Brief Reports

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Screened ion-ion interaction in mercury-chain compounds: Single chain

Minette M. Mohan and A. Griffin
Department of Physics and Scarborough College, University of Toronto, Toronto, Ontario, Canada M5S 1A7
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At room temperature, the mercury chains in $Hg_{3-\delta}AsF_6$ exhibit phonons characteristic of a one-dimensional lattice. We calculate the screening of the Hg ion-ion interaction in a single chain by electrons moving in a cylindrical potential of finite radius, within the random-phase approximation. The resulting Bohm-Staver-type expression for the phonon velocity is $(Z^2mN_I/MN_e)^{1/2}v_F$, where Z is the Hg ionic charge and N_I (N_e) is the number of ions (electrons) per unit length. Use of the Tomonaga-Luttinger solution for the electronic response function (keeping only the small-momentum scattering processes) just renormalizes the Fermi velocity in this expression.

A striking feature of the x-ray and neutron scattering studies of mercury-chain compounds like[1] $Hg_{3-\delta}AsF_6$ is the existence of intense sheets of diffuse scattering[2] corresponding to two perpendicular arrays of one-dimensional (1D) scatterers at room temperature. This scattering is due to chains of Hg atoms which lie in "channels" created by the body-centered tetragonal structure of the host AsF_6^- anions. The intensity of these sheets is virtually uniform, indicating no phase correlation in atomic positions between the chains. The Hg-Hg intrachain distance ($d_{\|}=a/3-\delta=2.67$ Å) is found to be incommensurate with the host-lattice parameter a along the chain direction, indicating that the interactions with the host AsF_6^- lattice are weak. Rasavi, Datars, Chartier, and Gillespie[3] used a free-electron dispersion relation for a Fermi-surface model of the chain lattice and obtained excellent agreement with the cross-sectional areas measured in the de Haas–van Alphen effect. Thus, the electronic states are well described[1,3] by 1D plane-wave states with energy $\epsilon(k)=\hbar^2k^2/2m$ parallel to the chain axis. At room temperatures, then, both the ions and the electrons of the Hg chains behave as one-dimensional entities, essentially independent of other Hg chains as well as of the host lattice. As the temperature approaches 120 K, the perpendicular arrays order to produce a 3D structure,[2] but our present discussion will be restricted to the high-temperature phase.

Hg-chain compounds at room temperature thus are quite different from almost all other quasi-one-dimensional metals, where the electrons are best described in the tight-binding approximation and the ions are part of a three-dimensional lattice.[4–6] Hg chains are a beautiful example of a one-dimensional two-component electron-ion plasma. In this paper, we apply the standard random-phase approximation (RPA) theory to a two-component plasma[7] restricted to a cylindrical potential and use the results to evaluate the long-wavelength phonon velocity in a single Hg chain. To deal with the long-range Coulomb screening in a well-defined way, it is crucial to work with a chain of finite radius r_0.[8,9] The phonon velocity is found to be given by a Bohm-Staver–type expression.[7] Using available data,[1] this formula gives $c_{1D}\simeq 2.9\times10^3$ m/s in comparison with $(4.4\pm0.8)\times10^3$ m/s obtained from neutron scattering data.[10] We also use our model to discuss the electron-phonon matrix element and the phonon dispersion relation at large momentum $\sim 2k_F$, where one expects phonon softening.[4,5]

As mentioned, the electrons and ions in a given Hg chain are viewed as a two-component plasma confined to a cylindrical potential well (of radius r_0) along the x axis. We treat the electron-electron, ion-electron, and ion-ion Coulomb interactions within the standard RPA. The coupled mean-field equations of motion are a straightforward generalization of those for a single-component electron gas in a cylindrical potential.[8] We assume that both electrons and ions are in their ground state as far as their transverse motion is concerned. Thus, the density response functions have the form

$$\chi_{i,j}(\mathbf{p},-\mathbf{p}',\omega)=f_i(\mathbf{p}_\perp)f_j(\mathbf{p}'_\perp)\chi_{i,j}(p_x,\omega)\ . \tag{1}$$

Here $\chi_{i,j}$ is the correlation function involving the densities $\hat\rho_i(\mathbf{r})$ and $\hat\rho_j(\mathbf{r})$ where i and j represent the species involved (electrons and ions). The form factors $f_i(\mathbf{p}_\perp)$ arise from the localized ground-state orbitals for transverse motion. For our present purposes, it is sufficient to use the Gaussian approximation, in which case

$$f_i(\mathbf{p}_\perp)=e^{-p_\perp^2r_0^2/4} \tag{2}$$

for both electrons and ions. Finally, $\chi_{i,j}(p_x,\omega)$ is the response function for a purely one-dimensional two-component plasma.

Within the standard mean-field approximation (MFA) one finds, after a little calculation,

$$\chi_{e,e}(p_x,\omega)=\frac{\tilde\chi_{e,e}(p_x,\omega)[1-Z^2u(p_x)\chi^0_{I,I}(p_x,\omega)]}{1-Z^2u(p_x)\chi^0_{I,I}-Z^2u(p_x)\chi^0_{I,I}u(p_x)\tilde\chi_{e,e}}\ , \tag{3}$$

where

$$u(p_x)=\frac{1}{A_\perp}\sum_{\mathbf{p}_\perp}|f(\mathbf{p}_\perp)|^2\frac{4\pi e^2}{p_x^2+p_\perp^2} \ , \tag{4}$$

$V=LA_\perp$ is the total volume, and $\tilde{\chi}_{e,e}(p_x,\omega)$ is the one-dimensional electron response function which includes *only* electron-electron interactions. In the RPA the latter is

$$\tilde{\chi}_{e,e}(p_x,\omega)=\frac{\chi^0_{e,e}(p_x,\omega)}{1-u(p_x)\chi^0_{e,e}(p_x,\omega)} \ ; \tag{5}$$

$\chi^0_{I,I}$ and $\chi^0_{e,e}$ are the noninteracting one-dimensional response functions of the ions and electrons, respectively. $\chi_{I,I}(p_x,\omega)$ and $\chi_{I,e}(p_x,\omega)$ have the same poles as $\chi_{e,e}(p_x,\omega)$ in (3), and thus need not be written down. We observe that the structure of the 1D $\tilde{\chi}_{e,e}(p_x,\omega)$ in (5) is precisely the same as the familiar expression in 3D metals, apart from the fact that the effective Coulomb potentials involve form factors [see (4)]. It is in these form factors that the finite chain radius enters. One easily verifies that

$$\begin{aligned}u(p_x)&=e^2e^{p_x^2r_0^2/2}E_1(p_x^2r_0^2/2)\\&\simeq 2e^2|\ln(p_xr_0)|+\cdots;\ p_xr_0\ll 1 \ ,\end{aligned} \tag{6}$$

where $E_1(x)$ is the exponential integral. If we set $r_0\to 0$ [in which case $|f(\mathbf{p}_\perp)|^2=1$], $u(p_x)$ in (4) diverges and is not well defined.

The collective modes of this two-component system are given by the solutions of

$$\begin{aligned}1=&\ Z^2u(p_x)\chi^0_{I,I}(p_x,\omega)\\&+Z^2u^2(p_x)\chi^0_{I,I}(p_x,\omega)\tilde{\chi}_{e,e}(p_x,\omega) \ .\end{aligned} \tag{7}$$

The phonon modes correspond to frequencies in the regime

$$\bar{v}_Ip_x\ll\omega\ll v_Fp_x \ , \tag{8}$$

where $\bar{v}_I$ is an average ionic speed. In this regime we can use the high-frequency approximation

$$\chi^0_{I,I}(p_x,\omega)=\frac{N_Ip_x^2}{M\omega^2};\ \omega\gg\bar{v}_Ip_x \ . \tag{9}$$

It is useful to introduce the high-frequency (unscreened) collective mode in a 1D ion plasma (moving in a uniform negative background)

$$\Omega_{\rm pl}^2(p_x)\equiv\frac{Z^2N_I}{M}u(p_x)p_x^2 \ . \tag{10}$$

Using the fact that

$$Z^2u(p_x)\chi^0_{I,I}(p_x,\omega)=\frac{\Omega_{\rm pl}^2(p_x)}{\omega^2} \ , \tag{11}$$

(7) can be written as

$$\omega^2=\Omega_{\rm pl}^2(p_x)+\frac{Z^2N_I}{M}u^2(p_x)p_x^2\tilde{\chi}_{e,e}(p_x,\omega) \ . \tag{12}$$

In turn, using (10) and (5), an alternate form is

$$\begin{aligned}\omega^2&=\Omega_{\rm pl}^2(p_x)[1+u(p_x)\tilde{\chi}_{e,e}(p_x,\omega)]\\&=\frac{\Omega_{\rm pl}^2(p_x)}{1-u(p_x)\chi^0_{e,e}(p_x,\omega)} \ ,\end{aligned} \tag{13}$$

where we have used (5) in the last step. In the frequency range (8), we can use the static approximation to the 1D Lindhard function

$$-\lim_{p_x\to 0}\chi^0_{e,e}(p_x,\omega=0)=\frac{2}{\pi\hbar v_F}=N(\epsilon_F) \ , \tag{14}$$

where $N(\epsilon_F)$ is the density of states for a 1D electron gas.

In the long-wavelength limit $p_xr_0\ll 1$ (since $r_0\sim 1$–2 Å, this condition is equivalent to $p_x\ll k_F$); $u(p_x)$ diverges as $|\ln(p_xr_0)|$, and hence (13) reduces to

$$\omega^2=\frac{Z^2N_I}{M}\frac{1}{N(\epsilon_F)}p_x^2 \ . \tag{15}$$

The effective screened ion-ion interaction is given by $U(p_x)=Z^2/N(\epsilon_F)$ for $p_x\to 0$. The phonon velocity is thus given by

$$c_{\rm 1D}=\left[\frac{N_I}{M}\frac{Z^2}{N(\epsilon_F)}\right]^{1/2}$$

or, equivalently,

$$c_{\rm 1D}=\left[\frac{Z^2m}{M}\frac{N_I}{N_e}\right]^{1/2}v_F \ . \tag{16}$$

We observe that the logarithmic factor dependent on r_0 cancels out of the numerator and denominator of (13).

In the specific case of $Hg_{3-\delta}AsF_6$, it is known experimentally[1,3] that $N_e=1.65N_I$ and $k_F=0.97$ Å^{-1}. In Table I, we give the predicted values of $c_{\rm 1D}$ using (16) as well as available experimental data from neutron scattering.[10] No ultrasonic data are available for $Hg_{3-\delta}AsF_6$. For comparison we show the analogous results for bulk mercury ($Z=2$) using the Bohm-Staver expression (see p. 240 of Ref. 7)

$$c_{\rm 3D}=\left[\frac{Z}{3}\frac{m}{M}\right]^{1/2}v_F \ , \tag{17}$$

together with experimental values obtained from neutron scattering[11] and ultrasonic[12] data.

We can use our model to discuss the electron-phonon interaction in a finite-radius chain. In standard notation, we have[7]

$$\hat{H}_{e\text{-ph}}=\sum_{p_x}Q(p_x)V^i(p_x)\hat{\rho}^+(p_x) \ , \tag{18}$$

where $\hat{\rho}(p_x)$ is the electronic density operator, $Q(p_x)$ is the normal mode coordinate, and $V^i(p_x)$ is the electron-phonon

TABLE I. Longitudinal sound velocities in Hg (in units of 10^3 m/s).

	Theoretical	Neutron scattering data	Ultrasonic data[a]
$c_{\rm 1D}$	2.9 ($k_F=0.97$ Å^{-1})	4.4 ± 0.8[b]	
$c_{\rm 3D}$	2.1 ($k_F=1.37$ Å^{-1})	2.45 (0,0,1)[c] 1.92 (1,0,0)[c]	1.76 (0,0,1) 1.80 (1,0,0)

[a]Reference 12. [b]Reference 10. [c]Reference 11.

matrix element. Calculation gives

$$V^I(p_x)=Z\left(\frac{N_I}{M}\right)^{1/2}\frac{ip_x}{A_\perp}\sum_{\mathbf{p}_\perp}\frac{4\pi e^2 f(\mathbf{p}_\perp)}{p_x^2+p_\perp^2} \quad . \tag{19}$$

We note that this involves $f(\mathbf{p}_\perp)$, while $u(p_x)$ in (4) involves $|f(\mathbf{p}_\perp)|^2$. However, using the fact that in our Gaussian approximation $|f(\mathbf{p}_\perp)|^2=f(\sqrt{2}\mathbf{p}_\perp)$, one has

$$\frac{1}{\sqrt{2}}V^I(\sqrt{2}p_x)=Z\left(\frac{N_I}{M}\right)^{1/2}ip_x u(p_x) \quad , \tag{20}$$

and thus

$$\tfrac{1}{2}|V^I(\sqrt{2}p_x)|^2=\Omega_{\rm pl}^2(p_x)u(p_x) \quad . \tag{21}$$

Consequently, the phonon dispersion relation in (13) can be written in the form

$$\omega^2=\Omega_{\rm pl}^2(p_x)+\tfrac{1}{2}|V^I(\sqrt{2}p_x)|^2\tilde{\chi}_{e,e}(p_x,\omega) \quad . \tag{22}$$

In the limit $p_x r_0 \ll 1$ (i.e., $p_x \ll k_F$), (19) simplifies to

$$V^I(p_x)=Z\left(\frac{N_I}{M}\right)^{1/2}ip_x 2e^2|\ln(p_x r_0)|+\cdots \quad , \tag{23}$$

and in this case (22) is equivalent to

$$\omega^2=\Omega_{\rm pl}^2(p_x)+|V^I(p_x)|^2\tilde{\chi}_{e,e}(p_x,\omega) \quad . \tag{24}$$

This type of expression is often written down in analogy to the 3D result[7] when discussing the softening of the phonon frequency at $p_x\simeq 2k_F$ due to the Peierls instability. However, the above calculation shows that (24) is not valid at *large* values of p_x in metallic chains when the electrons are described in the nearly-free-electron approximation (plane waves) as in Hg chains. [The tight-binding limit[4-6,8] is a different story. In that case, of course, $V^I(p_x)$ is not given by (19)]. The $p_x r_0 \ll 1$ results in (6) and (23) have been briefly noted by Levin, Mills, and Cunningham.[9,13] However, in discussing the phonon softening at $p_x=2k_f$ they used (24) rather than the correct RPA expression (22) for this model.

In place of the simple RPA expression (5) for the electronic response function, we may generalize the analysis to deal with the Tomonaga-Luttinger model.[5,14,15] Keeping only the small-momentum forward-scattering processes (g_2 and g_4 in the usual notation) one has[14,15]

$$\tilde{\chi}_{e,e}(p_x,\omega)=\frac{N(\epsilon_F)v_F^2p_x^2(1+\bar{g}_4-\bar{g}_2)}{\omega^2-v_F^2p_x^2[(1+\bar{g}_4)^2-\bar{g}_2^2]} \quad , \tag{25}$$

where

$$\begin{aligned}\bar{g}_4&\equiv\tfrac{1}{2}N(\epsilon_F)[g_{40}+u(p_x)]=\bar{g}_{40}+\bar{u}(p_x) \quad ,\\ \bar{g}_2&\equiv\tfrac{1}{2}N(\epsilon_F)[g_{20}+u(p_x)]=\bar{g}_{20}+\bar{u}(p_x) \quad .\end{aligned} \tag{26}$$

Here we have separated out the long-range Coulomb contribution (4) to g_2 and g_4.[14] For frequencies in the region (8), we can again use the static approximation to (25):

$$-\tilde{\chi}_{e,e}(p_x,\omega=0)=\frac{N(\epsilon_F)}{1+\bar{g}_{40}+\bar{g}_{20}+2\bar{u}(p_x)} \quad . \tag{27}$$

Using this in (12), the phonons are given by $\omega=\tilde{c}_{1D}p_x$, with

$$\tilde{c}_{1D}=\left(\frac{Z^2m}{M}\frac{N_I}{N_e}\right)^{1/2}(1+\bar{g}_{40}+\bar{g}_{20})^{1/2}v_F \tag{28}$$

in the limit $p_x r_0 \ll 1$ [where $u(p_x)$ is large]. The extra factor $(1+\bar{g}_{40}+\bar{g}_{20})^{1/2}$ is a typical renormalization factor that arises when dealing with a 1D interacting Fermi gas.[15]

In a separate paper[16] we discuss the electronic response function of an array of coupled chains. This can be used to show that the screening of the Hg ion-ion interaction in a given chain (which we have calculated in this paper) is not affected much by the electrons in *other* chains. A remaining problem is to obtain the long-wavelength screening of the Coulomb interaction between ions on *different* chains. Such results would provide microscopic estimates of the effective ion-ion interaction needed in theories of the phonon dynamics of the coupled Hg-chain system.[17,18]

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