonlinear response-function approach, the authors formulate an approximation scheme for the calculation of dynamical ionic polarizabilities in binary-mixture plasmas. Preliminary collective-mode calculations are presented in the weak- and very-strong-coupling regimes.

## I. INTRODUCTION

Using a nonlinear response-function approach, we formulate a promising new dynamical theory of binary-ionic-mixture plasmas. Preliminary calculations indicate that the theory will provide a reliable description of the longitudinal collective modes over a range of coupling strengths [characterized by the plasma parameter $\Gamma=\beta e^2/a$, $a=(3/4\pi n)^{1/3}$, $n=\Sigma_\sigma(N_\sigma/V)$] spanning the entire fluid regime. At long wavelengths [$kv_\sigma \ll |\omega|$, $v_\sigma=\sqrt{(1/\beta m\sigma)}$], these calculations reproduce the qualitative features of the molecular dynamics data for the dispersion of the optical mode in the strong-coupling ($\Gamma \gg 1$) regime,[1] while at the same time reproducing the $k=0$ weak-coupling ($\Gamma \ll 1$) collective-mode features inferred from a recent microscopic theory.[2] As far as we know, this is the first time a dynamical theory has succeeded in securing the correct collective-mode properties of binary ionic mixtures in these two extreme coupling regimes.

Our approximation scheme is a generalization of the earlier Golden-Kalman (GK) one-component-plasma (ocp) scheme.[3] The principal building blocks to its construction are (i) the first Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) kinetic equations linking nonequilibrium one- and two-particle distribution functions [labeled $F(1)$ and $G(12)$] and (ii) dynamical nonlinear fluctuation-dissipation theorems (NLFDT's)[4] linking three-point structure and quadratic response functions. The central hypothesis of the theory, the VAA (velocity-average approximation)[3,5,6] supposes that the non-random-phase-approximation part of $G(12)$ can be replaced by a suitably chosen velocity average.

The development of the theory is carried out in three stages which we summarize in Sec. II. Detailed derivations will be displayed in a more complete follow-up regular article.[7]

## II. APPROXIMATION SCHEME

Consider a mixture of $N_A$ and $N_B$ classical point ions in a uniform neutralizing background of rigid degenerate electrons; the entire system occupies the large but bounded volume $V$. Let $m_\sigma$ and $e_\sigma$ ($\sigma=A,B$) denote the mass and electrical charge; $n_\sigma=N_\sigma/V$ is the unperturbed density, $\kappa_\sigma=(4\pi\beta e_\sigma^2 n_\sigma)^{1/2}$ is the Debye wave number, $\Omega_\sigma=(4\pi n_\sigma e_\sigma^2/m_\sigma)^{1/2}$ is the plasma frequency, and $\kappa^2=\Sigma_\sigma\kappa_\sigma^2$, $\Omega^2=\Sigma_\sigma\Omega_\sigma^2$. Relevant two- and three-point structure functions $S_{\sigma\sigma'}(\mathbf{k}t)$ and $S_{\sigma\sigma'\sigma''}(\mathbf{q}t;\,\mathbf{k}-\mathbf{q}t)$ are defined in Ref. 4, while linear and quadratic polarizabilities are defined through the constitutive relation

$$\langle\phi_{\sigma,\mathbf{k}}\rangle^{(2)}(\omega)=-\alpha_\sigma(\mathbf{k}\omega)\Phi^{(2)}(\mathbf{k}\omega)+\frac{1}{V}\sum_{\mathbf{q}}\frac{iq|\mathbf{k}-\mathbf{q}|}{k}\int_{-\infty}^{\infty}\frac{d\mu}{2\pi}\alpha_\sigma(\mathbf{q}\mu;\mathbf{k}-\mathbf{q}\,\omega-\mu)\Phi^{(1)}(\mathbf{q}\mu)\Phi^{(1)}(\mathbf{k}-\mathbf{q}\,\omega-\mu)\quad(\sigma=A,B)\tag{1}$$

connecting the second-order response $\langle\phi_\sigma\rangle^{(2)}$ of type $\sigma$ ions to the total potential perturbation $\Phi=\phi^{\text{ext}}+\Sigma_\sigma\langle\phi_\sigma\rangle$; $\Phi^{(1)}(\mathbf{q}\mu)=\phi^{\text{ext}}(\mathbf{q}\mu)/\epsilon(\mathbf{q}\mu)$, $\epsilon(\mathbf{q}\mu)=1+\Sigma_\sigma\alpha_\sigma(\mathbf{q}\mu)$.

In the first stage, we introduce the VAA hypothesis into linearized first BBGKY equations in order to convert the velocity-dependent $G(12)$'s into velocity-independent nonequilibrium two-point density correlation functions. The latter are then expressed in terms of equilibrium three-point structure functions via routine statistical mechanical linear response calculations [see, e.g., Ref. 3, Appendix A]. These operations lead to the polarizability expression

$$\frac{\alpha_\sigma(\mathbf{k}\omega)}{\epsilon(\mathbf{k}\omega)}=\frac{\alpha_{\sigma0}(\mathbf{k}\omega)}{\epsilon_0(\mathbf{k}\omega)}[1-v_{\sigma\sigma}(\mathbf{k}\omega)]-\frac{\alpha_{\sigma0}(\mathbf{k}\omega)\alpha_{\eta0}(\mathbf{k}\omega)}{\epsilon_0(\mathbf{k}\omega)[1+\epsilon_0(\mathbf{k}\omega)]}[v_{\sigma\sigma}(\mathbf{k}\omega)-v_{\eta\eta}(\mathbf{k}\omega)]$$
$$-\frac{1+\alpha_{\eta0}(\mathbf{k}\omega)}{\epsilon_0(\mathbf{k}\omega)[1+\epsilon_0(\mathbf{k}\omega)]}[\alpha_{\eta0}(\mathbf{k}\omega)v_{\sigma\eta}(\mathbf{k}\omega)+\alpha_{\sigma0}(\mathbf{k}\omega)v_{\eta\sigma}(\mathbf{k}\omega)]\quad(\sigma,\eta=A,B:\eta\neq\sigma)\ ,\tag{2a}$$

where $\alpha_{\sigma0}(\mathbf{k}\omega)\equiv\alpha_\sigma(\mathbf{k}\omega)|_{\Gamma=0}$ is the random-phase-approximation (RPA) polarizability and

$$v_{\sigma\sigma'}(\mathbf{k}\omega)\equiv\frac{4\pi\beta}{k^2}\sum_{\sigma''}e_{\sigma'}e_{\sigma''}(n_\sigma n_{\sigma'}n_{\sigma''})^{1/3}\frac{1}{N_{\sigma'}}\sum_{\mathbf{q}}\frac{\mathbf{k}\cdot\mathbf{q}}{q^2}\left\{i\omega\int_0^\infty dt\,e^{i\omega t}S_{\sigma\sigma'\sigma''}(\mathbf{k}-\mathbf{q}t;\mathbf{q}t)+S_{\sigma\sigma'\sigma''}(\mathbf{k}-\mathbf{q}t=0;\mathbf{q}t=0)\right\}\tag{2b}$$
$$(\sigma,\sigma'=A,B)$$

is a $\Gamma$- dependent dynamical coupling correction. Equations (2) are valid for arbitrary $k$ values and over the entire frequency domain. At high frequencies $\omega \gg \Omega_\sigma$, one can rigorously demonstrate[3] that the three-point functions in (2b) collapse into two-point functions, whence

$$\mathrm{Re}\frac{\alpha_\sigma(\mathbf{k}\omega\to\infty)}{\epsilon(\mathbf{k}\omega\to\infty)}=\frac{\Omega_\sigma^2}{\omega^2}-\frac{\Omega_\sigma^{(4)}(\mathbf{k})}{\omega^4}-\cdots \tag{3a}$$

with

$$\Omega_\sigma^{(4)}(\mathbf{k})=\Omega_\sigma^2\Omega^2+\Omega_\sigma^4\{3(k/\kappa_\sigma)^2+\sum_{\sigma'}(e_{\sigma'}N_{\sigma'}/e_\sigma N_\sigma)\frac{1}{V}\sum_{\mathbf{q}}\chi^2[(e_{\sigma'}m_\sigma/e_\sigma m_{\sigma'})g_{\sigma\sigma'}(\mathbf{k}-\mathbf{q})-g_{\sigma\sigma'}(\mathbf{q})]\}\ ; \tag{3b}$$

$$g_{\sigma\sigma'}(\mathbf{q})=(n_\sigma n_{\sigma'})^{-1/2}\{S_{\sigma\sigma'}(\mathbf{q}t=0)-\delta_{\sigma\sigma'}\} \tag{4}$$

is the static pair correlation function and $\chi=\mathbf{k}\cdot\mathbf{q}/(kq)$. The VAA expression (3) is identical to the exact high-frequency sum-rule expansion through $O(1/\omega^4)$.

In the second stage, the three-point structure functions are traded for quadratic response functions by application of the ionic NLFDT's.[4] After some algebra, we obtain

$$v_{\sigma\sigma}(\mathbf{k}\omega)=-\frac{1+\alpha_\eta(\mathbf{k}\omega)}{\epsilon(\mathbf{k}\omega)}[u_\sigma(\mathbf{k}\omega)+w_\sigma(\mathbf{k}\omega)]-\frac{e_\eta N_\eta}{e_\sigma N_\sigma}\frac{\alpha_\sigma(\mathbf{k}\omega)}{\epsilon(\mathbf{k}\omega)}w_\eta(\mathbf{k}\omega)\ , \tag{5a}$$

$$v_{\eta\sigma}(\mathbf{k}\omega)=\frac{\alpha_\eta(\mathbf{k}\omega)}{\epsilon(\mathbf{k}\omega)}[u_\sigma(\mathbf{k}\omega)+w_\sigma(\mathbf{k}\omega)]+\frac{e_\eta N_\eta}{e_\sigma N_\sigma}\frac{1+\alpha_\sigma(\mathbf{k}\omega)}{\epsilon(\mathbf{k}\omega)}w_\eta(\mathbf{k}\omega)\quad(\sigma,\eta=A,B:\eta\neq\sigma)\ , \tag{5b}$$

where the dynamical coupling coefficients

$$u_\sigma(\mathbf{k}\omega)=\frac{i\kappa_\sigma^2}{k^2}\frac{1}{N_\sigma}\sum_{\mathbf{q}}\frac{\mathbf{k}\cdot\mathbf{q}}{q^2}\int_{-\infty}^{\infty}d\mu\,\delta_-(\mu)\left(\frac{a_\sigma(\mathbf{q}\mu;\mathbf{k}-\mathbf{q}\omega-\mu)}{\epsilon(\mathbf{q}\mu)\epsilon(\mathbf{k}-\mathbf{q}\omega-\mu)}+\frac{a_\sigma(\mathbf{q}\omega-\mu;\mathbf{k}-\mathbf{q}\mu)}{\epsilon(\mathbf{q}\omega-\mu)\epsilon(\mathbf{k}-\mathbf{q}\mu)}\right)\ , \tag{5c}$$

$$w_\sigma(\mathbf{k}\omega)=\frac{i\kappa_\sigma^2}{k^2}\frac{1}{N_\sigma}\sum_{\mathbf{q}}\frac{\mathbf{k}\cdot\mathbf{q}}{q^2}\int_{-\infty}^{\infty}d\mu\,\delta_-(\mu)\left(\frac{\alpha_\eta(\mathbf{k}-\mathbf{q}\omega-\mu)a_\sigma(\mathbf{q}\mu;\mathbf{k}-\mathbf{q}\omega-\mu)}{\epsilon(\mathbf{q}\mu)\epsilon(\mathbf{k}-\mathbf{q}\omega-\mu)}+\frac{\alpha_\eta(\mathbf{k}-\mathbf{q}\mu)a_\sigma(\mathbf{q}\omega-\mu;\mathbf{k}-\mathbf{q}\mu)}{\epsilon(\mathbf{q}\omega-\mu)\epsilon(\mathbf{k}-\mathbf{q}\mu)}\right) \tag{5d}$$

$$(\sigma,\eta=A,B:\eta\neq\sigma)$$

are structured by relative quadratic polarizabilities[3,6] $a_\sigma(\mathbf{q}\mu;\mathbf{p}\nu)=-qp|\mathbf{q}+\mathbf{p}|\alpha_\sigma(\mathbf{q}\mu;\mathbf{p}\nu)/(2\pi\beta^2e_\sigma^3n_\sigma)$. Equations (5a) and (5b), when substituted into (2a) lead to the VAA expression

$$\epsilon(\mathbf{k}\omega)=1+\sum_\sigma\alpha_{\sigma 0}(\mathbf{k}\omega)[1+u_\sigma(\mathbf{k}\omega)+w_\sigma(\mathbf{k}\omega)]-\sum_\sigma\frac{e_\sigma N_\sigma}{e_\eta N_\eta}\alpha_{\eta 0}(\mathbf{k}\omega)w_\sigma(\mathbf{k}\omega)\quad(\eta\neq\sigma) \tag{6}$$

for the dielectric response function. The formal operations which transform (2b) into (5) do not entail any restrictions on the range of $(k,\omega)$. Consequently, (5) and (6) are valid for arbitrary wave numbers and over the entire frequency domain. The static ($\omega=0$) limit of Eqs. (2a) and (5) [which we identify as Ref. 5, Eqs. (41)] is exact since the VAA itself is exact in this limit.[6]

In the third stage, we make the approximation scheme self-consistent at long wavelengths by supposing that the quadratic polarizability can be approximated by an RPA-like structure. The subsequent $kv_\sigma \ll |\omega|$ development of (5c) and (5d) according to the procedure of Ref. 3 then results in the dynamical superposition formulas

$$u_\sigma(\mathbf{k}\omega)=(\Omega_\sigma/\omega)^2[u_{\sigma_{\rm stat}}(\mathbf{k})+u_{\sigma_{\rm dyn}}(\mathbf{k}\omega)]\ , \tag{7a}$$

$$u_{\sigma_{\rm stat}}(\mathbf{k})=\sum_{\sigma'}\frac{e_{\sigma'}N_{\sigma'}}{e_\sigma N_\sigma}\frac{1}{V}\sum_{\mathbf{q}}\chi^2[g_{\sigma\sigma'}(\mathbf{k}-\mathbf{q})-g_{\sigma\sigma'}(\mathbf{q})]\ , \tag{7b}$$

$$\begin{aligned}u_{\sigma_{\rm dyn}}(\mathbf{k}\omega)=&-\frac{3}{5}\left(\frac{k}{\kappa_\sigma}\right)^2\frac{1}{N_\sigma}\sum_{\sigma'}\sum_{\mathbf{q}}\int_{-\infty}^{\infty}d\mu\,\delta_-(\mu)\hat\alpha_\sigma(\mathbf{q}\omega-\mu)\hat\alpha_{\sigma'}(\mathbf{q}\mu)\\&-\frac{7}{30}\left(\frac{k}{\kappa_\sigma}\right)^2\frac{1}{N}\sum_{\mathbf{q}}\int_{\infty}^{\infty}d\mu\,\delta_-(\mu)\{\hat\alpha_\sigma(\mathbf{q}\mu)\hat\alpha_\eta(\mathbf{q}\omega-\mu)-\hat\alpha_\eta(\mathbf{q}\mu)\hat\alpha_\sigma(\mathbf{q}\omega-\mu)\}-R_{\sigma\eta}\quad(\sigma,\eta=A,B:\eta\neq\sigma)\ ,\end{aligned} \tag{7c}$$

and

$$w_\sigma(\mathbf{k}\omega)=(\Omega_\sigma/\omega)^2[w_{\sigma_{\rm stat}}(\mathbf{k}\omega)+w_{\sigma_{\rm dyn}}(\mathbf{k}\omega)]=(\Omega_\sigma/\omega)^2[w_{\sigma_{\rm stat}}(\mathbf{k})+w_{\sigma_{\rm dyn}}(0\omega)]+O(k^2v_\sigma^2/\omega^2)+O[(k^2v_\sigma^2/\omega^2)(\Omega_\sigma^2/\omega^2)]\ , \tag{8a}$$

$$w_{\sigma_{\rm stat}}(\mathbf{k})=-\frac{e_\eta N_\eta}{e_\sigma N_\sigma}\left[\frac{1}{V}\sum_{\mathbf{q}}\chi^2g_{\sigma\eta}(\mathbf{k}-\mathbf{q})+\frac{2}{5}\left(\frac{\Omega_\sigma}{\omega}\right)^2\left(\frac{k}{\kappa_\sigma}\right)^2g_{\sigma\eta}(r=0)\right]\ , \tag{8b}$$

$$\begin{aligned}w_{\sigma_{\rm dyn}}(0\omega)=&-\frac{1}{3N_\sigma}\sum_{\mathbf{q}}(q/\kappa_\sigma)^2\int_{-\infty}^{\infty}d\mu\,\delta_-(\mu)[\hat\alpha_\sigma(\mathbf{q}\mu)\hat\alpha_\eta(\mathbf{q}\omega-\mu)+\hat\alpha_\eta(\mathbf{q}\mu)\hat\alpha_\sigma(\mathbf{q}\omega-\mu)]\\&-\frac{1}{3N_\sigma}\sum_{\sigma'}\sum_{\mathbf{q}}(q/\kappa_\sigma)^2\int_{-\infty}^{\infty}d\mu\,\delta_-(\mu)[\hat\alpha_\sigma(\mathbf{q}\omega-\mu)\alpha_\eta(\mathbf{q}\omega-\mu)\hat\alpha_{\sigma'}(\mathbf{q}\mu)+\hat\alpha_\sigma(\mathbf{q}\mu)\alpha_\eta(\mathbf{q}\mu)\hat\alpha_{\sigma'}(\mathbf{q}\omega-\mu)]\end{aligned} \tag{8c}$$

$$(\sigma,\eta=A,B:\eta\neq\sigma)$$

where, e.g., $\hat{\alpha}_\sigma(\mathbf{q}\mu)=\alpha_\sigma(\mathbf{q}\mu)/\epsilon(\mathbf{q}\mu)$ and $R_{\sigma\eta}$ is another polarizability pair cluster quantity similar in structure to but more involved than the second right-hand-side member of Eq. (7c). Equation (7) is a natural generalization of the Ref. 3 ocp dynamical coupling coefficient; as such, $u_\sigma(\mathbf{k}\omega)$ provides information only about $O(k^2)$ long-range correlational effects. Equation (8) goes much further: it provides information about $O(k^0)$ ionic interdiffusion and short-range static correlational effects on the collective mode structure.

The self-consistent pair of coupled ionic polarizability equations which results from the combination of (2a), (5a), (5b), (7), and (8) comprises the approximation scheme of the present paper. Since the VAA is exact at $\omega=0$, the dynamical coupling coefficients $u_\sigma(\mathbf{k}\omega)$ and $w_\sigma(\mathbf{k}\omega)$ can be inputted with static pair correlation function data which are assumed to be determined by Monte Carlo simulations or by an independent theoretical approach.[8] At high frequencies $\omega >> \Omega_\sigma$ and arbitrary $\Gamma$, the correct small-$k$ limit of the sum-rule coefficient $\Omega_\sigma^{(4)}(\mathbf{k})$ is readily recovered from the combination of (2a), (5a), (5b), (7), and (8); thus, internal consistency between the third-stage construction of our approximation scheme and the (exact) VAA expression (3) is guaranteed. Because of the inherent RPA-like character of the dynamical polarizability clusters, the Eqs. (7c) and (8c) $\mathbf{q}$ summations are cut off at the customary $q_{\max}\sim 1/a$ for strong coupling situations. The nature of the cutoff at weak coupling is discussed at some length below.

## III. COLLECTIVE-MODE BEHAVIOR

The collective-mode analysis of this section is preliminary. More comprehensive numerical calculations are deferred to a later work.[9]

### A. $\Gamma << 1$, $k=0$

First note from (7) that $u_\sigma(0\omega)=0$. We next observe from (8b) and (8c) that *both* $w_{\sigma_{\rm stat}}(0)$ and $w_{\sigma_{\rm dyn}}(0\omega)$ exhibit divergences when evaluated in the Debye-Hückel and RPA approximations, respectively; these divergences, however, exactly cancel each other under addition (with or without the screening) leaving us with the expression

$$w_\sigma(0\omega)=(\Omega_\sigma/\omega)^2[I_\sigma(\omega+J_\sigma(\omega)]\ , \tag{9a}$$

where

$$I_\sigma(\omega)=\frac{2\gamma}{3\pi}\frac{n}{n_\sigma}\left(\frac{\kappa_\eta}{\kappa}\right)^2 \times\int_0^{x_{\max}}dx\left(\frac{x^2}{(1+x^2)^2}-\frac{x^4}{(1+x^2)^2}y_\sigma Z(y_\sigma)\right) \tag{9b}$$

$$(\sigma,\eta=A,B:\eta\neq\sigma)$$

is expressed in terms of the plasma dispersion function

$$Z(y_\sigma)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dz\,\frac{e^{-z^2/2}}{z-y_\sigma-i0}$$

with

$$y_\sigma=\frac{\omega\kappa_\sigma}{\Omega_\sigma\kappa}\frac{1}{\sqrt{1+m_\sigma/m_\eta}}\frac{1}{x},\quad x=\frac{q}{\kappa}\ ;$$

$J_\sigma(\omega)$ is a similarly structured but more involved integral which is developed from the $\hat{\alpha}\alpha\hat{\alpha}$ cluster (convergent) sums in (8c). The plasma parameter $\gamma=\kappa^3/(4\pi n)$ appearing in (9b) more appropriately characterizes weak coupling situations. In deriving (9b) from (8b) and (8c) we have assumed that $\hat{\alpha}_\sigma(\mathbf{q}\mu)$ and $\hat{\alpha}_\sigma(\mathbf{q}\omega-\mu)$ can be replaced by $\alpha_\sigma(\mathbf{q}\mu)/\epsilon(\mathbf{q}0)$ and $\alpha_\sigma(\mathbf{q}\omega-\mu)/\epsilon(\mathbf{q}0)$. This static screening approximation, which is probably quite good except near $\omega=2\Omega$, has been used extensively.[10]

The integral $I_\sigma(\omega)$ still exhibits divergences in its real and imaginary parts. The divergence in the latter is the well-known logarithmic one which is handled by the usual $\gamma << 1$ cutoff $\mathbf{q}_{\max}=1/\beta e^2$. The familiar $\gamma\ln\gamma^{-1}$ expression

$$\mathrm{Im}\epsilon(0\omega)|_{\Gamma<<1}\simeq\sqrt{2/\pi}\frac{n}{3}\left[\left(\sum_\sigma m_\sigma\right)\left(\sum_\sigma(e_\sigma^2n_\sigma/m_\sigma)\right)\left(\sum_\sigma(e_\sigma^2n_\sigma)\right)\right]^{-1/2}\frac{\kappa_A\kappa_B}{\kappa^2}\left[e_A\left(\frac{m_B}{m_A}\right)^{1/2}-e_B\left(\frac{m_A}{m_B}\right)^{1/2}\right]^2\frac{\Omega\,\Omega_A\Omega_B}{\omega^3}\gamma\ln\gamma^{-1} \tag{10}$$

then follows [cf. Eq. (6)] from the subsequent evaluation of $\mathrm{Im}w_\sigma(0\omega)$. The divergence in the real part appears only at very high frequencies $\omega>\Omega/\gamma$ and would adversely affect the $1/\omega^4$ structure of $\mathrm{Re}\hat{\alpha}_{\rm VAA}(\omega\rightarrow\infty)$ were it not for the imposition of the cutoff: indeed at weak coupling, the $q_{\max}$ cutoff is required to maintain internal consistency with the VAA sum-rule coefficient $\Omega_\sigma^{(4)}(k)$. At the lower frequencies $\omega<<\Omega/\gamma$, the divergence in $\mathrm{Re}w_\sigma(0\omega)$ disappears and a numerical evaluation for the case of $H^+-He^{2+}$, $N_+=N_{2+}$ leads to

$$\mathrm{Re}\epsilon(0\omega)|_{\Gamma<<1}=1-\frac{\Omega^2}{\omega^2}-0.016\gamma\frac{\Omega^4}{\omega^4}\ , \tag{11}$$

whence $\Delta\omega'(k=0)\equiv\mathrm{Re}\omega(k=0)-\Omega=0.008\gamma\Omega$. Note that our real frequency shift $\Delta\omega'_{GGN}(k=0)=0.055\Gamma^{3/2}\Omega$ compares favorably with Baus's predicted[2] $\Delta\omega'_B(k=0)=0.08\Gamma^{3/2}\Omega$. At weak coupling, but only at weak coupling, our calculations support his contention that the (positive) shift in the plasma frequency is temperature dependent.[2]

### B. $\Gamma >> 1$

The dynamical $\hat{\alpha}\hat{\alpha}$ and $\hat{\alpha}\alpha\hat{\alpha}$ cluster terms, while they play an important role in the weak and intermediate coupling regimes, appear to contribute only negligibly to the structure of the optical mode at very strong coupling ($\Gamma>>1$). To see this, we first observe that the Golden-Kalman (GK) ocp theory[3] can be exactly recovered from the present theory simply by setting $m_A=m_B$ and $e_A=e_B$ with the concentrations left arbitrary. We next examine the Carini-Kalman-Golden $\Gamma=110.4$ dispersion curve[11] [which originated from the GK approximation scheme[3] and, consequently, from the ocp limit of Eqs. (7a)–(7c)] and observe that this high-$\Gamma$ curve can be quite accurately reproduced *solely* from the ocp version of (7b). Thus, in binary ionic mixtures, $\mathrm{Re}u_{\sigma_{\rm dyn}}(\mathbf{k}\omega)$ should not significantly affect the dispersion of the optical mode for $\Gamma>>1$. The same holds true for $\mathrm{Re}w_{\sigma_{\rm dyn}}(\mathbf{k}\omega)$: our preliminary compressibility-sum-rule-based estimate indicates that it drops off like $1/\Gamma$ as $\Gamma\rightarrow\infty$. It therefore follows that the correlational corrections to the dielectric response function

$$\begin{aligned}\mathrm{Re}[\epsilon(\mathbf{k}\omega)|_{\Gamma>>1}-\epsilon_0(\mathbf{k}\omega)] &= \left(\frac{e_A m_B}{e_B m_A}+\frac{e_B m_A}{e_A m_B}-2\right)\frac{\Omega_A^2\Omega_B^2}{\omega^4}\frac{1}{V}\sum_q \chi^2 g_{AB}(\mathbf{k}-\mathbf{q}) \\ &\quad -\sum_{\sigma,\sigma'}\frac{e_\sigma m_{\sigma'}}{e_{\sigma'} m_\sigma}\frac{\Omega_\sigma^2\Omega_{\sigma'}^2}{\omega^4}\frac{1}{V}\sum_{\mathbf{q}}\chi^2[g_{\sigma\sigma'}(\mathbf{k}-\mathbf{q})-g_{\sigma\sigma'}(\mathbf{q})] \\ &\quad +\left\{\frac{7}{5}\left[\frac{e_A}{e_B}\left(\frac{m_B}{m_A}\right)^{3/2}+\frac{e_B}{e_A}\left(\frac{m_A}{m_B}\right)^{3/2}-\left(\frac{m_B}{m_A}\right)^{1/2}-\left(\frac{m_A}{m_B}\right)^{1/2}\right]\right\}\frac{\Omega_A^3\Omega_B^3}{\omega^6}\frac{k^2}{\kappa_A\kappa_B}g_{AB}(r=0)\end{aligned} \tag{12}$$

can be constructed solely from (7b) and (8b). Since $(1/V)\sum_{\mathbf{q}} g_{AB}(\mathbf{q}) = g_{AB}(r=0) = -1$ for $\Gamma\neq 0$,[8,12,13] the $k=0$ collective mode formula

$$\mathrm{Re}\,\omega(k=0)|_{\Gamma>>1}=\frac{\Omega}{\sqrt{2}}\left\{1+\left[1+\frac{4\Omega_A^2\Omega_B^2}{3\Omega^4}\left(\frac{e_A m_B}{e_B m_A}+\frac{e_B m_A}{e_A m_B}-2\right)\right]^{1/2}\right\}^{1/2} \tag{13}$$

follows from (12). For the $H^+-He^{2+}$ mixture with $N_+ = N_{2+}$, Eq. (13) provides $\omega(k=0)=1.0198\Omega$ in exact agreement with the result of the Hansen-McDonald-Vieillefosse (HMV) memory function analysis.[1] Our result (13) certainly supports HMV's contention that, at strong coupling ($\Gamma >> 1$), the positive shift in $\Omega$ is $\Gamma$ independent. For $0\neq kv_\sigma << |\omega|$, the last right-hand-side group ($\propto 1/\omega^6$) in (12) contributes only negligibly to the dispersion. This leaves us with a dispersion relation which is almost entirely controlled by the correlational parts of the third frequency moment sum rule coefficient $\Omega_\sigma^{(4)}(\mathbf{k})$. Inputting with the static pair-correlation function data from Ref. 8 would therefore result in a dispersion curve for the optical mode which should coincide with HMV's Fig. 6 sum-rule-moment-based theory curve,[1] and which therefore reproduces the qualitative features of their molecular dynamics data[1] for $\Gamma >> 1$. We have rigorously demonstrated near-coincidence of the two curves at the longer wavelengths $ka \leq 0.5$ where one can justifiably input with the more accessible correlation-energy-density formulas of Refs. 8 and 14.

A comprehensive collective mode analysis at intermediate coupling states and concomitant numerical calculations of $\Gamma_{\mathrm{crit}}$ marking the crossover from plasmonlike to phononlike dispersion are deferred to a later work.[9]

## IV. CONCLUSIONS

Following the Golden-Kalman ocp nonlinear response function approach,[3] we have formulated a promising sum-rule conserving approximation scheme for the calculation of ionic polarizabilities in binary mixture plasmas. Our preliminary collective mode calculations indicate that the (positive) shift in the plasma frequency is $\Gamma$ dependent at weak coupling and $\Gamma$ independent at very strong coupling. In the latter regime, the dispersion of the optical mode appears to be almost entirely structured by the correlational contributions to the third frequency moment sum rule.

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[1] I. R. McDonald, P. Vieillefosse, and J. P. Hansen, Phys. Rev. Lett. **39**, 271 (1977); J. P. Hansen, I. R. McDonald, and P. Vieillefosse, Phys. Rev. A **20**, 2590 (1979).

[2] M. Baus, Phys. Rev. Lett. **40**, 793 (1978); M. Baus and J. P. Hansen, Phys. Rep. **59**, 3 (1980).

[3] K. I. Golden and G. Kalman, Phys. Rev. A **19**, 2112 (1979).

[4] K. I. Golden and Lu De-xin, J. Stat. Phys. **29**, 281 (1982).

[5] K. I. Golden and G. Kalman, Phys. Rev. A **14**, 1802 (1976).

[6] K. I. Golden and G. Kalman, Ann. Phys. (N.Y.) **143**, 160 (1982).

[7] K. I. Golden, F. Green, and D. Neilson (unpublished).

[8] J. P. Hansen, G. M. Torrie, and P. Vieillefosse, Phys. Rev. A **16**, 2153 (1977).

[9] K. I. Golden, F. Green, and D. Neilson (unpublished).

[10] M. Baus, Phys. Rev. A **15**, 790 (1977).

[11] P. Carini, G. Kalman, and K. I. Golden, Phys. Lett. **78A**, 450 (1980).

[12] J. F. Springer, M. A. Pokrant, and F. A. Stevens, Jr., J. Chem. Phys. **58**, 4863 (1973).

[13] J. P. Hansen and I. R. McDonald, Phys. Rev. A **23**, 2041 (1981).

[14] H. E. DeWitt and Y. Rosenfeld, Phys. Lett. **75A**, 79 (1977).