

from:

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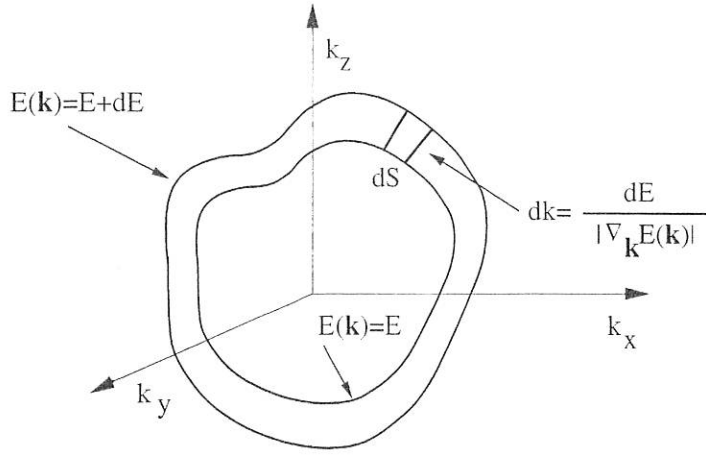


Fig. 21 Schematic representation of two isoenergetic surfaces in the  $k$  space.

Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling "Numerical Recipes" (Cambridge University Press 1986); J. L. Martins and M. L. Cohen, Phys. Rev. **B37**, 6134 (1988) and references quoted therein].

## 7 Density-of-states and critical points

In several problems the primary interest is not in the detailed wavevector dependence of the crystal band structure but only on the density-of-states in a given energy range. Consider for simplicity a non-degenerate band  $E(\mathbf{k})$ ; the corresponding density-of-states for this band is given by

$$D(E) = 2 \sum_{\mathbf{k}} \delta(E(\mathbf{k}) - E) = 2 \int_{B.Z.} \frac{V}{(2\pi)^3} \delta(E(\mathbf{k}) - E) d\mathbf{k}, \quad (50)$$

where  $d\mathbf{k}$  is the volume element of the reciprocal space and the factor 2 accounts for the spin degeneracy (we suppose this degeneracy is not removed). Equation (50) shows that contributions to the density-of-states  $D(E)$  at energy  $E$  occur from the band states (if any) such that  $E(\mathbf{k}) = E$ ; the factor  $V/(2\pi)^3$  gives the uniform density of allowed  $\mathbf{k}$  vectors in  $\mathbf{k}$ -space, as discussed in Eq. (43).

In Fig. 21 we indicate schematically the two isoenergetic surfaces  $E(\mathbf{k}) = E$  and  $E(\mathbf{k}) = E + dE$ . The distance  $dk$  between the two isoenergetic surfaces is obtained by observing that  $dE = \nabla_{\mathbf{k}} E(\mathbf{k}) \cdot d\mathbf{k} = |\nabla_{\mathbf{k}} E(\mathbf{k})| dk$ . Counting the volume in  $\mathbf{k}$ -space enclosed between the two surfaces, the expression (50) for the density-of-states can be transformed into the integral on the constant energy surface  $E(\mathbf{k}) = E$  in the form

$$D(E) = 2 \int_{E(\mathbf{k})=E} \frac{V}{(2\pi)^3} \frac{dS}{|\nabla_{\mathbf{k}} E(\mathbf{k})|}. \quad (51)$$

Expression (51) clearly shows that singularities in the density-of-states are expected at the *critical points*, defined as those points in  $\mathbf{k}$ -space for which

$$\nabla_{\mathbf{k}} E(\mathbf{k}) = 0 ; \quad (52)$$

for these points the density-of-states is expected to exhibit anomalies as a function of energy.

At the critical points, Eq. (50) or Eq. (51) can be integrated analytically. In more general situations the density-of-states can be obtained numerically by appropriate sampling of the  $\mathbf{k}$  vectors in the Brillouin zone.

Near a critical point, where Eq. (52) holds, we can expand the energy as a function of the wavevector, in quadratic form. Indicating with  $k_x, k_y, k_z$  the principal axes of the quadratic form and taking the origin at the critical point itself, we have

$$E(\mathbf{k}) = E_c \pm \frac{\hbar^2}{2m_x} k_x^2 \pm \frac{\hbar^2}{2m_y} k_y^2 \pm \frac{\hbar^2}{2m_z} k_z^2 \quad (53)$$

(where we choose  $m_x, m_y, m_z > 0$ , while the occurrence of plus or minus sign specifies the kind of critical point). The critical point  $M_0$  denotes zero negative signs in expression (53) and is thus a minimum of  $E(\mathbf{k})$ ; the critical point  $M_3$  denotes three negative signs in expression (53) and is thus a maximum;  $M_1$  and  $M_2$  denote one and two negative signs, respectively, and are thus two saddle points. Thus in three dimensions we have four types of critical points. Similarly, in two-dimensional crystals we have three types of critical points  $M_0, M_1$  and  $M_2$ : a minimum, a saddle point and a maximum, respectively. In one-dimensional crystals we have two types of critical points: a minimum  $M_0$  and a maximum  $M_1$ .

Near a three-dimensional critical point, the expression (50) for the density-of-states becomes

$$D(E) = \frac{2V}{(2\pi)^3} \int \delta(E_c \pm \frac{\hbar^2 k_x^2}{2m_x} \pm \frac{\hbar^2 k_y^2}{2m_y} \pm \frac{\hbar^2 k_z^2}{2m_z} - E) dk_x dk_y dk_z . \quad (54a)$$

For the two-dimensional case we have

$$D(E) = \frac{2L_x L_y}{(2\pi)^2} \int \delta(E_c \pm \frac{\hbar^2 k_x^2}{2m_x} \pm \frac{\hbar^2 k_y^2}{2m_y} - E) dk_x dk_y . \quad (54b)$$

For the one-dimensional case we have

$$D(E) = \frac{2L_x}{2\pi} \int \delta(E_c \pm \frac{\hbar^2 k_x^2}{2m_x} - E) dk_x . \quad (54c)$$

All types of integrals (54) can be easily calculated analytically with the help of the following property of the delta function

$$\delta[f(x)] = \sum_n \frac{\delta(x - x_n)}{|f'(x_n)|} . \quad (55)$$

where  $x_n$  are the simple zeroes of the function  $f(x)$ .

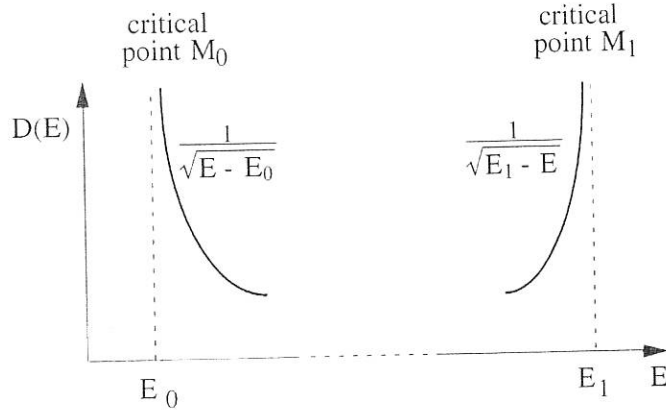


Fig. 22 Density-of-states at the critical points  $M_0$  (minimum) and  $M_1$  (maximum) of a one-dimensional crystal.

### Critical points in one-dimensional crystals

In one-dimensional crystals, for the critical point of type  $M_0$  at energy  $E_0$ , we consider the integral

$$D(E) = \frac{2L_x}{2\pi} \int \delta(E_0 + \frac{\hbar^2 k_x^2}{2m_x} - E) dk_x = L_x \frac{\sqrt{2m_x}}{\pi\hbar} \int \delta(E_0 + q_x^2 - E) dq_x \quad (56)$$

where the change of variable  $q_x = (\hbar/\sqrt{2m_x})k_x$  has been performed. Consider the function  $f(q_x) = E_0 + q_x^2 - E$ : the zeroes of this function occur for  $q_{x0} = \pm\sqrt{E - E_0}$  and  $f'(q_{x0}) = 2q_{x0} = \pm 2\sqrt{E - E_0}$ . The integral (56) then becomes

$$D(E) = L_x \frac{\sqrt{2m_x}}{\pi\hbar} \frac{1}{\sqrt{E - E_0}} \quad E > E_0. \quad (57)$$

Similarly for a critical point of type  $M_1$  at energy  $E_1$  we have

$$D(E) = L_x \frac{\sqrt{2m_x}}{\pi\hbar} \frac{1}{\sqrt{E_1 - E}} \quad E < E_1. \quad (58)$$

In Fig. 22 we give the behaviour of the density-of-states for the two possible critical points in one-dimensional crystals. It can be noticed that the singularities appearing in Fig. I-11a, which gives the bulk density-of-states for a linear chain evaluated with the Green's function technique, are (as expected) of the type illustrated in Fig. 22.

### Critical points in two-dimensional crystals

In two-dimensional crystals, for a critical point of type  $M_0$  at energy  $E_0$ , we have to calculate the integral

$$D(E) = \frac{2L_x L_y}{(2\pi)^2} \int \delta(E_0 + \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} - E) dk_x dk_y. \quad (59)$$

It is convenient to introduce the variable  $q_x = (\hbar/\sqrt{2m_x})k_x$  and  $q_y = (\hbar/\sqrt{2m_y})k_y$  in Eq. (59), and denote by  $S=L_xL_y$  the surface of the two-dimensional crystal; we have

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi^2 \hbar^2} \int \delta(E_0 + q_x^2 + q_y^2 - E) dq_x dq_y .$$

We pass to cylindrical coordinates and easily obtain

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi \hbar^2} \quad \text{for } E > E_0 . \quad (60)$$

A similar expression holds for the critical point which is a maximum, for  $E < E_2$ . Thus the density-of-states is step-like at the points  $M_0$  and  $M_2$  of a two-dimensional crystal.

For the saddle critical point  $M_1$  we have to evaluate the expression

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi^2 \hbar^2} \int \delta(E_1 + q_x^2 - q_y^2 - E) dq_x dq_y . \quad (61)$$

We suppose momentarily  $E > E_1$ . Consider the function  $f(q_x) = E_1 + q_x^2 - q_y^2 - E$ : the zeroes of this function occur for  $q_{x0} = \pm \sqrt{E - E_1 + q_y^2}$  and  $f'(q_{x0}) = 2q_{x0}$ . The integral (61) thus becomes

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi^2 \hbar^2} \int_{-q_c}^{q_c} \frac{1}{\sqrt{E - E_1 + q_y^2}} dq_y .$$

where the integral has been confined to a cutoff where the series expansion is supposed to hold. With the help of the indefinite integral

$$\int \frac{dx}{\sqrt{a^2 + x^2}} = \ln(x + \sqrt{a^2 + x^2}) ,$$

we obtain

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi^2 \hbar^2} \ln \frac{q_c + \sqrt{E - E_1 + q_c^2}}{-q_c + \sqrt{E - E_1 + q_c^2}} . \quad (62)$$

For  $E \approx E_1$ , with appropriate series development in the second member of Eq. (62), we obtain

$$D(E) = S \frac{\sqrt{m_x m_y}}{\pi^2 \hbar^2} \ln \frac{4q_c^2}{|E - E_1|} . \quad (63)$$

and we see that a logarithmic divergence occurs at the critical point (with the absolute value  $|E - E_1|$ , Eq. (63) holds also for  $E < E_1$ ). In Fig. 23 we show the behaviour of the density-of-states at the two-dimensional critical points.

### *Critical points in three-dimensional crystals*

For three-dimensional crystals we have four types of critical points:  $M_0$  (minimum),  $M_1$  and  $M_2$  (saddle points),  $M_3$  (maximum). The analytic behaviour at the three-dimensional critical points can be obtained with procedures similar to the previous

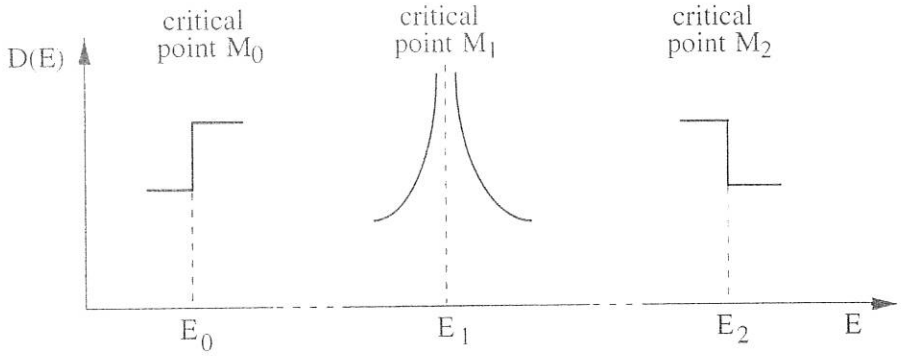


Fig. 23 Density-of-states at the critical points of type  $M_0$  (minimum),  $M_1$  (saddle point), and  $M_2$  (maximum) of a two-dimensional crystal.

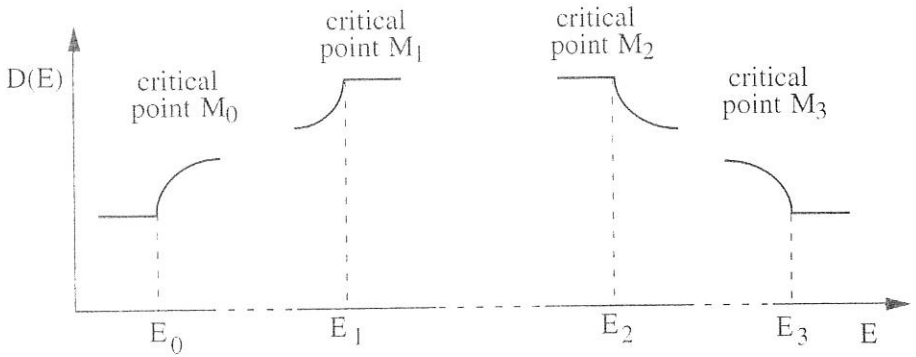


Fig. 24 Density-of-states at the critical points of type  $M_0$  (minimum),  $M_1$  and  $M_2$  (saddle points), and  $M_3$  (maximum) of a three-dimensional crystal.

reported calculations; we have:

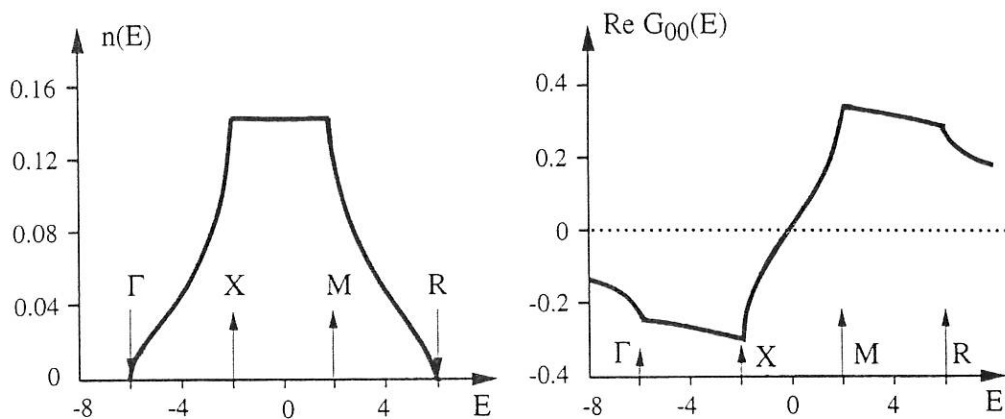
$$\text{critical point } M_0 \quad D(E) = C_0 + V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E - E_0} \quad \text{for } E > E_0 \quad (64a)$$

$$\text{critical point } M_1 \quad D(E) = C_1 - V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E_1 - E} \quad \text{for } E < E_1 \quad (64b)$$

$$\text{critical point } M_2 \quad D(E) = C_2 - V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E - E_2} \quad \text{for } E > E_2 \quad (64c)$$

$$\text{critical point } M_3 \quad D(E) = C_3 + V \frac{\sqrt{2m_x m_y m_z}}{\pi^2 \hbar^3} \sqrt{E_3 - E} \quad \text{for } E < E_3 \quad (64d)$$

In the above expressions  $C_i$  indicate either a constant (including zero) or a smoothly energy dependent quantity, while the terms with the square root are present only when the argument is positive. The results (64) are schematically indicated in Fig. 24.



**Fig. 25** Density-of-states of the cubium, to illustrate the three-dimensional critical points. The energy  $E$  is in units of  $|\gamma|$ , and  $n(E)$  is normalized to one. Besides  $n(E) = -(1/\pi)\text{Im } G_{00}(E)$ , also the real part of the Green's function diagonal matrix element  $G_{00}(E)$ , on a localized orbital of the cubium, is reported for convenience [from D. J. Lohrmann, L. Resca, G. Pastori Parravicini and R. D. Graft, Phys. Rev. B40, 8404 (1989); copyright 1989 by the American Physical Society].

As an example of three-dimensional density-of-states consider the case of the cubium, a simple cubic crystal with a single s-like orbital per site, and nearest neighbour interactions only. With a straightforward generalization of the procedures leading to Eq. (I-37), we have that the band energy  $E(\mathbf{k})$  of the cubium is given by the expression

$$E(\mathbf{k}) = \alpha + 2\gamma (\cos k_x a + \cos k_y a + \cos k_z a) \quad (65)$$

(for simplicity we take  $\alpha = 0$ ; the hopping parameter  $\gamma$  is supposed to be negative). The Brillouin zone of the cubium is indicated in Fig. 17, together with the symmetry points  $\Gamma$ ,  $X$ ,  $M$  and  $R$ . It is seen by inspection of Eq. (65) that  $\Gamma$  is a critical point of type  $M_0$  and energy  $E_0 = -6|\gamma|$ . Similarly,  $X$  and  $M$  are saddle points of type  $M_1$  and  $M_2$ , and energy  $E_1 = -2|\gamma|$  and  $E_2 = 2|\gamma|$ , respectively. The point  $R$  is a critical point of type  $M_3$  and energy  $E_3 = 6|\gamma|$ . The density-of-states corresponding to the energy band (65) can be computed numerically, for instance via the general definition (50) and appropriate sampling of the Brillouin zone, or by means of the Green's function technique and Lanczos procedure (see Section V-8.2). The computed density-of-states of cubium is reported in Fig. 25, and the presence of the critical points of the type and energy discussed above can be clearly noticed.

## Further reading

S. L. Altmann "Band Theory of Solids: an Introduction from the Point of View of Symmetry" (Clarendon Press, Oxford 1994)

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