1. Phonons at low temperatures

In the long-wave limit, the dispersion relations of the $\nu$-th acoustic branch of a three-dimensional crystal can be written as

$$\omega_{\nu}^2(q) = v_{\nu x}^2 q_{\nu x}^2 + v_{\nu y}^2 q_{\nu y}^2 + v_{\nu z}^2 q_{\nu z}^2.$$  

(Speaking generally, the appropriate choice of the Cartesian axes is unique for each mode.) This expression defines the thermodynamic properties of the phonon system at sufficiently low temperatures.

(a) Find corresponding expressions for thermal energy, entropy, and heat capacity.

(b) Consider the same problem in one and two dimensions.

(c) Compare the three-dimensional results to their photon (black body radiation) counterparts.

(d) Suppose the long-wave acoustic dispersion is written in a generic form:

$$\omega_{\nu}^2(q) = \sum_{ij} \gamma_{ij}(\nu) q_i q_j.$$  

How does one find $v_{\nu x}$, $v_{\nu y}$, and $v_{\nu z}$ from the matrix $\gamma_{ij}(\nu)$? How can the above-discussed thermodynamic functions be written in terms of the matrices $\gamma_{ij}(\nu)$ (in any dimensions)?

Solution

(a) First, calculate the spectral density function $D(\varepsilon)$:

$$D(\varepsilon) = \sum_{\nu=1}^{3} D_\nu(\varepsilon), \quad D_\nu(\varepsilon) = \frac{V}{(2\pi)^3} \int_{BZ} d^3 q \delta(\varepsilon - \omega_{\nu}(q)).$$
Introduce the new integration variable, \( p \), such that

\[
q_i = p_i / v_{\nu i}.
\]

Then take into account that we are dealing with the limit of low temperatures where the relevant value of \( \varepsilon \) are small enough so that the upper limit of the integration over \( p \) can be safely set equal to infinity. We get

\[
D_\nu(\varepsilon) = \frac{V}{2\pi^2 \Delta_\nu} \int dp \, p^2 \delta(\varepsilon - p) = \frac{V \varepsilon^2}{2\pi^2 \Delta_\nu}, \quad \Delta_\nu = v_{\nu x} v_{\nu y} v_{\nu z}.
\]

Hence,

\[
D(\varepsilon) = \frac{V \varepsilon^2}{2\pi^2 \Delta_*}, \quad \frac{1}{\Delta_*} = \frac{1}{\Delta_1} + \frac{1}{\Delta_2} + \frac{1}{\Delta_3}.
\]

Then calculate the free energy (the low-temperature limit allows us to formally extend the integration over \( \varepsilon \) to infinity and then non-dimensionalize the integral by introducing the new integration variable \( x = \varepsilon / T \)):

\[
F = T \int d\varepsilon D(\varepsilon) \ln \left(1 - e^{-\varepsilon / T}\right) = \frac{VT^4}{2\pi^2 \Delta_*} \int_0^\infty dx \, x^2 \ln (1 - e^{-x}) = -\frac{\pi^2 VT^4}{90 \Delta_*}.
\]

Here we used the known integral

\[
\int_0^\infty dx \, x^2 \ln (1 - e^{-x}) = -\frac{\pi^4}{45}.
\]

Now we straightforwardly calculate \( S, E, \) and \( C_V \):

\[
S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{2\pi^2 VT^3}{45 \Delta_*}
\]

\[
E = F + TS = \frac{\pi^2 VT^4}{30 \Delta_*},
\]

\[
C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{2\pi^2 VT^3}{15 \Delta_*}.
\]

(b) In \( d \) dimensions we have

\[
D(\varepsilon) = \sum_{\nu=1}^d D_\nu(\varepsilon), \quad D_\nu(\varepsilon) = \frac{V}{(2\pi)^d} \int_{BZ} d^d q \, \delta(\varepsilon - \omega_\nu(q)),
\]
and using the same type of argument as in $d = 3$, we get

$$D_{\nu}(\varepsilon) = \frac{A_d \varepsilon^{d-1}}{(2\pi)^d \Delta_{\nu}}, \quad \Delta_{\nu} = \prod_{j=1}^{d} v_{\nu j},$$

$$D(\varepsilon) = \frac{A_d \varepsilon^{d-1}}{(2\pi)^d \Delta_{*}}, \quad \frac{1}{\Delta_{*}} = \sum_{\nu=1}^{d} \frac{1}{\Delta_{\nu}},$$

where

$$A_1 = 2, \quad A_2 = 2\pi, \quad A_3 = 4\pi.$$

Here we took into account that

$$\int d^d p \delta(\varepsilon - p) = A_d \int_{0}^{\infty} dp p^{d-1} \delta(\varepsilon - p) = A_d \varepsilon^{d-1}.$$

For the free energy we then have

$$F = -\frac{A_d I_d}{(2\pi)^d \Delta_{*}} \frac{V}{T^{d+1}}, \quad I_d = -\int_{0}^{\infty} dx x^{d-1} \ln (1 - e^{-x}).$$

Now we calculate $S$, $E$, and $C_V$:

$$S = -\left( \frac{\partial F}{\partial T} \right)_V = \frac{(d + 1) A_d I_d}{(2\pi)^d \Delta_{*}} \frac{V}{T^d},$$

$$E = F + TS = \frac{d A_d I_d}{(2\pi)^d \Delta_{*}} \frac{V}{T^{d+1}},$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{d(d + 1) A_d I_d}{(2\pi)^d \Delta_{*}} \frac{V}{T^d}.$$

(c) For photons we have two rather than three branches and all the velocities are equal to the speed of light $c$. Hence, to convert all the relations into their black-body radiation analogs we just need to use

$$\frac{1}{\Delta_{(*)}} = \frac{1}{c^3} + \frac{1}{c^3} = \frac{2}{c^3}.$$
(d) Without loss of generality, we assume that the matrix $\gamma_{ij}$ is symmetric, because we can always symmetrize it,

$$\gamma_{ij} \rightarrow (\gamma_{ij} + \gamma_{ji})/2,$$

without changing the value of

$$\omega^2_\nu(q) = \sum_{ij} \gamma_{ij}(\nu)q_iq_j.$$

Then we rotate the axes in the reciprocal space (below $U_{is}$ is a real unitary matrix the explicit form of which is not relevant),

$$q_i = \sum_s U_{is} \tilde{q}_s,$$

so that in the new basis the matrix is diagonal,

$$\tilde{\gamma}_{sr} = \sum_{ij} \gamma_{ij} U_{is} U_{jr} = v^2_s \delta_{sr}$$

and we arrive at the above-discussed form

$$\omega^2_\nu(\tilde{q}) = \prod_{j=1}^d v^2_{\nu j} \tilde{q}_{\nu j}^2.$$

Finally, we recall that the rotation of the matrix does not change its determinant, and, since

$$\Delta_\nu = \prod_{j=1}^d v_{\nu j} = \sqrt{\det \tilde{\gamma}},$$

realize that we can use all the above-derived results by simply writing

$$\Delta_\nu = \sqrt{\det \gamma}.$$

2. Van Hove singularities

The points of extrema (maxima, minima, and saddle points) of the dispersion $\omega(q)$ result in the (Van Hove) singularities of the spectral function
In 3D, the behavior of $\omega(q)$ at an extremal point $\omega_\ast = \omega(q_\ast)$ can be represented as (note that $\omega_\ast \neq 0$)

$$\omega(q) = \omega_\ast + \lambda_x(q_x - q_{x\ast})^2 + \lambda_y(q_y - q_{y\ast})^2 + \lambda_z(q_z - q_{z\ast})^2,$$

provided the Cartesian axes are chosen appropriately. There are four different cases defined by the signs of $\lambda$’s:

(i) Local minimum $(+++)$,
(ii) Local maximum $(- - -)$,
(iii) and (iv) Saddle points $(+ + -)$ and $(+ - -)$.

(a) For each of the cases (i)-(iv), find corresponding type of Van Hove singularity of the function $D(\varepsilon)$.

(b) Do the same for one- and two-dimensional cases.

**Solution**

We start with shifting and re-scaling the wave vectors (the procedure is the same in any dimensions):

$$q_j = q_{j\ast} + p_j / \sqrt{|\lambda_j|} \quad (j = 1, \ldots, d).$$

As a result we have

$$\omega(p) = \omega_\ast + \xi_1 p_1^2 + \ldots + \xi_d p_d^2,$$

where

$$\xi_j = \lambda_j / |\lambda_j| = \pm 1.$$

Then for the density of states (for a given branch) we will have

$$D(\varepsilon) = \frac{V}{(2\pi)^d} \int_{BZ} d^d q \delta(\varepsilon - \omega(q)) = .$$

$$= \frac{V}{(2\pi)^d \Lambda} \int d^d p \delta(\varepsilon - \omega_\ast - \xi_1 p_1^2 - \ldots - \xi_d p_d^2),$$

where

$$\Lambda = \sqrt{|\lambda_1 \lambda_2 \cdots \lambda_d|}.$$
We do not care about the amplitudes, only about the shape of the singularities, and from now on will be omitting all the pre-factors:

\[ D(\varepsilon) \propto \int d^d p \delta(\varepsilon - \omega_s - \xi_1 p_1^2 - \ldots - \xi_d p_d^2). \]

We are interested only in the behavior of \( D(\varepsilon) \) at \( \varepsilon \to \omega_s \), so that the limits of integration are irrelevant (can be set equal to infinity).

(i) (a)-(b). Local minimum in all dimensions.

We have

\[ D(\varepsilon) \propto \int dp \, p^{d-1} \delta(\varepsilon - \omega_s - p^2) \propto \begin{cases} 0, & \varepsilon \leq \omega_s, \\ (\varepsilon - \omega_s)^{d/2-1}, & \varepsilon > \omega_s. \end{cases} \]

In particular,

\[ \varepsilon > \omega_s : \quad D(\varepsilon) \propto \begin{cases} \sqrt{\varepsilon - \omega_s}, & d = 3, \\ \text{const}, & d = 2, \\ 1/\sqrt{\varepsilon - \omega_s}, & d = 1. \end{cases} \]

That is in 3D we have a square-root cusp, in 2D we have a jump by a constant, and in 1D there is a one-over-the-square-root singularity.

(ii) (a)-(b). Local maximum in all dimensions.

This case is very close to the previous one, because \( \delta(\varepsilon - \omega_s + p^2) = \delta(\omega_s - \varepsilon - p^2) \), and we just need to change \( \varepsilon \leftrightarrow \omega_s \):

\[ D(\varepsilon) \propto \int dp \, p^{d-1} \delta(\omega_s - \varepsilon - p^2) \propto \begin{cases} 0, & \varepsilon \geq \omega_s, \\ (\omega_s - \varepsilon)^{d/2-1}, & \varepsilon < \omega_s. \end{cases} \]

That is

\[ \varepsilon < \omega_s : \quad D(\varepsilon) \propto \begin{cases} \sqrt{\omega_s - \varepsilon}, & d = 3, \\ \text{const}, & d = 2, \\ 1/\sqrt{\omega_s - \varepsilon}, & d = 1. \end{cases} \]
and, similarly to the previous case, in 3D we have a square-root cusp, in 2D we have a jump by a constant, and in 1D there is a one-over-the-square-root singularity.

(iii) (a) Saddle point (+ + −).

\[ D(\varepsilon) \propto \int dp_x dp_y dp_z \delta(\varepsilon - \omega_\ast - p_x^2 - p_y^2 + p_z^2). \]

Integrate over \( dz \):

\[ \int dp_z \delta(\varepsilon - \omega_\ast - p_x^2 - p_y^2 + p_z^2) \propto \begin{cases} (p_x^2 + p_y^2 + \omega_\ast - \varepsilon)^{-\frac{1}{2}}, & p_x^2 + p_y^2 + \omega_\ast - \varepsilon > 0, \\ 0, & p_x^2 + p_y^2 + \omega_\ast - \varepsilon \leq 0. \end{cases} \]

Consider the case \( \varepsilon < \omega_\ast \). Here we have (introducing polar coordinates in the \( xy \) plane):

\[ D(\varepsilon) \propto \int_0^{\text{cutoff}} \frac{d(\rho^2)}{\sqrt{\rho^2 + \omega_\ast - \varepsilon}} \propto \int_0^{\text{cutoff}} \frac{dt}{\sqrt{t + \omega_\ast - \varepsilon}} \quad (\varepsilon < \omega_\ast). \]

Hence,

\[ D(\varepsilon) \propto \sqrt{t + \omega_\ast - \varepsilon}\bigg|_0^{\text{cutoff}} \propto (\text{regular part}) - \sqrt{\omega_\ast - \varepsilon} \quad (\varepsilon < \omega_\ast). \]

That is we get an upward square-root cusp at \( \varepsilon \to \omega_\ast - 0 \).

Now consider the case \( \varepsilon > \omega_\ast \).

\[ D(\varepsilon) \propto \int_{\varepsilon - \omega_\ast}^{\text{cutoff}} \frac{dt}{\sqrt{t + \omega_\ast - \varepsilon}} \propto \sqrt{t + \omega_\ast - \varepsilon}\bigg|_{\varepsilon - \omega_\ast}^{\text{cutoff}} \propto \text{regular} \quad (\varepsilon > \omega_\ast). \]

Hence, there is no singularity at \( \varepsilon > \omega_\ast \).

(iv) (a) Saddle point (− − +). This case is readily reduced to the previous one by \( \varepsilon \leftrightarrow \omega_\ast \). Hence, the singularity is absent at \( \varepsilon < \omega_\ast \), and there is an upward square-root cusp at \( \varepsilon \to \omega_\ast + 0 \).

(b) We have already discussed the maxima and minima in \( d = 1, 2, 3 \). There are no saddle points in 1D. And in 2D there is only one type of saddle point,
because the difference between $(+−)$ and $−(−)$ is in $p_x ↔ p_y$. For precisely the same reason of $p_x ↔ p_y$ (quasi-)symmetry—and in a remarkable contrast to all the cases we considered before—the spectral density $D(ε)$ now depends only on the absolute value of the difference $(ε − ω_∗)$. Indeed, using a formal trick of renaming the integration variables, $p_x ↔ p_y$, we get

\[ D(ε) ∝ \int dp_x dp_y \delta(ε − ω_∗ − p_x^2 + p_y^2) \equiv \int dp_y dp_x \delta(ε − ω_∗ − p_y^2 + p_x^2) \]

\[ \equiv \int dp_x dp_y \delta(ω_∗ − ε − p_x^2 + p_y^2), \]

meaning

\[ D(ε) ∝ \int dp_x dp_y \delta(|ε − ω_∗| − p_x^2 + p_y^2). \]

Now integrate over $dp_x$:

\[ \int dp_x \delta(|ε − ω_∗| − p_x^2 + p_y^2) ∝ (p_y^2 + |ε − ω_∗|)^{−\frac{d}{2}} \]

Then, introducing the variable $t ≡ |p_y|$, we obtain

\[ D(ε) ∝ \int_0^{cutoff} \frac{dt}{\sqrt{t^2 + |ε − ω_∗|}} ∝ \ln \left( t + \sqrt{t^2 + |ε − ω_∗|} \right) \bigg|_0^{cutoff} \]

This brings us to the final answer

\[ D(ε) ∝ \text{(regular part)} − \ln |ε − ω_∗| \quad (d = 2). \]