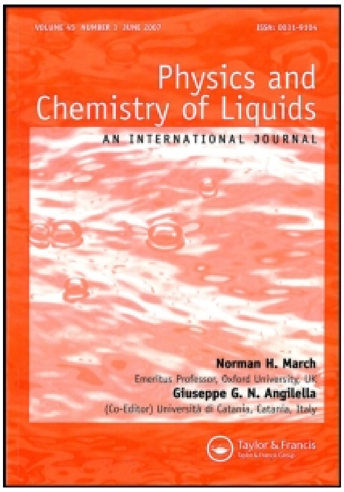

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P. V. Giaquinta[a]; M. Parrinello[a]; M. P. Tosi[a]; N. H. March[a]
[a] Department of Phyiscs, The Blackett Labortory Imperial College, London

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Frequency Spectra of Transport Properties in Ionic Liquids: Contribution of Charge Fluctuation Modes

P. V. GIAQUINTA, M. PARRINELLO, M. P. TOSI† and N. H. MARCH,
Department of Physics, The Blackett Laboratory, Imperial College, London SW7 2BZ

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The influence of charge fluctuation modes on the frequency spectra for shear viscosity, self-diffusion and thermal diffusion is discussed. Both the one-component plasma, and modifications which are anticipated in real ionic liquids to the charge fluctuation modes, are considered. The latter treatment utilizes a simple model into which is incorporated plasmon dispersion and plasmon damping, the damping being both at zero wave number k and at order k^2.

The main emphasis of the paper is on non-analytic behaviour with frequency, and the modifications which occur for damped charge fluctuation modes. Because of the dominant influence of mass fluctuation modes at very long time, which are not considered quantitatively here, the theory discussed should have relevance at intermediate times, such as are treated in present molecular dynamical calculations. Contact is made with such computer simulation of molten BeF_2 and a model of molten salts.

1 INTRODUCTION

This paper represents a start of a programme we are undertaking to study the frequency spectra of a variety of transport properties in ionic liquids. We recognize that, for a full discussion of specific systems, it will be essential to supplement the present treatment, based on an analytic development of a very simple (plasmon) model for the charge fluctuation modes, by molecular dynamical calculations. Indeed, such calculations have already been undertaken, though they deal with development in time (for example, the velocity auto-correlation function) whereas our prime interest in this paper is with frequency dependence. However, the two variables are, of course, related via Fourier transform. This is, at once, an advantage and a limitation.

†Permanent address: Istituto di Fisica dell'Università, Roma. The contribution of MPT to this work was made during a visit to Imperial College in the Winter 1975/6.

The advantage comes because it is well known from the work of Lighthill,[1] and many others, that the long-time behaviour of a quantity like the velocity auto-correlation function is dominated by singularities in the frequency-dependent analogue. The limitation is that full knowledge for all time is required to get the entire frequency spectrum.

Thus, work initiated by Alder and Wainwright,[2] by computer calculations, and developed theoretically by Ernst *et al.*[3] and later workers, has revealed the so-called long-time tails of various properties like the velocity auto-correlation function, which falls off with time like $t^{-3/2}$. This is reflected in frequency, as pointed out by Gaskell and March,[4] by a cusp proportional to $|\omega|^{1/2}$ at the low-frequency limit $\omega = 0$. This discussion was for neutral fluids, but similar properties will obtain for the mass fluctuation modes in two-component systems.

These modes, however, though we expect them to dominate the long-time behaviour of the velocity auto-correlation function in ionic liquids, and again to lead to a decay like $t^{-3/2}$, are not the prime interest of this paper. Rather we want to discuss the peculiar spectral features arising from the charge fluctuation modes.

Though, naturally, our interest is in the properties of real ionic liquids, like the molten alkali halides, a useful starting-point for the theory is the one-component plasma. Here, classical ions execute dynamical motions in a uniform, non-responsive neutralizing charge background. This system was treated in the pioneering work of Brush, Sahlin and Teller,[5] and has been extensively considered by Hansen and co-workers.[6] We take up this model at first, and briefly summarize what is already known about the time-dependent transport associated with the charge fluctuation modes.

2 ONE-COMPONENT PLASMA

The molecular dynamical calculations for a classical one-component plasma referred to above[6] reveal that the velocity auto-correlation function for a liquid one-component plasma[7] has a slowly decaying oscillatory long-time tail. Gould and Mazenko,[8] within the framework of mode-mode coupling theory,[9] and in particular on the basis of coupling between the diffusive mode and a plasma oscillation, have proposed an explanation. Such a treatment gives for the long-time behaviour of the velocity auto-correlation function the form (actually Gould and Mazenko give the memory function)

$$t^{-3/2} \cos \omega_p t \tag{2.1}$$

where ω_p is the usual plasma frequency given by

$$\omega_p^2 = \frac{4\pi n e^2}{M} \tag{2.2}$$

e being the charge on the ions, n the particle density and M the ionic mass.

The considerations of Lighthill allow one to show readily that there is a singularity in the frequency spectrum $f(\omega)$ for diffusion at $\pm\omega_p$, the behaviour of $f(\omega)$ near to ω_p having the form

$$|\omega - \omega_p|^{1/2} \tag{2.3}$$

which we shall discuss more fully as a limiting case of a damped plasmon model treated below.

It is interesting to compare and contrast this result of Gould and Mazenko in Eq. (2.1) with the corresponding long-time tail of the frequency spectrum for shear viscosity in the one-component plasma as given very recently by Baus and Wallenborn.[10] Their result shows important differences from the Gould-Mazenko form (2.1), namely the characteristic frequency of the oscillation in the long-time tail is the harmonic $2\omega_p$, and also there is a phase shift. The precise form given by Baus and Wallenborn is in fact

$$\eta(t) = \frac{(2\pi\Gamma t)^{-3/2}}{120\beta}\left[1 + \left(1 + \left|\frac{c}{\Gamma}\right|^2\right)^{-3/4} \cos\left(2\omega_p t + \frac{3}{2}\arctan\frac{c}{\Gamma}\right)\right] \tag{2.4}$$

where c and Γ represent the dispersion and the damping respectively of the plasmon modes (see Eq. 3.2 below).

This form of the long-time tail becomes in frequency space, following again the methods of Lighthill,[1] an asymmetrical singularity around $\pm 2\omega_p$, having the form near the singular point $2\omega_p$

$$|\omega - 2\omega_p|^{1/2}. \tag{2.5}$$

There is, in addition, a singularity of the form $|\omega|^{1/2}$ near to $\omega = 0$.

The work of the present paper is motivated by this singular behaviour in ω space, derived for diffusion in Eq. (2.3) and for shear viscosity in Eq. (2.5), from the long-time oscillatory tails given by Gould and Mazenko[8] and Baus and Wallenborn[10] respectively. Our main concern is to enquire just what qualitative features of these one-component plasma results might be expected to persist in real, two-component molten alkali halides, for example. To do this, one would require the full hydrodynamics of the two-component charged liquid. While this is under consideration in future work, in the present discussion we shall consider, as a step towards this goal, the introduction of static scattering into the one-component plasma. This model is introduced, and its consequences worked out, in Section 3 immediately below.

3 ONE-COMPONENT PLASMA, WITH STATIC SCATTERERS

Given that there are additional scattering mechanisms introduced into the one-component plasma, we can set up a model without the need to enquire closely into the precise microscopic model. The important qualitative change from the model of Section 2 is then that the plasmon is damped even in the zero wave-number limit. We stress that we still focus on charge fluctuation modes, and that in real charged fluids the mass fluctuation modes will dominate with $t^{-3/2}$ tails, as in neutral fluids.

The model we have in mind is one of weak scattering by static impurities. It is thereby implied that the spectral features pointed out in Section 2 for the ideal one-component plasma will not be completely washed out. There are molten charged fluids (see section 7 below) in which there is strong scattering and a different model is then doubtless needed.

3.1 Longitudinal current

Following the techniques used by Ernst *et al.*,[3] we can write down the variation with time of the current $\mathbf{u}_{\mathbf{k}}^{c}(t)$ associated with the charge fluctuations. In particular, the longitudinal part of the current takes the form

$$\hat{k} \cdot \mathbf{u}_{\mathbf{k}}^{c}(t) = A_{\mathbf{k}}^{+}(0)\, e^{-\omega_k^{+} t} - A_{\mathbf{k}}^{-}(0)\, e^{-\omega_k^{-} t};$$
$$A_{\mathbf{k}}^{\pm}(0) = \pm\tfrac{1}{2}\hat{k} \cdot \mathbf{u}_{\mathbf{k}}^{c}(0) \equiv \pm\tfrac{1}{2} u_{\mathbf{k}l}^{c}(0) \tag{3.1}$$

where $\omega_k^{\pm}$ describes a plasmon excitation, with dispersion and damping given by

$$\omega_k^{\pm} = \pm i(\omega_p + ck^2) + (\gamma + \Gamma k^2). \tag{3.2}$$

Here, $\hat{k}$ denotes a unit vector while $u_{\mathbf{k}l}^{c}(0)$ denotes the longitudinal part of the current at time $t = 0$.

Some comments are called for at this point on the meaning of the damping as introduced in Eq. (3.2) and the related point of the connection between with the one-component plasma of section 2. For the ideally pure one-component fluid, $\gamma = 0$. For the impure one-component fluid (which is our first step towards the two-component ionic melts) γ represents the plasmon damping at the extreme long wavelength limit $\mathbf{k} = 0$. This should not be confused with the low-frequency resistivity. There are cases when the two things are not correlated; a well-localized system has a very well-defined plasmon excitation ($\gamma \cong 0$) and a very low conductivity. In the case $\gamma \neq 0$, on the other hand, the system has certainly other hydrodynamic modes which are important (and most probably dominant) in determining the spectra near $\omega \cong 0$. Therefore, since we are examining here only the charge-mode contribution to the spectra in a mode-mode coupling theory, it is clearly not a complete account of the low-frequency behaviour. The emphasis, therefore, as we stressed above already, is on behaviour related to the plasma frequency ω_p and its harmonics, which we expect to play a role at intermediate times, but to become progressively less important at really long time.

3.2 Transverse currents

The parallel assumption made on the transverse currents is

$$u^c_{kt}(t) = u^c_{kt}(0) \exp\{-(\sigma + \lambda k^2)t\} \tag{3.3}$$

where σ is the d.c. electrical conductivity in a uniform field, while λ accounts for (non-local) inhomogeneity effects. Clearly, in (3.3) the mode is assumed to be of a pure relaxation type. This expression (3.3) for the transverse currents in the charged fluid should be contrasted with the expression for the transverse currents associated with mass fluctuations, namely

$$u^m_{kt}(t) = u^m_{kt}(0) \exp\{-\nu k^2 t\} \tag{3.4}$$

As we shall see, the presence of the k-independent term in the exponent in Eq. (3.3) will lead to damping of this contribution to the long-time behaviour of the transport functions.

3.3 Diffusion

Likewise for diffusion, we follow Ernst *et al.*[3] by working with the probability density of a labelled particle $P_k(t)$ which we take as

$$P_k(t) = P_k(0) \exp(-Dk^2 t) \tag{3.5}$$

where D is the self-diffusion constant. We now work out the frequency spectrum for diffusion and since we are interested in displaying the general features of our plasmon model with static scatterers, we omit all inessential normalization constants from the argument. Then the time-dependent property, namely the velocity auto-correlation function $C_D(t)$, for which we require the Fourier transform $f(\omega)$, can be written, since we must couple P with the total charge fluctuation current, as

$$\begin{aligned}
C_D(t) &\cong n^{-1}\int dv_0\, f_0(v_0)\, v_{0x}(2\pi)^{-3}\int dk\, u^c_{kx}(t)\, P_{-k}(t) \\
&\sim \frac{n^{-1}}{9(2\pi)^3}\int dv_0\, f_0(v_0)\, v_0^2 \int dk' \left\{ \frac{1}{2}\left[\frac{e^{-i(\omega_p - i\gamma)t}}{(ic + \Gamma + D)^{3/2} t^{3/2}} \right.\right. \\
&\quad \left.\left. + \frac{e^{i(\omega_p + i\gamma)t}}{(-ic + \Gamma + D)^{3/2} t^{3/2}}\right] + \frac{2e^{-\sigma t}}{(\lambda + D)^{3/2} t^{3/2}} \right\} e^{-k^{\prime 2}} \\
&\sim \frac{k_B T}{24\pi^{3/2} n} t^{-3/2} \left\{ e^{-\delta t} \frac{\cos\left(\omega_p t + \dfrac{3}{2}\arctan\dfrac{c}{D + \Gamma}\right)}{[c^2 + (D + \Gamma)^2]^{3/4}} + \frac{2e^{-\sigma t}}{(\lambda + D)^{3/2}} \right\},
\end{aligned} \tag{3.6}$$

where n as usual is the particle density. For the one-component fluid, without scattering mechanisms, $\sigma = \infty$ (no transverse contribution) and $\gamma = 0$ (non-analytic behaviour around $\omega = \pm\omega_p$). In essence, apart from a phase factor, Eq. (2.1) is then regained.

4 FREQUENCY SPECTRA: EFFECT OF SCATTERING ON SINGULARITIES

We now turn to discuss the consequences of these results for the frequency spectrum for diffusion.

4.1 Case $\gamma = 0$

Here we can write for the longitudinal contribution to Eq (3.6)

$$f(t) \propto \cos\left[\omega_p|t| + \phi\right]|t|^{-\frac{3}{2}} \tag{4.1}$$

and the Fourier transform $f(\omega)$ is evidently given by

$$f(\omega) \propto \int_{-\infty}^{\infty} dt\, e^{i\omega t}\left[\Theta(t)\cos(\omega_p t + \phi)t^{-\frac{3}{2}} + \Theta(-t)\cos(\omega_p t - \phi)(-t)^{-\frac{3}{2}}\right] \tag{4.2}$$

Using the result of Lighthill[1] that

$$\text{F.T}\,\{e^{ikx}|x|^{\alpha}\Theta(x)\} = e^{-\frac{\pi}{2}i(\alpha+1)\mathrm{sgn}(y-k)}\alpha!\,|y-k|^{-1-\alpha} \tag{4.3}$$

we get for $f(\omega)$ the forms around $\pm\omega_p$, aside from additive constants as

$$f(\omega)|_{\omega\sim\omega_p} \sim \frac{-k_BT}{12\pi M}\frac{|\omega-\omega_p|^{1/2}}{\left[c^2+(D+\Gamma)^2\right]^{3/4}}\cos\left[\frac{3}{2}\arctan\frac{c}{D+\Gamma}+\frac{\pi}{4}\mathrm{sgn}(\omega-\omega_p)\right] \tag{4.4}$$

$$f(\omega)|_{\omega\sim-\omega_p} \sim \frac{-k_BT}{12\pi M}\frac{|\omega+\omega_p|^{1/2}}{\left[c^2+(D+\Gamma)^2\right]^{3/4}}\cos\left[\frac{3}{2}\arctan\frac{c}{D+\Gamma}-\frac{\pi}{4}\mathrm{sgn}(\omega+\omega_p)\right] \tag{4.5}$$

Figure 1 shows the schematic form of $f(\omega)$ for $\gamma = 0$. The reservations made above must be recalled; the important point we wish to make is that the cusps at $\pm\omega_p$, which are certainly present in the ideal one-component plasma, will be rounded off by damping.

As an alternative way of expressing the velocity autocorrelation function, let us consider the memory function. Thus, we take the Laplace transform of $f(t)$ with respect to z, and then with $z = i\omega$ we find

$$\tilde{f}(\omega)|_{\omega\approx\omega_p} = \tilde{f}(\omega_p) - \sqrt{\pi}\,e^{i\phi}\,e^{\pi/4\,i\,\mathrm{sgn}(\omega-\omega_p)}|\omega-\omega_p|^{1/2} \tag{4.6}$$

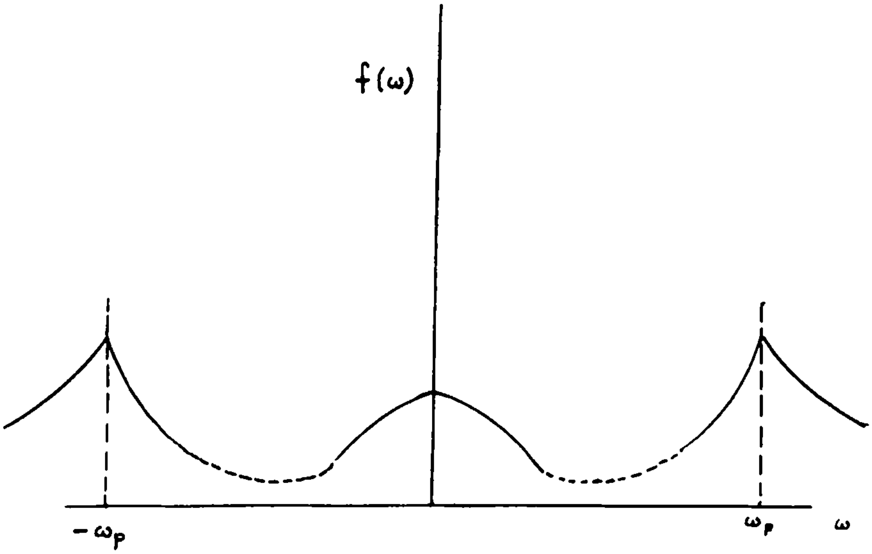

FIGURE 1 Purely schematic form for frequency spectrum $f(\omega)$ for diffusion. (Case plotted for $\gamma = 0$ and σ finite).

Note that $f(\omega)$ is an even function of ω. With no damping, there are cusps as shown at ω_p and $-\omega_p$ associated with charge fluctuation modes. With conductivity $\sigma = 0$, the peak shown at $\omega = 0$ becomes an $|\omega|^{1/2}$ cusp (see Eq. 3.6).

The effect of small plasmon damping ($\gamma \neq 0$) is to round off the cusps at $\pm\omega_p$.

and the relation to the memory function $\tilde{M}(\omega)$ is

$$\tilde{f}(\omega) \,\alpha\, [-i\omega + \tilde{M}(\omega)]^{-1}. \tag{4.7}$$

For $\omega \cong \omega_p$, the result takes the form

$$\tilde{M}(\omega) - \tilde{M}(\omega_p) \,\alpha\, e^{i\phi} e^{\pi/4 i \,\mathrm{sgn}(\omega - \omega p)} |\omega - \omega_p|^{1/2}. \tag{4.8}$$

5 THERMAL DIFFUSION

We next sketch the calculation of the kinetic contribution to the thermal diffusion spectrum. The temperature fluctuations $T_k(t)$ are described by the equation

$$T_k(t) = T_k(0) \exp\{-D_T k^2 t\} \tag{5.1}$$

where the thermal diffusivity $D_T = K/n\,c_p$, K being the thermal conductivity and c_p the heat capacity at constant pressure.

The kinetic part of the time-correlation function between temperature fluctuations is then written, following Ernst *et al*,[3] as

$$C_T(t) \approx \tfrac{5}{2} k_B \int dv_0\, f_0(v_0)\, v_{0x} \left[\tfrac{1}{2} M v_0^2 - \tfrac{5}{2} k_B T\right] (2\pi)^{-3} \int dk\, u_{kx}(t)\, T_{-k}(t). \tag{5.2}$$

It is clear, by comparison with the first line of Eq. (3.6) that, aside from a multiplying constant, the result has the same form as (3.6) for self-diffusion, with D however in (3.6) being replaced by D_T. The peaks in the frequency spectrum lie therefore at $\pm\omega_p$.

6 SHEAR VISCOSITY

Finally we calculate the spectrum for the kinetic contribution to viscosity, again following the methods of Ernst *et al.*[3] We can write the appropriate time-correlation function for shear viscosity which involves coupling of current along the x axis with that in the y direction as

$$C_\eta(t) \approx nM^2 \int dv_0\, f_0(v_0) v_{0x}\, v_{0y}\, (2\pi)^{-3} \int dk\, u_{kx}(t)\, u_{-ky}(t) \tag{6.1}$$

and after some manipulation we obtain

$$C_\eta(t) \cong \frac{(nk_BT)^2 t^{-3/2}}{60(2\pi)^{3/2}} \left\{ \frac{1}{2} e^{-2\mu} \left[\frac{1}{\Gamma^{3/2}} + \frac{\cos\left(2\omega_p t + \frac{3}{2}\arctan\frac{c}{\Gamma}\right)}{(c^2+\Gamma^2)^{3/4}} \right] + \frac{7}{2}\frac{e^{-2\sigma t}}{\lambda^{3/2}} + 3e^{-(\sigma+2\gamma)t} \frac{\cos\left(\omega_p t + \frac{3}{2}\arctan\frac{c}{\Gamma+\lambda}\right)}{[c^2+(\Gamma+\lambda)^2]^{3/4}} \right\} \tag{6.2}$$

To see that we regain the result of Baus and Wallenborn[10] we note that when $\gamma \to 0$ and $\sigma \to \infty$ we get back singularities at $\omega = 0$ and $\omega = \pm 2\omega_p$. Thus the time-dependence of the shear viscosity has the form

$$C_\eta(t) \approx \frac{(nk_BT)^2 t^{-3/2}}{120(2\pi)^{3/2}} \left[\frac{1}{\Gamma^{3/2}} + \frac{\cos\left(2\omega_p t + \frac{3}{2}\arctan\frac{c}{\Gamma}\right)}{(c^2+\Gamma^2)^{3/4}} \right] \tag{6.3}$$

in agreement with Baus and Wallenborn.[10] The changes in going from Eqs. (6.3) to (6.2) are naturally to blur out the cusps in ω space at $\omega = 0$ and $\pm 2\omega_p$. However the last term in the curly bracket in Eq. (6.2) is associated with additional structure in the frequency spectrum around $\pm\omega_p$, damped by conductivity σ and plasmon damping γ.

7 DISCUSSION AND FUTURE WORK

As we emphasized, this discussion has been concerned with the role of charge fluctuation modes in frequency spectra. The model used does not have the richness of modes undoubtedly present in real two-component ionic liquids. Below therefore we emphasize what features of our model we expect to be reflected in such charged liquids, and what modifications must be made to the results for the one-component plasma with scattering.

The first point to be made is that the charge fluctuation mode of the one-component plasma undoubtedly leads to undamped oscillatory behaviour in the long-time tails of the Fourier transform of the frequency spectra for diffusion and viscosity, as well as to a non-oscillatory $t^{-3/2}$ behaviour in the shear viscosity. The present model strongly suggests that, when scattering processes are introduced, the plasmon singularities, along with any singularities at hormonics of ω_p, will be smeared out. Our model is valid for small smearing and shows that exponential damping will occur at sufficiently long times. Thus the whole question of the influence of the charge fluctuation modes on the frequency spectra of the various transport properties would seem to hinge on just how much the cusps at ω_p, and multiples of it, are washed out by scattering processes. Of course, even after this blurring out of the singularities due to the charge fluctuation modes, there will remain undamped long-time tails associated with a cusp at $\omega = 0$ from mass fluctuation modes in all liquids.

In conclusion, we believe this discussion of the charge fluctuation modes is very relevant to the molecular dynamical results of Rahman *et al.*[11] on molten BeF_2. Here it appears that the small Be ion behaves somewhat as if it is in a cage, enclosed by F ions, and its velocity auto-correlation function is reported to show oscillatory behaviour at the intermediate times investigated in the computer simulation. This, it seems to us, is at least compatible with our model, based on small damping. In contrast the F ion velocity auto-correlation function is reported to show no such oscillatory behaviour at intermediate times. Here, we seem to be in the region of critical damping. It would seem that the structure of molten BeF_2, consistent with the Be ions rapidly vibrating in a structure determined for them by the F ions, implies that the Be ions would make the dominant contribution to the plasma mode.

A further example from computer calculations is that for a simple model of a molten salt in which the ions differ only in their charge, investigated by Hansen and McDonald.[12] In this case, there is only one velocity auto-correlation function, and this does not show oscillatory behaviour at intermediate times $\sim 10^{-12}$ sec. Our model would suggest that in such a system, with the interaction potential used by Hansen and McDonald, the effects of the plasmon mode are substantially damped.

We are currently attempting to generalize the present approach to treat the problem of the dielectric loss properties of ionic liquids, and it is intended to publish these results at a later date. The relevance of all this, and in particular singularity structure at small ω, to the dielectric properties of superionic conductors, and related systems, is also under consideration.

Acknowledgements

One of us (NHM) wishes to acknowledge that his interest in the dielectric loss properties was stimulated by discussion of data on a wide variety of dielectric solids with Professor A.K. Jonscher and Dr. R. Hill of Chelsea College, London University. We hope to take up this problem in detail elsewhere.

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