

Density of States in Disordered Systems with Short-Range Order

Moon Sung Chung

Dept. of Materials Science and Engineering

<Abstract>

The density of states in disordered systems with short-range order were derived in the exact form using the tight-binding model and selfconsistent approximation and then calculated numerically. The forms for the short-range order and interactions were assumed to be Gaussian.

The numerical results obtained seem to agree with other recent works.

Short-Range Order가 존재하는 비정질계에서의 에너지 상태밀도

鄭 文 成

材 料 工 學 科

<요 약>

tight-binding model과 selfconsistent approximation을 이용하여 거의 정확한 형태로 에너지 상태밀도를 구하고 수치해석적인 방법으로 값을 계산하였다. short-range order와 상호작용은 Gaussian 형태로 가정하였다. 계산된 값은 현재 일반적으로 인정되고 있는 형태와 유사한 그래프를 그려주었다.

I. Introduction

For last several decades, researches in crystals have made remarkable progresses by using Bloch theorem for periodicity. In the natural world, however, there exists an enormous amount of important materials whose microscopic structure are far from periodic. Among them are included alloys, mixed crystals, doped semiconductors, amorphous solids, liquid metals, and even biological substances.

Therefore, many researchers have studied on the methods for deriving macroscopic properties of those materials from the quantum mechanical rules governing the microscopic world or alternatively for deducing microscopic behaviors of those systems from the macroscopic informations which are observable by experim-

ents. Since Anderson's paper⁽¹⁾, creditable for the first time, was published, a few decades has passed and the study on the method has been carried out steadily, but the theory making an era like Bloch theorem, has not been found. Almost every theory developed till now is associated with a single-site description of the electronic structure and based on the multiple scattering theory.^{(2)~(4)} In recent years, the tight-binding model of liquid metals introduced by Roth^{(5)~(6)} yields good result.

Though various methods calculating the level density of electron moving under the influence of random potential were developed, many of them are mainly concerned with one-dimensional model. For the three-dimensional problem of random lattice, Green's function formalism^{(7)~(8)} has been known as the most powerful method. In this article the density of states

are derived from the ensemble-averaged Green's function.,

Given the fact that short-range order plays an important role in a certain disordered material, the formalism has been worked including correlation between atoms. The amorphous states do not exhibit the long-range order but a certain degree of short-range order. That is, the ideal amorphous state has the same number of coordinates for the nearest neighbor as the crystal, but has not for the next nearest neighbors. Especially in liquid metal the short-range order is always present.

The model of electronic structure calculated in this paper has been studied by many workers⁽⁹⁾⁻⁽¹¹⁾ but discussed till now, i.e. no work dealing the full formalism of the density of states has been found.

II. Tight-Binding Model

The wave function is assumed to be expanded in terms of atomic orbitals $\phi_j(\vec{r}) = \phi(\vec{r} - \vec{R}_j)$ located on the various atomic sites and an LCAO expansion for the one-electron Green's function $\bar{G}(\vec{r}, \vec{r}')$ is also assumed to be possible, i.e.

$$g(\vec{r}, \vec{r}') = \sum_{ij} \phi_i(\vec{r}) g_{ij} \phi_j(\vec{r}'). \quad (1)$$

Following the notation of Schwartz and Ehrenreich, we shall use script letters for the Configuration dependent quantities.

In general, the Green's function satisfies the equation

$$(E - \mathcal{H}) g(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'), \quad (2)$$

Multiplying Eq.(2) by $\phi_i^*(\vec{r})$ on the left and $\phi_m(\vec{r}')$ on the right and integrating over the whole \vec{r} and \vec{r}' , we have

$$\sum_{ij} \int d^3r \phi_i^*(\vec{r}) (E - \mathcal{H}) \phi_j(\vec{r}) g_{ij} \int d^3r' \phi_j(\vec{r}') \phi_m(\vec{r}') \\ = \int d^3r \phi_i^*(\vec{r}) \phi_m(\vec{r}) d^3r. \quad (3)$$

Introducing overlap and transfer matrices

$$S_{ij} \equiv S(\vec{R}_i - \vec{R}_j) = \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d^3r$$

and

$$\mathcal{H}_{ij} = \int \phi_i^*(\vec{r}) \mathcal{H} \phi_j(\vec{r}) d^3r,$$

Eq.(3) then yields

$$\sum_{ij} (ES_{ij} - \mathcal{H}_{ij}) g_{ij} S_{jm} = S_{im}. \quad (4)$$

For the distribution of atoms, S_{ij} can be shown to be positive definite and to have an inverse. Then Eq.(4) becomes

$$\sum_i (ES_{ii} - \mathcal{H}_{ii}) g_{ij} = \delta_{ij}. \quad (5)$$

This is the basic equation of the present model. If we assume that the matrix element \mathcal{H}_{ij} depends upon the distance between atoms i and j , $\mathcal{H}_{ij} = \mathcal{H}(\vec{R}_{ij})$ and assume that $\mathcal{H}_{ii} = H_0$ is independent, of the distribution, we can lump the overlap term in \mathcal{H}_{ij} as follows,

$$\mathcal{H}'_{ij} = H'(\vec{R}_{ij}) = \mathcal{H}_{ij} - ES_{ij}.$$

Eq.(5) then becomes

$$(E - H_0) g_{ij} - \sum_{i \neq j} H'(\vec{R}_{ij}) g_{ij} = \delta_{ij}. \quad (6)$$

Let us multiply by $\delta(\vec{r} - \vec{R}_i) \delta(\vec{r}' - \vec{R}_j)$ and sum over i and j . Then

$$(E - H_0) g(\vec{r}, \vec{r}') - \sum_{i \neq j} \delta(\vec{r} - \vec{R}_i) H'(\vec{R}_{ij}) \\ g_{ij} \delta(\vec{r}' - \vec{R}_j) = \rho(\vec{r}) \delta(\vec{r} - \vec{r}'), \quad (7)$$

where $\rho(\vec{r})$ is the density function,

$$\rho(\vec{r}) = \sum_i \delta(\vec{r} - \vec{R}_i) = \sum_i \rho_i(\vec{r}).$$

Eq.(7) can be shown to become

$$(E - H_0 + H'(0)) g(\vec{r}, \vec{r}') - \rho(\vec{r}) \int d^3r'' H'(\vec{r}'' - \vec{r}') \\ \times g(\vec{r}'' - \vec{r}') = \rho(\vec{r}) \delta(\vec{r} - \vec{r}'). \quad (8)$$

This equation shows that the dependence on the position of atoms occurs only through the density function, $\rho(\vec{r})$ and the interaction $H'(\vec{r} - \vec{r}')$ is a continuous quantity.

The density of states is obtained from the one-electron Green's function as follows.

$$N(E) = -\frac{1}{\pi N} I_m \int G(\vec{r}, \vec{r}) d^3r \\ = -\frac{1}{\pi N} I_m \int \langle g(\vec{r}, \vec{r}) \rangle d^3r \quad (9)$$

where $G(\vec{r}, \vec{r})$ is the ensemble averaged quantity of $g(\vec{r}, \vec{r}')$, i.e. $G(\vec{r}, \vec{r}') = \langle g(\vec{r}, \vec{r}') \rangle$.

Here, the (squared) bracket refers to the ensemble average. Since the macroscopic properties of the amorphous material represent average quantities, we must take the quantity averaged over the whole configuration. If we assume spatial homogeneity for our ensemble,

$$G(\vec{r}, \vec{r}') = G(\vec{r} - \vec{r}').$$

Then Eq. (9) becomes

$$N(E) = -\frac{1}{\pi n} I_m \int S(\vec{r}) G(\vec{r}) d^3 r, \quad (10)$$

where n is the density, N/Ω or $\langle \rho(\vec{r}) \rangle$.

If we take the Fourier transformation of Eq. (10), it becomes

$$N(E) = -\frac{1}{\pi n} I_m \int S G \frac{d^3 k}{8\pi^3}$$

Taking a limit $S_{ij} = \delta_{ij}$, we have

$$N(E) \Big|_{S_{ij}=\delta_{ij}} = -\frac{1}{\pi n} I_m G_k \Big|_{k \rightarrow \infty}$$

The large- k limit means the localization of the wavefunction.

III. Selfconsistent Approximation (SCA)⁽¹²⁾

We consider a quantity I similar to the exact Green's function used in Schwartz and Ehrenreich, i.e.

$$I = H + HGH, \quad (1)$$

Where I is called interaction operator.

Here, the prime on H' is dropped. Let us now define a quantity D such that

$$G = D(1 + HG), \quad (2)$$

where D shall be called medium locator or simply locator and it is the analog quantity of the self energy in the paper of Schwartz. The locator can be decomposed in the contribution from the individual atom by writing

$$d_i = \langle g_i \rangle_i H I^{-1}, \quad (3)$$

in terms of which

$$D = \frac{1}{\Omega} \sum_i \int d_i d^3 R_i = n \int d_i d^3 R_i, \quad (4)$$

where $\langle g_i \rangle_i$ is the ensemble averaged quantity of Green's function of i th atom with i th atom

fixed.

Using Eqs. (II. 8) and (III. 3), we have

$$\langle g_i \rangle_i = -\frac{\rho_i}{E} (1 + H \langle g \rangle_i), \quad (5)$$

where ρ_i is a locator satisfying $\rho = \sum_i \rho_i$ and $\langle g \rangle_i$ denoting G_i is the ensemble averaged quantity of g with i th atom fixed. We then have

$$d_i = \frac{\rho_i}{E} (1 + H G_i) H I^{-1}. \quad (6)$$

In terms of G_i , we can define I_i and D_i

$$I_i = H^{-1} H G_i H, \quad (7)$$

$$D_i = G_i H I^{-1} = H^{-1} - I_i^{-1} \quad (8)$$

Now G_i can be written as follows

$$G_i = \langle g_i \rangle_i + n \int g(\vec{R}_{ij}) \langle g_j \rangle_j d^3 R, \quad (9)$$

so that we have for D_i

$$D_i = \langle g_i \rangle_i H I^{-1} + n \int d^3 R_j g(\vec{R}_{ij}) \langle g_j \rangle_j H I^{-1} \quad (10)$$

The results of this procedure are a hierarchy of equations, the first of which describes the total wave in terms of the effective potential of the medium with one atom fixed, the second describes the effective field with one atom fixed in terms of the effective field with two atoms fixed, etc. Then Truncation is needed. The SCA means that the hierarchy of equation is decoupled as follows,

$$G_{ij} \longrightarrow G_i G^{-1} G_j.$$

Defining a quantity q_i to simplify the selfconsistent equations, we then have the SCA equations

$$q_i = d_i - \tilde{d}_i (1 + I q_i), \quad (11)$$

$$d_i = -\frac{\rho_i}{E} (1 + I q_i), \quad (12)$$

$$\tilde{d}_i = -n \int h(\vec{R}_{ij}) d_j d^3 R_j, \quad (13)$$

$$D = n \int d_i d^3 R_i, \quad (14)$$

$$G = (D^{-1} - H)^{-1}, \quad (15)$$

$$I = H + HGH, \quad (16)$$

where $h(\vec{r}) = g(\vec{r}) - 1$ is the short-range order.

To reduce the SCA equations to simpler and more useful forms, we make use of coordinate representation using the δ -function nature of

ρ_i . Now we can assume that

$$q_i(\vec{r}, \vec{r}') = q(\vec{r} - \vec{R}_i, \vec{r}' - \vec{R}_i)$$

and similarly for d , and \vec{d} , and also

$$G(\vec{r}, \vec{r}') = G(\vec{r} - \vec{r}')$$

and similarly for H, D and I .

Taking Fourier transformation of these equation, We have the following selfconsistent set of equations, restoring the prime omitted previously.

$$G_k = n(E - H_0 - nH'_k - \Sigma_k)^{-1} \quad (17)$$

$$\Sigma(\vec{k}) = n \int \vec{H}'_k H'_k G_k F(\vec{k}', \vec{k}) \frac{d^3 k'}{8\pi^3} \quad (18)$$

$$nF(\vec{k}, \vec{k}') = 1 + nh(\vec{k} - \vec{k}') + n \int h(\vec{k} - \vec{k}'') H'_k G_k F(\vec{k}'', \vec{k}') \frac{d^3 k''}{8\pi^3} \quad (19)$$

These are the final results. Therefore we can find that the SCA results in an integral equation with a Kernel determined selfconsistently. Because of isotropy, these equations can be put in one-dimensional form and solved numerically.

IV. Results for Density of States

There exists a little correlation even though ions are very highly randomly distributed. Therefore, we cannot put the short-range order, h , to be zero but the interaction can be assumed to be localized. Since

$$\begin{aligned} \langle \rho(\vec{r}) \rho(\vec{r}') \rangle &= \sum_{ij} \langle \rho_i(\vec{r}) \rho_j(\vec{r}') \rangle \\ &= \sum_i \langle \rho_i(\vec{r}) \rangle \delta(\vec{r} - \vec{r}') + \sum_{i \neq j} \langle \rho_i(\vec{r}) \rho_j(\vec{r}') \rangle \\ &= n\delta(\vec{r} - \vec{r}') + n^2 g(\vec{r} - \vec{r}'). \end{aligned}$$

The short-range order parameter $h(\vec{r})$ has a value between -1 (at $r=0$) and 0 (at $r=\infty$). If we assume that the correlation is Gaussian, we have

$$h(\vec{r}) = -\exp(-\alpha r^2).$$

We also assume that the interaction is Gaussian,

$$H'(\vec{r}) = H_1 \exp(-\lambda r^2).$$

Taking the Fourier transformation of $h(\vec{r})$ and $H'(r)$, we have

$$h(\vec{k}) = \int h(\vec{r}) e^{i \cdot \vec{r}} d^3 r.$$

$$H_k = \int H(\vec{r}) e^{i \cdot \vec{r}} d^3 r.$$

From the SCA results, we have

$$\begin{aligned} \vec{H}_k &= \int H'(\vec{r}) g(\vec{r}) e^{i \cdot \vec{r}} d^3 r \\ &= H'_k + \int H'_k h(\vec{k} - \vec{k}') \frac{d^3 k'}{8\pi^3} \quad (1) \\ nF(\vec{k}, \vec{k}') &= 1 + nh(\vec{k} - \vec{k}') \\ &\quad + n \int h(\vec{k} - \vec{k}'') H'_k G_k F(\vec{k}'', \vec{k}') \frac{d^3 k''}{8\pi^3} \\ &= 1 + n \left[h(\vec{k} - \vec{k}') + \int h(\vec{k} - \vec{k}'') H'_k G_k h(\vec{k}'', \vec{k}') \frac{d^3 k''}{8\pi^3} \right. \\ &\quad \left. + \int h(\vec{k} - \vec{k}'') H'_k G_k h(\vec{k}'', \vec{k}') \right. \\ &\quad \left. H'_k G_k h(\vec{k}'' - \vec{k}') \frac{d^3 k''}{8\pi^3} \frac{d^3 k'''}{8\pi^3} + \dots \right] \quad (2) \end{aligned}$$

$$\begin{aligned} \Sigma(\vec{k}) &= n \int \vec{H}'_k H'_k G_k F(\vec{k}', \vec{k}) \frac{d^3 k'}{8\pi^3} \\ &= \int \frac{d^3 k'}{8\pi^3} \left(H'_k + \int H'_k h(\vec{k}' - \vec{k}_0) \frac{d^3 k_0}{8\pi^3} \right) \\ &\quad H'_k G_k \left[1 + n \left(h(\vec{k} - \vec{k}') \right. \right. \\ &\quad \left. \left. + \int h(\vec{k} - \vec{k}'') H'_k G_k h(\vec{k}'' - \vec{k}') \frac{d^3 k''}{8\pi^3} + \dots \right) \right] \\ &= \Sigma_0 + \Sigma_k, \quad (3) \end{aligned}$$

where

$$\begin{aligned} \Sigma_0 &= \int H'_k G_k \frac{d^3 k'}{8\pi^3} \\ &\quad + \int H'_k h(\vec{k}' - \vec{k}_0) H'_k G_k \frac{d^3 k_0}{8\pi^3} \frac{d^3 k'}{8\pi^3} \end{aligned}$$

and

$$\begin{aligned} \Sigma_k &= n \int \frac{d^3 k'}{8\pi^3} \left(H'_k + \int H'_k h(\vec{k}' - \vec{k}_0) \frac{d^3 k_0}{8\pi^3} \right) H'_k G_k \\ &\quad \times \left[h(\vec{k} - \vec{k}') + \int h(\vec{k} - \vec{k}'') H'_k G_k h(\vec{k}'' - \vec{k}') \right. \\ &\quad \left. \frac{d^3 k''}{8\pi^3} + \dots \right] \\ &\equiv \Sigma_k^{(1)} + \Sigma_k^{(2)} + \dots \end{aligned}$$

Here the superscript numbers refer to the order of terms in the square bracket. Since the above equations can be expanded in perturbation series, we can calculate the self-energy $\Sigma(\vec{k})$ numerically using the iteration method.

As mentioned above we have Gaussian forms for the correlation and interaction, Then

$$h(\vec{k}) = -\left(\frac{\pi}{\alpha}\right)^{3/2} \exp(-k^2/4\alpha),$$

$$H'_k = \left(\frac{\pi}{\lambda}\right)^{3/2} H_1 \exp(-k^2/4\lambda)$$

Substituting these value into Eq. (3), the first term of self-energy Σ_0 and Σ_k are as follow

$$\begin{aligned} \Sigma_0 &= \frac{H_1^2 \pi^{3/2}}{G_0^{-1} - \Sigma_0} \left(\frac{1}{(2\lambda)^{3/2}} - \frac{1}{(4\alpha + 5\lambda)^{3/2}} \right) \\ &+ \frac{H_1^2 \pi}{2\lambda^3 (G_0^{-1} - \Sigma_0)} \int dk \frac{k^2 \Sigma_k}{G_0^{-1} - \Sigma_0 - \Sigma_k} \\ &\left[\frac{\exp\left(-\frac{2\lambda + \alpha}{4\lambda(\alpha + \lambda)} k^2\right)}{\exp(-k^2/2\lambda) - \frac{(\alpha + \lambda)^{3/2}}{4\lambda(\alpha + \lambda)^{3/2}}} \right] \\ \Sigma_k &= -\frac{H_1^2 n \pi^3}{G_0^{-1} - \Sigma_0} \left[\frac{\exp(-k^2/(4\alpha + 2\lambda))}{(\lambda^2 + 2\alpha\lambda)^{3/2}} \right. \\ &\quad \left. - \frac{\exp\left(-\frac{\alpha + 2\lambda}{4(3\alpha\lambda + \alpha^2 + \lambda^2)} k^2\right)}{(\alpha^2 + \lambda^2 + 3\alpha\lambda)} \right] \end{aligned}$$

Here, G_0 satisfies the following equation $G = G_0 + G_0 \Sigma G_0$, where Σ is the self-energy.

Results obtained by numerical method yielded a form of the density of states curve quite similar to those of recent works. The above perturbation series, however, was found to have poor convergency. It is considered that the introduction of more realistic correlation and interaction functions right improve the convergency.

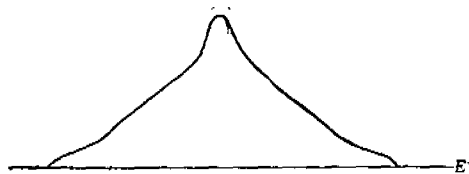


Fig. Density of states for $H_0=0$, $H'=-1$, $n=0.8$, $\alpha=4.0$, and $\lambda=2.0$

Reference

1. P.W. Anderson, Phys. Rev. **109**, 1492(1953)
2. M. Lax, Phys. Rev. **85**, 621(1952)
3. J.L. Beedy, Phys. Rev. **135**, A130(1964)
4. P. Seven, Phys. Rev. **156**, 809(1967)
5. L.M. Roth, Phys. Rev. **B7**, 4321(1973)
6. L.M. Roth, Phys. Rev. **B9**, 2476(1974)
7. B.I. Halperin, Phys. Rev. **139**, A104(1965)
8. R.A. Abraham and S.F. Edwards, J. Phys. **C5**, 1183(1972)
9. N.F. Mott, Phil. Mag. **17**, 1259(1968)
ibid, **22**, 903.
J. Noncryst. Solids **8-10**, 1(1972)
10. M.H. Cohen, J. Noncryst. Solids **4**, 391 (1970)
11. Yonezawa and Morigaki, Prog Theor. Phys. Supplement No.53, **1** (1973)
12. L. Schwartz and H. Ehrenreich, Ann. Phys. (N. Y.) **64**, 100(1971)