The colour of charge density wave order

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Charge density waves and their optical response

The charge density wave (CDW) phase is a nice example whose theoretical proposal was proposed long before its experimental discoveries. The toy model considered by Fröhlich and Peierls turns out to be more powerful than it appeared [31, 32], which was thought to be a "doubly degenerate" surprise\(^1\) [33]. In this chapter, we will first introduce the mechanism of CDW phase formation from several different perspectives. Then we will discuss its typical optical response in the second part of this chapter.

2.1. THEORETICAL DESCRIPTIONS OF CDWs

There are various equivalent ways to approach CDW physics. One could start from a single particle Hamiltonian with the explicit electron-phonon coupling term or consider a BCS-type Hamiltonian with the CDW phase treated as a specific pairing Ansatz. Then either the divergence of the electronic susceptibility [34] or the softened phonon spectrum [35, 36] gives hints of the instability of the parental state. In order to remind the readers of the similarity between CDW and superconductivity, here we shall follow the BCS framework by using the mean-field treatment of the effective electron-electron interaction which causes the instability of the Fermi surface. Then the anomaly in the electronic and phonon spectra will be discussed in sequence.

\(^1\)Peierls wrote in his retrospective summary: ‘In this case the first surprise was in the mathematical result for the one-dimensional case; a second surprise was that this had some connection with reality.’
2.1.1. The BCS Instability of the Fermi Surface

Let us consider the electronic Hamiltonian with an effective electron-electron interaction term:

\[ H_e = \sum_{k,\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{N} \sum_{k,k',l,l',\sigma,\sigma'} V_{k,k',l,l',\sigma,\sigma'} c_{k\sigma}^\dagger c_{k'\sigma'}^\dagger c_{l\sigma'} c_{l\sigma} \]  

(2.1)

where \( V_{k,k',l,l',\sigma,\sigma'} \) is the effective interaction coefficient which could be positive or negative. Depending on the pairing Ansatz, this Hamiltonian could describe singlet/triplet superconductivity, charge density wave or spin density wave \([37,38]\). For example, the BCS Ansatz for a singlet superconductor would be:

\[
\langle c_{k'\uparrow}^\dagger c_{-k'\downarrow} \rangle \neq 0 \\
\langle c_{-k'\downarrow} c_{k'\uparrow} \rangle \neq 0
\]  

(2.2)

which describes the creation and annihilation of singlet Cooper pairs. With this Ansatz, the BCS Hamiltonian for the singlet superconductor is written as (\( V_{k,k',l,l',\sigma,\sigma'} < 0 \) in this case):

\[ H = \sum_{k,\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{N} \sum_{k,k'} V_{k,k'} c_{k\uparrow}^\dagger c_{k'\uparrow}^\dagger c_{-k'\downarrow} c_{-k\downarrow} \]  

(2.3)

Then the BCS Ansatz can be substituted into the Hamiltonian for the mean-field approximation. As the central topic of this thesis, CDW physics is given by a different set of Ansatz \([39]\):

\[
\Delta_k = -\frac{1}{N} \sum_{k',\sigma} V_{k,k'} \langle c_{k'\uparrow+q,\sigma} c_{k',\sigma} \rangle \\
\Delta_k^* = -\frac{1}{N} \sum_{k,\sigma} V_{k,k'} \langle c_{k\uparrow,\sigma} c_{k+q,\sigma} \rangle
\]  

(2.4)

This Ansatz describes that electron-hole pairs are formed from two states in the reciprocal space via a nesting vector \( \mathbf{q} \). We only keep the relevant terms of Eq. 2.1:

\[ H_e = \sum_{k,\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{N} \sum_{k,k',\sigma} V_{k,k'} c_{k+q,\sigma}^\dagger c_{k',\sigma}^\dagger c_{k',\sigma} c_{k,\sigma} \]  

(2.5)

We consider an arbitrary small interaction \( V_{k,k'} \), thus the mean-field approximation can be deployed:

\[
c_{k+q,\sigma}^\dagger c_{k,\sigma} = \langle c_{k+q,\sigma}^\dagger c_{k,\sigma} \rangle + \phi
\]  

(2.6)
\( \phi \) is the fluctuation of the electron-hole pair. Then the 4-operator interaction term can be expanded as\(^2\):

\[
\begin{align*}
    c_{k+q,\sigma}^\dagger c_{k',\sigma'}^\dagger c_{k',+q,\sigma} c_{k,\sigma'} &= \langle c_{k+q,\sigma}^\dagger c_{k,\sigma'} \rangle \langle c_{k',+q,\sigma}^\dagger c_{k',\sigma} \rangle + \\
    &+ \langle c_{k+q,\sigma}^\dagger c_{k',\sigma} \rangle \langle c_{k,\sigma'}^\dagger c_{k'+q,\sigma} \rangle + \phi^2
\end{align*}
\]

\(2.7\) Replace \( \phi \) with Eq. 2.6, we obtain:

\[
\begin{align*}
    c_{k+q,\sigma}^\dagger c_{k',\sigma'}^\dagger c_{k',+q,\sigma} c_{k,\sigma'} &= \langle c_{k+q,\sigma}^\dagger c_{k,\sigma'} \rangle c_{k',+q,\sigma}^\dagger c_{k',\sigma} + \\
    &+ c_{k+q,\sigma} c_{k',\sigma} \langle c_{k',+q,\sigma}^\dagger c_{k',\sigma}^\dagger c_{k'+q,\sigma} \rangle - \langle c_{k+q,\sigma}^\dagger c_{k,\sigma'} \rangle \langle c_{k',+q,\sigma}^\dagger c_{k',\sigma} \rangle + \phi^2
\end{align*}
\]

\(2.8\) Here we drop the \( \phi^2 \) as it is small in the mean-field approximation. Combine with the CDW Ansatz Eq. 2.4, we obtain the effective mean-field Hamiltonian for CDW:

\[
H_e = \sum_{k,\sigma} \xi_k c_{k,\sigma}^\dagger c_{k,\sigma} - \sum_{k,\sigma} \Delta_k c_{k,\sigma}^\dagger c_{k+q,\sigma} - \sum_{k,\sigma} \Delta_k^* c_{k+q,\sigma}^\dagger c_{k,\sigma} + \\
\frac{1}{N} \sum_{k,k',\sigma} V_{k,k'} \langle c_{k+q,\sigma}^\dagger c_{k,\sigma} \rangle \langle c_{k',+q,\sigma}^\dagger c_{k',\sigma} \rangle
\]

\(2.9\)

One can see that the second and the third terms have very similar form of a typical three-branch vertex of fermion-boson interaction, such as electron-phonon interaction term. We ignore the fourth term that only contributes a constant. Then the BCS Hamiltonian Eq. 2.9 of the charge density wave can be related with the classic Fröhlich Hamiltonian with the CDW ground state \([15, 31]\):

\[
H = \sum_{k,\sigma} \xi_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_q \hbar \omega_q b_q^\dagger b_q + \sum_{k,q,\sigma} g(k,q)(b_{-q}^\dagger + b_q) c_{k+q,\sigma}^\dagger c_{k,\sigma}
\]

\(2.10\)

If we take the average of the phonon field \( \langle b_{-q}^\dagger + b_q \rangle \) to obtain the mean-field electron Hamiltonian, the gap function \( \Delta \) of the Fröhlich Hamiltonian can be written as:

\[
\Delta = g(k,q) \langle b_{-q}^\dagger + b_q \rangle
\]

\(2.11\) so that the mean-field Fröhlich Hamiltonian has the same form with Eq. 2.9. By diagonising Eq. 2.9 one can obtain the electronic spectra. We rewrite it in the matrix product form:

\[
H = \sum_{k,\sigma} \begin{pmatrix} c_{k,\sigma}^\dagger & c_{k+q,\sigma}^\dagger \end{pmatrix} \begin{pmatrix} \xi_k & \Delta_k \\ \Delta_k^* & \xi_{k+q} \end{pmatrix} \begin{pmatrix} c_{k,\sigma} \\ c_{k+q,\sigma} \end{pmatrix}
\]

\(2.12\)

\(^2\)When we flip the order of the operators to make pairs in the Ansatz Eq. 2.4, a term \( c_{k+q,\sigma}^\dagger c_{k',+q,\sigma}^\dagger \delta_{k,k'} \) is obtained as the result of the anti-commutation relation of fermionic operators. It is only a single particle term which can be absorbed into the first term in Eq. 2.5. Thus we ignore it here, which does not change the physics to be discussed.
which can be diagonalised directly to obtain the electronic spectra\(^3\):

\[
E(k) = \frac{(\xi_{k+q} + \xi_k)}{2} \pm \sqrt{\frac{(\xi_{k+q} - \xi_k)}{2}^2 + |\Delta_k|^2}
\]  

(2.13)

Therefore, the two states at \(k\) and \(k+q\), one of which is filled and the other is empty, repel from each other. Such band repulsion lowers the energy on the electron side. Normally, it is the phonon that provides the finite momentum \(q\) to couple the two states, whose energy is small compared with the bandwidth. Thus, only the states that are near the Fermi surface are nested. The new eigenstates are linear compositions of the original states at \(k\) and \(k+q\).

### 2.1.2. The divergence in electronic response functions

This Fermi surface instability can also be measured by the electronic susceptibility, which can be evaluated by considering an electron-hole scattering process shown in Fig. 2.1.

![Figure 2.1: The density-density correlation function expanded with the random phase approximation (RPA) [39].](image)

The renormalised interaction \(U\) is represented as the circle on the left side, which includes all possible intermediate processes following the interaction part of the effective Hamiltonian Eq. 2.5. Each vertex in Fig. 2.1 can be expanded into an interaction boson line, which we ignore its internal structure here since the nesting instability does not rely on the origin of the effective electron-electron interaction. In the random phase approximation (RPA), the interaction is expanded in a series of electron-hole bubbles, i.e. the polarisation operator \(\Pi_0(q, \omega)\) [39]. As we shall see later, this RPA is identical to the mean-field approximation which we just used in Eq. 2.4.

\[
U(q, \omega) = V(q) + V(q)\Pi_0(q, \omega)V(q) + V(q)\Pi_0(q, \omega)V(q)\Pi_0(q, \omega)V(q) + ... = \frac{V(q)}{1 - \Pi_0(q, \omega)V(q)}
\]

(2.14)

The dielectric function \(\epsilon(q, \omega)\) is defined as the screening coefficient which

\(^3\)The diagonalisation is essentially doing a CDW version of the Bogolyubov transformation [39]:

\[
\begin{pmatrix}
\alpha_{k, \sigma} \\
\beta_{k+q, \sigma}
\end{pmatrix} =
\begin{pmatrix}
u_k & v_k \\
v_k & -u_k
\end{pmatrix}
\begin{pmatrix}
\alpha_{k+q, \sigma} \\
\beta_{k, \sigma}
\end{pmatrix}
\]
2.1. Theoretical descriptions of CDWs

renormalised the bare interaction $V$:

$$\varepsilon = \frac{V}{U} = 1 - V\Pi_0$$  \hspace{1cm} (2.15)

The polarisation operator $\Pi_0(q, \omega)$ is represented by electron-hole bubbles in Fig. 2.1, which is given by:

$$\Pi_0(q, \omega_n) = \frac{2T}{N} \sum_{\mathbf{k}, \epsilon_m} G_0(\mathbf{k}, \epsilon_m)G_0(\mathbf{k} + \mathbf{q}, \epsilon_m + \omega_n)$$  \hspace{1cm} (2.16)

The single bubble diagram is the mean field of the electron-hole pair as the CDW Ansatz shown in Eq. 2.4. The Matsubara Green’s function of a bare electron $G_0(\mathbf{k}, \epsilon_m)$ is given by:

$$G_0(\mathbf{k}, \epsilon_m) = \frac{1}{i\epsilon_m - \xi_k}$$  \hspace{1cm} (2.17)

By working out the summation of Matsubara frequency $\epsilon_m$ in Eq. 2.16 [40], one obtains:

$$\Pi_0(q, \omega_n) = \frac{2}{N} \sum_{\mathbf{k}} \frac{n(\mathbf{k}) - n(\mathbf{k} + \mathbf{q})}{\xi_k - (\xi_{k+q} + i\omega_n)}$$  \hspace{1cm} (2.18)

which can be calculated by inserting a specific electron spectrum. For tight-binding model in 1D, $\Pi_0(q, \omega_n)$ was shown to have the logarithmic divergence behaviour for $q \rightarrow 2k_F$ [39]:

$$\Pi_0(q, \omega = 0) \sim \frac{1}{\pi v_F} \frac{2k_F}{q} \ln\left|\frac{1 + q/2k_F}{1 - q/2k_F}\right|$$  \hspace{1cm} (2.19)

Therefore, the interaction $U(q, \omega_n)$ is strongly renormalised in the nesting condition. Starting from the homogeneous metal, we arrive at the anomaly of the electronic response function around $q$, which leads to the new CDW phase. The idea would be that the nesting vector $q$ now mixes states $|k\rangle$ and $|k + q\rangle$, which strongly enhanced the transition probability between these states.

In order to give readers a clearer picture, we now discuss the Fermi surface instability and the electronic susceptibility anomaly in the half-filled 1D tight-binding model. The 1D nesting vector $Q$, which is able to couple electron states with hole states over a large area in the reciprocal space, is $2k_F$. The paired states repel to give rise to the CDW gap as shown in Fig. 2.2. At the same time, the size of the Brillouin zone is reduced from $\frac{2\pi}{a}$ to $\frac{\pi}{a}$. 
2. Charge density waves and their optical response

Figure 2.2: (a) The dispersion relation of the half-filled 1D atomic chain with the nesting vector $Q$. (b) The mixture of the two states at the boundary of the Brillouin zone opens the CDW gap. The dashed line denotes the band folding after the Brillouin zone is changed.

On one hand, the CDW gap is opened in the reciprocal space, and in the real space, charge density modulation is induced on the other hand. The charge density in real space $\rho_x$ can be obtained through Fourier transform:

$$\rho_x = \langle c_x^+ c_x \rangle = \frac{1}{N} \sum_{k,q} \langle c_k^+ c_{k+q} \rangle e^{-iqx}$$

(2.20)

$\langle c_k^+ c_{k+q} \rangle$ is only nonzero for the nesting case $q = Q$ as in the CDW Ansatz Eq. 2.4. If we neglect the $k$-dependence of the coupling coefficient $V_k$ and the CDW gap $\Delta_k$, the real space charge density is shown as:

$$\rho_x = \frac{1}{N} \frac{\Delta}{V} e^{-iQx}$$

(2.21)

which has the periodic modulation with the nesting wave vector $Q$. The real space charge density wave can be observed using microscopic techniques. The real space periodicity of the lattice is enlarged to $\frac{2\pi}{Q}$ as the reduced Brillouin zone suggests.

2.1.3. The renormalisation of the phonon spectra

As discussed above, phonons could provide the finite nesting vector $Q$ and energy $\omega$ to couple the electron-hole pairs, which leads to the divergence of the polarisation operator $\Pi_0$. In the real materials, the electron-phonon coupling always exists even for the materials which are said to have alternative CDW mechanisms [41–43]. Therefore, the strongly modified phonon spectra are almost always associated with the CDW order.

As mentioned before, the electron-phonon coupling term Eq. 2.10 have the similar form with the mean-field BCS Hamiltonian Eq. 2.9:

$$H_{int} = -\frac{g}{N} \sum_{k,q,\sigma} b_q c_{k+q,\sigma}^+ c_{k,\sigma} + h.c.$$
where we ignore the $k$-dependence of the coupling coefficient $g$ for simplicity. A recent study shows that the $k$-dependence of $g$ is important when considering the real materials [14], while it does not affect the physics we are going to discuss. The phonon’s propagator is then renormalised by the electron-phonon coupling. For small $g$, we could consider the RPA method likewise. Fig. 2.3 shows the recursive form of the RPA expansion of the electron-hole bubbles. Thus the Green’s function of the dressed phonon $D(q, \omega_n)$ is then the function of the polarisation operator $\Pi(q, \omega_n)$ and the Green’s function of the bare phonon $D_0(q, \omega_n)$ [44]:

\[
D(q, \omega_n) = D_0(q, \omega_n) + D_0(q, \omega_n)g^2 \Pi_0(q, \omega_n)D(q, \omega_n)
\]

\[
= \frac{1}{D_0^{-1}(q, \omega_n) - g^2 \Pi_0(q, \omega_n)}
\]

(2.23)

The Green’s function of the bare phonon $D_0(q, \omega) = \frac{1}{\omega_n^2 + \Omega_0^2 + g^2 \Pi_0(q, \omega_n)}$ is plugged in to obtain:

\[
D(q, \omega_n) = -\frac{1}{\omega_n^2 + \Omega_0^2 + g^2 \Pi_0(q, \omega_n)}
\]

(2.24)

Thus the retarded Green’s function can be obtained by doing an analytical continuation of Matsubara frequency, which directly gives us the renormalised spectra of the dressed phonon:

\[
D_R(q, \omega) = \frac{1}{\omega^2 - \Omega_0^2 - g^2 \Pi_0(q, \omega)}
\]

(2.25)

The spectra of dressed phonon is given by the pole in a self-consistent form:

\[
\Omega_q^2 = \Omega_0^2 + g^2 \Pi_0(q, \Omega_q)
\]

(2.26)

The polarisation operator $\Pi_0(q, \Omega_q)$ is negative according to Eq. 2.18. Thus the renormalised energy is smaller than the bare phonon energy. More specifically, the enhancement of $\Pi_0(q, \Omega_q)$ shown in the previous section 2.1.2 gives rise to a dip in the phonon spectra, which is called phonon softening. The phase transition happens when the phonon energy $\Omega_Q$ at the nesting vector $Q$ reduces to zero, which suggests the structural instability of the normal state:

\[
0 = \Omega_0^2 + g^2 \Pi_0(q, 0)
\]

(2.27)

Here we can see that the structural instability is obtained as long as the product of the coupling strength $g$ and the polarisation operator $\Pi_0(q, \Omega_q)$ is strongly enhanced at proper $q$. Therefore, the divergence of $\Pi_0(q, \Omega_q)$, which suggests
the perfect nesting on the Fermi surface, is not necessary if we also have en-
hanced electron-phonon coupling near to the nesting vector.

By solving Eq. 2.27, one can obtain the equation of $T_c$ of the CDW phase. Using the simplest example of a half-filled 1D chain:

$$\begin{align*}
\mu &= 0 \\
2k_F &= \pi / a \\
\epsilon_{k+2k_F} &= -\epsilon_k
\end{align*}$$

Combining with the 1D polarisation operator Eq. 2.18, we obtain:

$$1 = \frac{g^2}{\Omega_0^2}N \sum_k \frac{1}{\epsilon_k} \tanh \frac{\epsilon_k}{2k_BT_c}$$

### 2.1.4. Peierls Mechanism

We already show that the instability of the normal metal is so intrinsic that arbitrary small interaction could induce the reconstruction of the Fermi surface as well as the lattice structure. Since the nesting vector $Q$ is normally provided by phonons, the feasibility of the phase transition will depend on the competition between the energy earned from the electronic band repulsion and the energy cost from the lattice distortion. In this section, we will evaluate the CDW phase transition from the energy perspective following the derivation in [44].

The Landau free energy of the system with Hamiltonian Eq. 2.22 consists of electronic and lattice parts:

$$F = \Omega_e + E_{lat}$$

where the grand canonical potential $\Omega_e$ can be obtained from the grand canonical partition function:

$$\Omega_e = -k_BT \ln \Xi_e$$

The grand partition function can be calculated for the system with the electron spectra $E_k$:

$$\Xi_e = \prod_{k \in \text{1st BZ}} (1 + e^{-\beta E_k})^2 (1 + e^{\beta E_k})^2$$

where "2" in the exponent comes from the spin degeneracy. Thus we could work out Eq. 2.31:

$$\Omega_e = -4k_BT \sum_{k \in \text{1st BZ}} \ln(2\cosh \frac{\beta E_k}{2})$$

Here $E_k$ is the electronic spectra in the CDW phase obtained in Eq. 2.13. In the 1D chain case we consider, the mirror symmetry of the spectrum (Eq. 2.28) simplifies the formula:

$$E_k = \sqrt{\epsilon_k^2 + \Delta^2}$$
As for the lattice part, the phonon energy could be evaluated using \( H_{\text{lat}} = \frac{1}{2} \sum_q \Omega_q^2 P^\dagger_q P_q \) where \( P_q \) is the Fourier transform of the lattice distortion. The lattice distortion is related with the creation and annihilation operators of the phonon:

\[
P_q = b_q + b^\dagger_{-q}
\]  

(2.35)

As mentioned before, the average of the phonon operator gives the mean-field approximation of the Fröhlich Hamiltonian:

\[
\Delta = g \langle b^\dagger_{-q} + b_q \rangle
\]  

(2.36)

Therefore, the lattice distortion energy can be calculated using the average of the operator \( \langle P^\dagger_q P_q \rangle \):

\[
E_{\text{lat}} = \frac{N \Omega_0^2 \Delta^2}{g^2}
\]  

(2.37)

The minimisation of the free energy \( \frac{\partial F}{\partial \Delta} \) gives the gap function of the CDW phase:

\[
\frac{2g^2}{\Omega_0^2 N} \sum_{k \in 1^{st}\text{ BZ}} \frac{1}{E_k} \tanh \frac{E_k}{2k_B T} = 1
\]  

(2.38)

Peierls transition thus happens when electronic energy saving prevails over the structural energy cost. Now we compare this gap function with Eq. 2.29 obtained in the last section. We should notice that the coefficient '2' in front of Eq. 2.38 comes from the reduction of the Brillouin zone in the CDW phase. The \( T_c \) function Eq. 2.29 sums over the Brillouin zone of the normal state which is twice as large as the Brillouin zone in the CDW phase. Then we could find that Eq. 2.29 is indeed the gap function Eq. 2.38 at \( T = T_c \) when \( \Delta = 0 \).

The gap function of the CDW phase has the same form as the BCS gap function [45]:

\[
V_0 \sum_k \frac{1}{E_k} \tanh \frac{E_k}{2k_B T} = 1
\]  

(2.39)

Likewise, for the weakly coupled CDW phase we find the same kind gap to \( T_c \) relation:

\[
\frac{2|\Delta|}{k_B T_c} \approx 3.5
\]  

(2.40)

Here one can see the close relationship between the BCS superconductivity and the weakly coupled CDW from the identical form of their gap functions. Both phenomena are included in the picture of the Fermi surface instability as discussed at the beginning of this chapter. Their distinctive pairing mechanisms account for the more detailed differences between these two states. In the next section, we shall discuss their connections and differences from another perspective.
2.2. OPTICAL RESPONSE OF CHARGE DENSITY WAVES

The previous section introduces the theoretical description of the CDW phase from a microscopic perspective. The reconstruction of the Fermi surface as well as the band structure naturally opens a window for detecting the CDW phase with optics. The phenomenological view of CDW also gives insight into the optical response of the CDW without going into the detailed calculations of the electronic structure.

In the scenario of Peierls mechanism, the homogeneous electron gas in a normal metal changes to a periodically modulated charge density wave. The continuous translational invariant symmetry of charge density is then spontaneously broken. Instead, a new discrete translational symmetry is established. As suggested in Eq. 2.21, we could use a sinusoidal function to describe the periodic charge density wave in the real space:

$$\rho_e = \rho_0 \cos(Q \cdot x + \phi_0)$$  \hspace{1cm} (2.41)

where $Q$ is the nesting vector. As the result of spontaneous symmetry breaking, the phase of the charge density $Q \cdot x + \phi_0$ is not well defined. This suggests that the relative position between the periodic charge density and the lattice is a free parameter. Thus, the collective motion of the charge density wave relative to the lattice background gives rise to a gapless excitation, i.e. the Goldstone mode, according to the Goldstone theorem [46]. The charge density can slide as a whole in the background of the lattice. Thus it is also called sliding mode. One could anticipate that such collective charge motion responds to light. The total displacement of the charge density relative to the lattice background involves the change of dipole moments, which makes the Goldstone mode IR active.

2.2.1. THE DYNAMICS OF THE GOLDSTONE MODE

The CDW gap $\Delta$ is a good order parameter of the CDW phase. Its phase fluctuation corresponds to the gapless excitation Goldstone mode (phason) and its amplitude fluctuation gives rise to the gapped excitation Higgs mode (amplitudon) [47]:

$$\Delta(x, t) = (\Delta_0 + \delta(x, t)) e^{i\phi(x, t)}$$  \hspace{1cm} (2.42)

As mentioned above, the phason mode describes the relative motion between the charge density and the lattice background, which is IR active. The Higgs mode, however, is only Raman active since the oscillation of the amplitude of the charge density does change the dipole moment. The Higgs mode is therefore not observed in the experiments shown in this thesis. We will focus on the dynamics of the phason mode then.

By expanding the free energy with respect to the order parameter, one can write down the Lagrangian equation for $\phi(x, t)$\textsuperscript{4}. For simplicity, the following

---

\textsuperscript{4}For a detailed derivation of the equation of motion Eq. 2.43 as well as the conductivity equation, please refer to ref. [47] Chap. 6 & Chap. 9.
derivation is done for the typical 1D case, where the nesting vector is the $2k_F$. With applied electric field $E(q, \omega)$, the equation of motion of the Goldstone mode is then given by [47]:

$$\frac{d^2 \phi}{dt^2} - \hbar v_F^2 \frac{m}{m^*} \frac{d^2 \phi}{dx^2} = \frac{2k_F e}{m^*} E(q, \omega)$$  \hspace{1cm} (2.43)

$m$ is the band mass while $m^*$ is the renormalised mass including the electron-phonon interaction, and $v_F$ is the Fermi velocity. The charge current of the phason model can be obtained using Eq. 2.41:

$$j = -en\dot{x} = e \frac{n_{\text{charge}} d\phi}{2k_F} \frac{d}{dt}$$  \hspace{1cm} (2.44)

The conductivity is defined as the susceptibility of the current in response to the applied electric field:

$$j = \sigma E$$  \hspace{1cm} (2.45)

Combining Eq. 2.43, 2.44 and 2.45, we obtain the conductivity of the Goldstone mode:

$$\sigma(q, \omega) = \frac{m}{4\pi m^*} \frac{i\omega \omega_p^2}{\omega^2 - \hbar v_F m^* q^2}$$  \hspace{1cm} (2.46)

in which the plasma frequency $\omega_p = \frac{4\pi n_0 e^2}{m}$. The momentum of photon $q$ is generally very small compared with any length scale in the reciprocal space of the solids. By neglecting the $q$ related term:

$$\sigma(\omega) = \frac{m \omega_p^2}{4\pi m^*} \lim_{\omega \to 0} \frac{i}{\omega + i\epsilon} = \frac{m \omega_p^2}{4\pi m^*} \left( \pi \delta(\omega) + \frac{i}{\omega} \right)$$  \hspace{1cm} (2.47)

Therefore, we notice that the Goldstone mode contributes a Delta function to the real part of the optical conductivity $\sigma_1(\omega)$ and the $\frac{1}{\omega}$ divergence to the imaginary part of the optical conductivity $\sigma_2(\omega)$. $\sigma_1(\omega)$ and $\sigma_2(\omega)$ naturally follow the Kramers-Kronig relation. This distinct behaviour allows us to distinguish the Goldstone mode from the normal electronic contributions in the optical spectra.

Generally, the dielectric function $\varepsilon(\omega)$ is connected with the optical conductivity $\sigma(\omega)$:

$$\varepsilon(\omega) = i \frac{4\pi \sigma(\omega)}{\omega} + 1$$  \hspace{1cm} (2.48)

Thus the dielectric function of the phason mode is:

$$\varepsilon(\omega) = 1 - \frac{m}{m^*} \frac{\omega_p^2}{\omega^2} + i \frac{\pi m \omega_p^2}{m^*} \frac{\delta(\omega)}{\omega}$$  \hspace{1cm} (2.49)

Compared to the $\delta(\omega)$ peak in $\sigma_1(\omega)$ and $\varepsilon_2(\omega)$ that is local and resides at the ultra-low energy range, the non-local asymptotic behaviour in $\sigma_2(\omega)$ and $\varepsilon_1(\omega)$
Charge density waves and their optical response is much easier to probe and examine:

\[
\sigma_{2,\text{CDW}}(\omega) \propto \frac{1}{\omega}
\]
\[
\varepsilon_{1,\text{CDW}}(\omega) \propto \frac{1}{\omega^2}
\] (2.50)

As the comparison, the single particle optical response has a different asymptotic behaviour at low energy range\(^5\):

\[
\lim_{\omega \to 0} \sigma_{2,\text{DL}}(\omega) \propto \omega
\]
\[
\lim_{\omega \to 0} \varepsilon_{1,\text{DL}}(\omega) \sim \text{Const.}
\] (2.51)

We now compare the different optical response functions of the normal metal and the CDW state. Fig. 2.4(a) shows the low energy \(\sigma_1(\omega)\). The single particle response gives rise to the Drude peak in the normal metal, and the CDW phason mode accounts for the \(\delta(\omega)\) function at zero energy accompanied by an optical gap. In panel (b), \(\sigma_2(\omega)\) of the CDW phase diverges as \(\frac{1}{\omega}\) while the Drude-Lorentz response converges to zero. In panel (c), we show the function \(-\omega^2\varepsilon_1(\omega)\). As we know from Eq. 2.50 and 2.51, this function converges to a finite number for the CDW phase, which is proportional to the spectral weight of the phason mode. The single particle contribution converges to zero, which allows us to separate the phason response from other single particle responses. We shall use this feature to study a specific material in Chap. 4. Finally, because of the existence of the optical gap and the narrow phason mode, the reflectivity approaches 1 below \(2\Delta\), reflecting the absence of excitations below the gap.

It is not a coincidence that a similar infrared response has been generally observed in superconductors, where the optical gap opens in \(\sigma_1(\omega)\) and the similar unity reflectivity plateau below the gap is formed [49–52]. We have already emphasized the connection between CDW and superconductivity from the perspective of the Fermi surface instability as their common origin. The infrared spectra based on the Goldstone theorem suggest a different angle to the similarity between CDW and superconductivity. Both of them are the results of the spontaneous symmetry breaking that gives rise to the emergence of the charged Goldstone boson. The difference between these two phenomena can thus be found in the different symmetry they break. For CDW, it is the translational symmetry that is broken, while for superconductivity it is the global \(U(1)\) symmetry of the phase [46].

The \(\delta(\omega)\) function in \(\sigma_1(\omega)\) gives unique transport behaviour. By definition, it is with zero width, which describes a collective excitation with an infinite lifetime and free from any scattering process. The conductivity is infinite at \(\omega = 0\), which gives zero DC resistivity, while the spectral weight, i.e. the integral of \(\sigma_1(\omega)\) over \(\omega\) is still finite. One would expect a superconductivity-like phase transition where the resistivity drops to zero below \(T_c\). However,

\(^5\)The single particle optical response is discussed in the section 3.2.1, and its asymptotic behaviour can be obtained from the Drude-Lorentz model Eq. 3.14
2.2. Optical response of charge density waves

Figure 2.4: The optical functions of the normal metal and the CDW state calculated using Zimmermann model [48]. Here a small width is added to the phason mode to make it observable in the graph. $\frac{T}{T_c} \approx 0$.

materials in the CDW phase always have a finite DC resistivity. The CDW phase transition generally gives rise to a small kink to the DC resistivity $R(T)$ at $T_c$ instead of jumping to zero resistivity.

Several possibilities could account for the finite DC resistivity of the CDW state. In the incommensurate CDW phase, the periodicity of the charge density modulation does not match the lattice periodicity. The phason mode can be gapped and scattered due to the fragility of the long-range order with respect to impurities. In this case, the translational invariance symmetry is only broken locally. Domains are formed where each domain is associated with different order parameters. As the result, the Goldstone mode is no longer massless, and its interaction with impurities also introduces the finite lifetime [53]. As for the commensurate CDW case, the phase of the order parameter $\phi$ is not translational invariant due to the match of the periodic charge density and the lattice. Thus the sliding phason mode is pinned by the lattice, which also gaps the phason mode.

2.2.2. Phason observed in materials

Due to impurities and commensurability, the CDW phason mode cannot give rise to zero DC resistivity. Its eigenfrequency is typically in the GHz range. Thus it is not trivial to observe the phason mode directly.

The first detection of the phason mode in a CDW material is quasi-1D NbSe$_3$, which features the strongly non-Ohmic DC conductivity and anom-
Charge density waves and their optical response

lous AC transport behaviour in the microwave range [54, 55]. Applying a moderate DC electric field provides energy to de-pin the phason mode, which gives nonlinear IV characteristics. More direct measurement on phason is to use millimeter wave configurations [56]. In the AC impedance measurements, the complex conductivity of materials can be inferred and the phason mode can be directly observed. In the 1980s and 1990s, several groups of CDW materials have been shown to feature pinned phason modes in millimeter-wave measurements. Examples are doped blue bronze $K_{0.3}Mo_{1-x}W_xO_3$, Bechgaard salts $(TMTSF)_2PF_6$, transition metal trichalcogenides $TaS_3$ and Weyl semimetal $(TaSe_4)_2I$ [57–62]. The common feature of these materials is that they all have quasi-1D crystal structures, where the Peierls mechanism is most favourable to be applied.

![Figure 2.5: The millimeter wave range reflectivity and $\sigma_1(\omega)$ in the millimeter wave range. The reflectivity curves on the left panel are calculated using the measured complex conductivity. On the right panel, $\sigma_1(\omega)$ curves are with two peaks, in which the one with the lowest energy is identified as the phason mode while the other one’s origin is controversial. The figures are taken from [58]](image)

To give readers some idea about the phason mode, its eigenfrequency observed in the materials mentioned above, as shown in the right panel of Fig. 2.5, is $1 \sim 10 \text{ cm}^{-1}$. Fitted with the Lorentzian function, the strength of the phason mode $\omega^2_{ph}$ $30000 \sim 400000 \text{ cm}^{-2}$ and broadening $\sim 1 \text{ cm}^{-1}$ [58] are extracted.

On the other hand, the presence of the phason mode in materials with 2D or 3D CDWs is seldom mentioned. Measurements on quasi-2D materials MoSe$_2$ and 1T-TaS$_2$ indirectly suggest that the phason mode might be responsible for the anomalous transport behaviour [23, 63, 64], where the non-Ohmic I-V
curves are observed. Apart from that, early optics measurements on bulk 2H-TaSe$_2$ and 1T-TaS$_2$ were used to infer the existence of the phason mode from the spectral weight transfer analysis [65], while later measurements with higher precision rule out this interpretation [66, 67]. Concerning the work presented in this thesis, we demonstrate conclusively that the phason mode contributes to the optical conductivity of 1T-VSe$_2$ in Chap. 4.

One question might naturally appear here: Since the phason mode observed in the real materials are all pinned and broadened by interaction, does the analysis of the optical response function in the previous section still hold? The answer is yes. One could show that the phason mode described by a sharp Lorentzian peak at very low energy still gives qualitatively the same results as shown in Fig. 2.4 at the energy range far above$^6$. This is essential for the later analysis in VSe$_2$, which shall be discussed in Chap. 4.

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$^6$In other words, in the limit of $\omega_{\text{observing}} \gg \omega_0$ and $\omega_0 \gg \gamma$, where $\omega_0$ and $\gamma$ are the eigenfrequency and the scattering rate of the phason mode.