

Coarse-Grained Quantities in Aperiodic Systems. III

—Monte-Carlo Calculation of the Impurity Band States—

Kenkichi OKADA* and Hirotsugu MATSUDA**

**Department of Chemistry, Faculty of Science, Kyoto University, Kyoto*

***Research Institute for Fundamental Physics, Kyoto University, Kyoto*

(Received January 8, 1968)

The coarse-grained density of states is computed for an electron in a three-dimensional random array of impurities by the method of ensemble average of periodic systems (MEAPS) combined with the Monte Carlo method. The model on which the calculation is made is due to Matsubara and Toyozawa (M-T) based on the tight binding approximation for the impurity band states. The result of the calculation qualitatively agrees with that of the Monte-Carlo calculation of Majlis based on the ensemble average of small systems. It shows how the perturbative approach of M-T is good at high concentration of impurities but it is a poor approximation at low concentration. A merit of the MEAPS compared with the method of ensemble average of small systems is discussed.

§ 1. Introduction

In the first paper of the present series¹⁾ it has been proved that in an aperiodic linear chain the state density of phonons or electrons coarse-grained over a certain energy interval can be approximated by a suitable ensemble average of the state densities of periodic systems. In the second paper²⁾ histograms of frequency spectra of isotopically disordered diatomic linear chains for various sets of long and short range order parameters have been calculated by using the above-mentioned method of ensemble average of periodic systems (MEAPS) and have been compared with the result calculated by the negative-factor-counting method developed by Dean et al.³⁾ It has been numerically shown that the suitable choice of the width of histograms is very important for the result of the MEAPS to be a good approximation; the choice can be done by referring to the stability of the histogram with the change of the ensembles. The comparison then indicates that the MEAPS using periodic chains with not more than 8 atoms in a unit cell gives better approximation than the moment method using 20 moments. In view of such satisfactory results in a linear chain we have tried to apply this method to three-dimensional systems.

Various approximation methods have been devised and developed for what they call the random lattice problem. Among others the method for obtaining Green's function by summing up certain types of terms in the perturbation expansion^{4),5)} seems to have a wide range of applicability. However, in such

methods so far the nature of the approximation is not so clear that one must worry about the reliability of the results. In fact such a method predicted qualitatively wrong frequency spectra for isotopically disordered linear chain.⁵⁾

In this paper we calculate as an example of three-dimensional random systems the coarse-grained energy spectra of the model of a doped valence semiconductor exhibiting impurity band conduction which was introduced by Matsubara and Toyozawa.^{6),*)} Their model Hamiltonian is given by

$$H = \sum_{m \neq n} V_{mn} a_m^* a_n, \quad (1.1)$$

where a_m^* and a_m denote the operators for creating and annihilating an electron at the m -th impurity site. It is assumed that V_{mn} depends only upon the distance between the relevant sites such that

$$V_{mn} = V(|\mathbf{R}_{mn}|), \quad (1.2)$$

$$\mathbf{R}_{mn} = \mathbf{R}_m - \mathbf{R}_n, \quad (1.3)$$

$$V(R) = -V_0(1 + \alpha R)e^{-\alpha R}, \quad (1.4)$$

where V_0 and α are positive constants. By comparing our results with those of Matsubara and Toyozawa's obtained from the above mentioned perturbative approach, we numerically show that how their approximation is good at high concentration of impurities but poor at low concentration.

After our main result had been read at the annual meeting of the physical society of Japan held in Sapporo in October 1966, Monte-Carlo calculations of the impurity band states using the same model were published by Majlis.⁷⁾ His conclusion is qualitatively the same as ours. However, the method is somewhat different. He determined the positions of N impurities in a volume L^3 of the crystal, using a special computer library subroutine to generate $3N$ random Cartesian coordinates inside the volume such that $c = N/L^3 =$ (impurity concentration); the maximum number of N was 80. Then he calculated the density of states of such a system. He approximated the density of states of random systems with a given impurity concentration by taking an average over the ensemble of such systems. Since the system on which he calculated is a small one, the size effect may give a systematic error. One must note, for instance, that the simple cubic Bravais lattice containing $5 \times 5 \times 5 = 125$ atoms has as many as $5^3 - 3^3 = 98$ atoms on its surface.

On the other hand, since we deal with periodic systems in the MEAPS, we have no surface effect at all. Indeed, as shown in Appendix the MEAPS can give a correct second moment of energy eigenvalues while Majlis's method should give it a non-negligible error. Of course, our result, too, is an approximation for the energy spectrum since we have represented the random systems by an

*) Hereafter reference 6) is referred to as M-T.

ensemble average of a finite number of periodic systems with unit cells containing a finite number of atoms. However, we emphasize that our approach is of the nature such that one can reduce the error by increasing the width of histograms, that is, by increasing the degree of coarse-graining in energy as proved and demonstrated in the previous papers.

In §2 we describe our method of calculating the coarse-grained spectrum of Matsubara and Toyozawa's model. In §3 the results of the numerical calculation are given and §4 is devoted to discussion.

§ 2. Calculation of coarse-grained spectrum of Matsubara and Toyozawa's model

Let us assume that impurities are located only at the lattice points of a simple cubic lattice with a lattice constant equal to 1. Each lattice point is assumed to contain at most one impurity atom, and the probability of a lattice point being occupied by an impurity is equal to c independent of the configuration of impurities occupying the other lattice points.

We try to approximate such infinite random system by an ensemble average of periodic systems whose unit cell has $10 \times 10 \times 10$ lattice points. For the periodic system we may rewrite the Hamiltonian introduced in (1.1) as

$$H = \sum_{i,\mu} \sum_{j,\nu} V(r_{i\mu,j\nu}) a_{j\nu}^* a_{i\mu}, \quad (2.1)$$

where $a_{i\mu}$ denotes an annihilation operator of an electron at the μ -th site of the i -th unit cell, and

$$r_{i\mu,j\nu} = |\mathbf{r}_{i\mu} - \mathbf{r}_{j\nu}|. \quad (2.2)$$

We decompose the position vector as

$$\mathbf{r}_{i\mu} = \mathbf{R}_i + \mathbf{r}_\mu, \quad (2.3)$$

where \mathbf{R}_i is the position vector of the fixed point of the i -th unit cell, so that the set of \mathbf{R}_i 's constitutes the set of lattice vectors of the periodic system.

It is convenient to expand the operator $a_{i\mu}$ in the form

$$a_{i\mu} = L^{-3/2} \sum_{\mathbf{k}} A_\mu(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_i), \quad (2.4)$$

where L is an appropriately large integer and \mathbf{k} a wave vector whose component is one of $(2\pi/LM)l$, ($l=0, 1, 2, \dots, L-1$); M is a linear dimension of a unit cell and here $M=10$. Equation (2.1) is now written as

$$H = \sum_{\mathbf{k}} \sum_{\mu,\nu} V_{\mu\nu}(\mathbf{k}) A_\nu^*(\mathbf{k}) A_\mu(\mathbf{k}), \quad (2.5)$$

where we put

$$V_{\mu\nu}(\mathbf{k}) = \sum_{\mathbf{R}} V(|\mathbf{R} + \mathbf{r}_\mu - \mathbf{r}_\nu|) \exp(i\mathbf{k} \cdot \mathbf{R}) \quad (2.6)$$

the summation being taken over the lattice vectors of the periodic system. The relations

$$V_{\mu\nu}^*(\mathbf{k}) = V_{\mu\nu}(-\mathbf{k}) = V_{\nu\mu}(\mathbf{k}) \quad (2.7)$$

hold as a consequence of Eq. (2.6).

Introduce a dimensionless concentration

$$p = 32\pi c\alpha^{-3} \quad (2.8)$$

following $M-T$. The normalized energy level density is a function of only energy E and p , and is denoted by $D(E; p)$.

For the sake of convenience of numerical computation henceforth we usually set $c=0.01$, so that for given p we determine α by (2.8). By making use of a standard subroutine to generate a uniform pseudo-random number with the method of mixing, we construct a unit cell structure containing n impurities. We then solve the eigenvalue problem for the n -dimensional matrix $V_{\mu\nu}(\mathbf{k})$ given by (2.6) and from the dispersion relation thus obtained we calculate the level density of the periodic system with the given unit cell structure.

Let $D_n(E; p)$ be the level density averaged over the periodic system with all the possible unit cell structure consisting just of n impurities. One may expect in view of the results of the MEAPS for one-dimensional systems that under suitable coarse-graining with respect to energy E the state density $D(E; p)$ can be approximated by

$$D(E; p) = \sum_n \tau_n D_n(E; p), \quad (2.9)$$

where τ_n is the binomial distribution for the weight factor, that is,

$$\tau_n = \binom{1000}{n} (0.01)^n (1-0.01)^{1000-n}. \quad (2.10)$$

Since $\sum_{n=5}^{15} \tau_n \simeq 0.92$, in the practical calculation we have restricted the value of n from 5 through 15 and replaced (2.9) by

$$D(E; p) \simeq \sum_{n=5}^{15} \tau_n D_n(E; p) / 0.92. \quad (2.9')$$

Even so, since it is a formidable task to exhaust all the possible unit cell structure, we use the Monte Carlo method for obtaining $D_n(E; p)$. In order to determine the suitable number of samples, and suitable width of coarse-graining (histogram), we have applied the stability test which was proved effective in the previous works. We must determine the width of histograms of density of states so as to reproduce the histograms for different sets of samples within a limited error, say, of 10%. Moreover the width W of histograms must be so chosen that the histogram is stable for a change of the average number of impurities in a unit cell, that is, in the present case stable for a change of the value of c around 0.01 for given value of p . Next, for fixed width W of histograms the

Table I. Number of samples, $S(p, n)$, necessary to be ensemble-averaged for a given set of both concentration p and number of impurities n under fixed energy width ($W/V_0=0.1$) and error criterion (10%). $T(p, n)$ indicates total number of samples used in the present calculation for given p and n .

p	1/16	1/8	1/4	1/2	1	2	4	8	16	32	
$S(p, 10)$	50	50	50	30	20	15	10	10	5	5	
$T(p, 10)$	140	140	140	140	50	50	40	35	15	15	
$S(p, 5)$	100	100	100	50	40	30	20	15	10	10	
$T(p, 5)$	280	280	280	280	100	60	40	30	20	20	
n	5	6	7	8	9	10	11	12	13	14	15
$S(32, n)$	10	10	10	10	5	5	5	4	4	3	3
$T(32, n)$	20	20	20	20	20	15	15	15	10	5	5

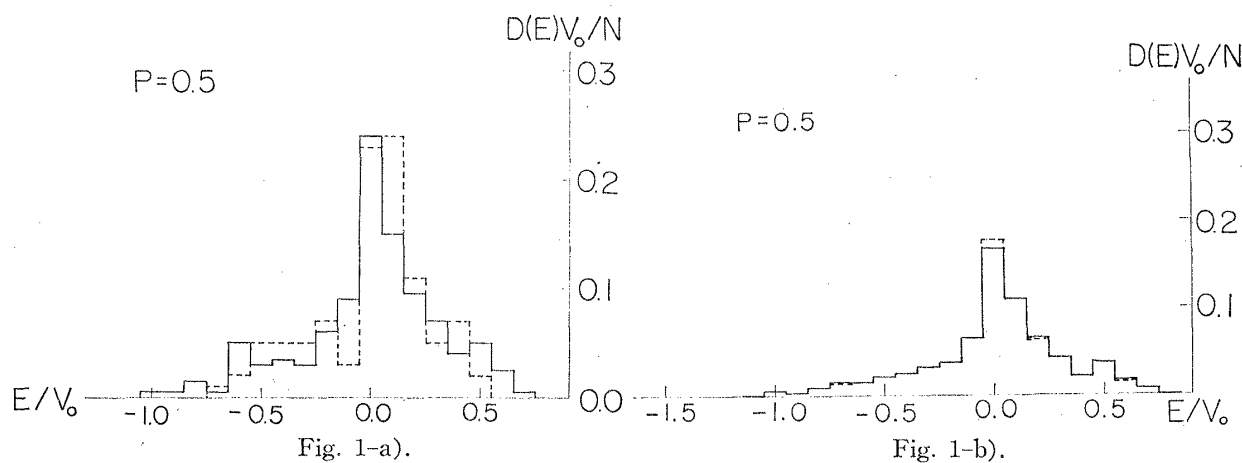


Fig. 1. An example of histograms of state density $D(E)$ for $p=0.5$ obtained from different set of values for c and α , where they are related to by Eq. (2.8). Solid lines correspond to $c=0.01$ and broken lines to $c=0.005$. Curve a) shows a pattern with 20 samples for both c values and b) exhibits stability of the coarse-grained spectrum averaged over larger ensembles: 140 samples for $c=0.01$ and 280 samples for $c=0.005$.

necessary number of samples $S(p, n)$ to be contained in a set depends both on the values of p and n . For $W=0.1V_0$, as we have found suitable, the number of samples used was as shown in Table I. Stability of the coarse-grained quantity for change of both c and α for a given value of p is tested as shown in Fig 1.

§ 3. Results of calculation

Our calculation was made for p which is equal to 2^m , ($m = -4, -3, \dots, 5$), and the result is given in Figures for the density of states. Figures 1 and 2 may serve to illustrate how individual samples exhibit eigenvalues and how to choose the width of histograms.

i) Low concentration cases ($p=1/16, 1/8, 1/4$).

The density of states shows a symmetric feature since most impurities are iso-

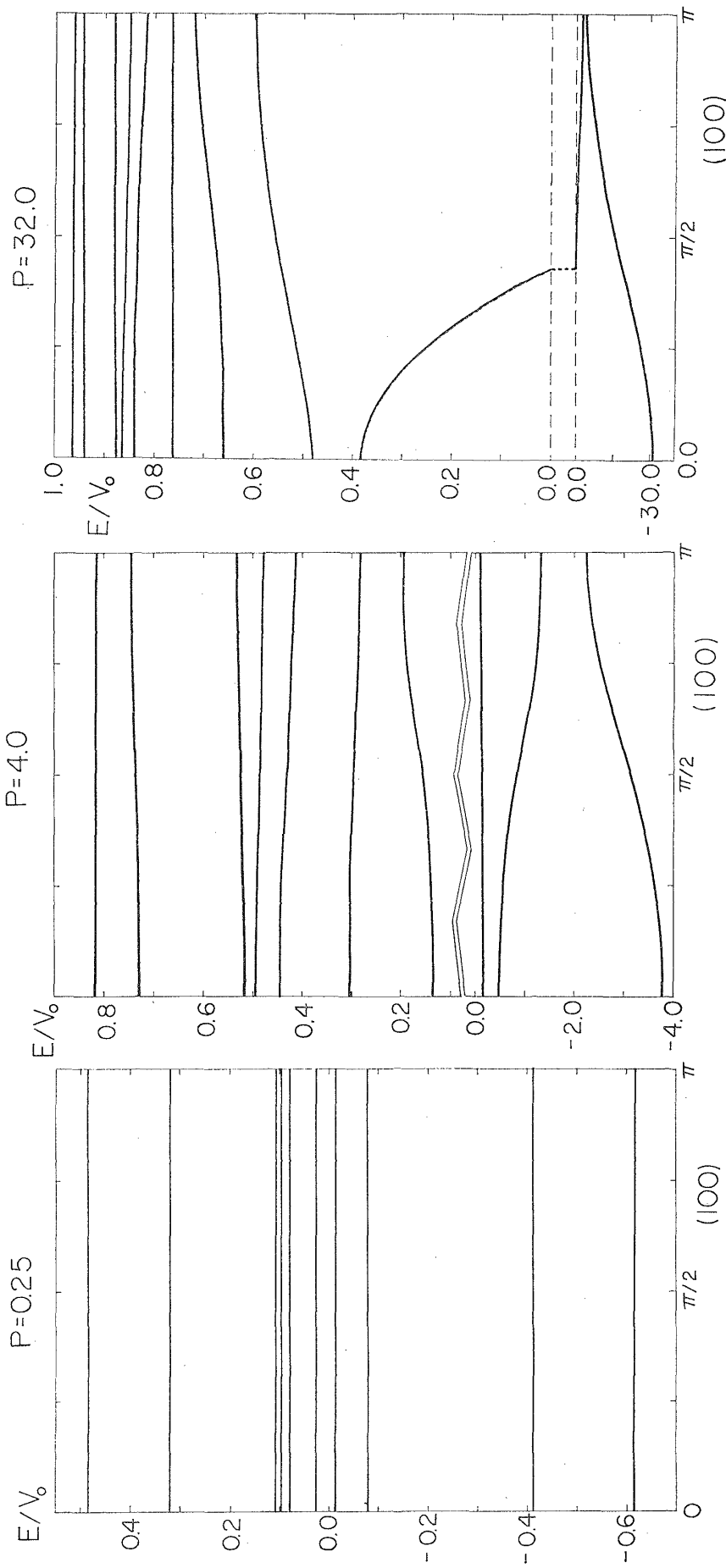


Fig. 2-a).

Fig. 2-b).

Fig. 2-c).

Fig. 2. Dispersion relations obtained from eigenvalues of the 10-dimensional matrix corresponding to the following pattern of coordinates of impurities in the unit cell: (4, 0, 1) (2, 1, 1) (0, 2, 1) (6, 3, 2) (5, 4, 2) (1, 9, 2) (4, 4, 4) (2, 5, 5) (0, 7, 6, 9). Curve a) for $p=0.25$, b) for $p=4.0$ and c) for $p=32.0$.

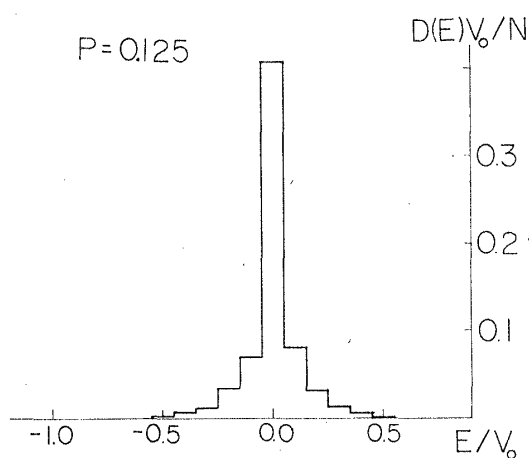


Fig. 3-a).

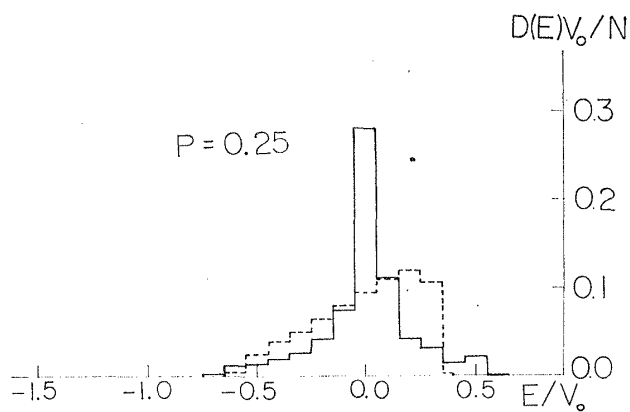


Fig. 3-b).

Fig. 3. Coarse-grained density of states $D(E)$ for low concentration is shown as histograms. Curve a) for $p=0.125$ and b) for $p=0.25$. For reference $D(E)$ from M-T are drawn as broken lines in Figs. 3b) to 5b).

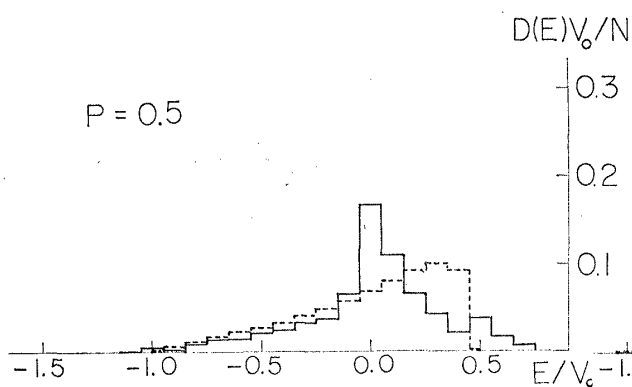


Fig. 4-a).

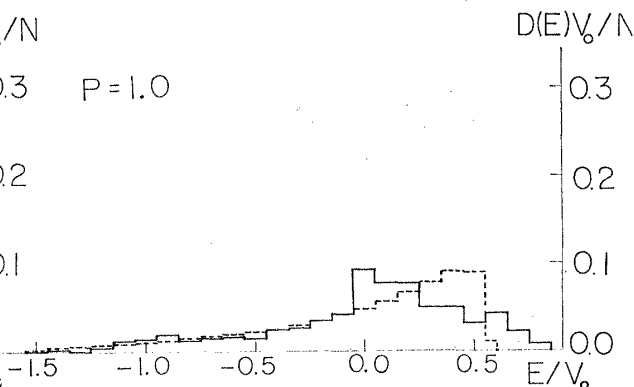


Fig. 4-b).

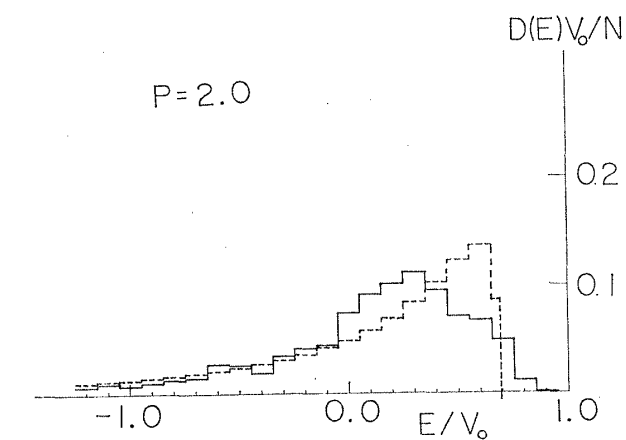


Fig. 4-c).

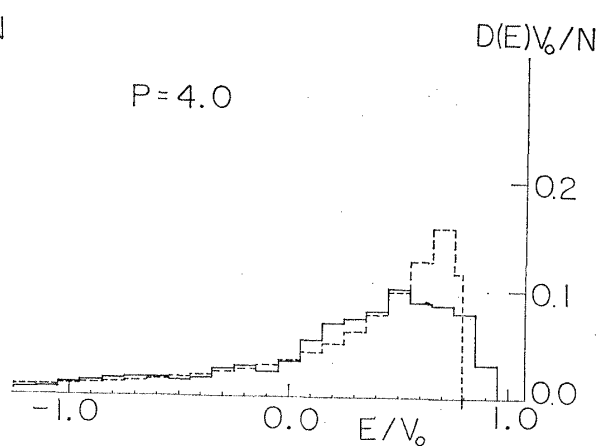


Fig. 4-d).

Fig. 4. Coarse-grained density of states $D(E)$ for intermediate concentration is shown as histograms. Curve a) for $p=0.5$, b) for $p=1.0$, c) for $p=2.0$ and d) for $p=4.0$.

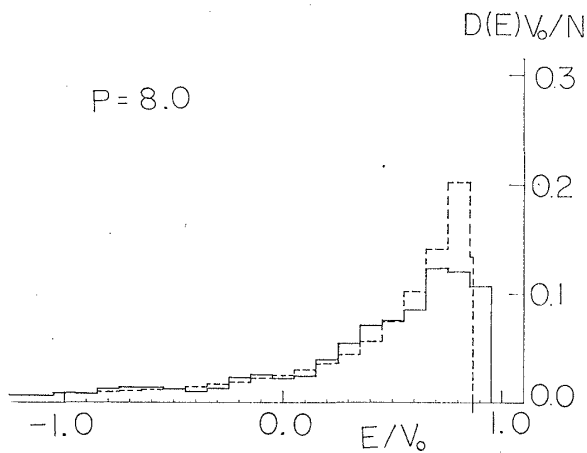


Fig. 5-a).

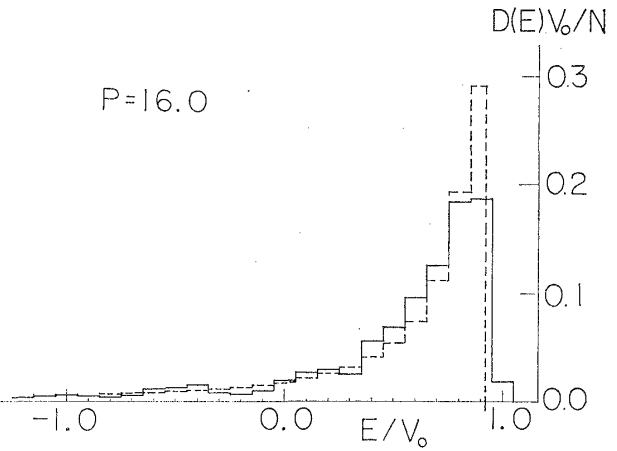


Fig. 5-b).

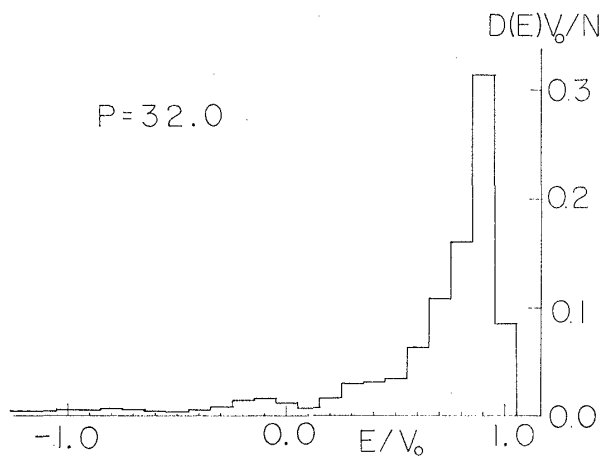


Fig. 5-c).

Fig. 5. Coarse-grained density of states $D(E)$ for high concentration is shown as histograms. Curve a) for $p=8.0$, b) for $p=16.0$ and c) for $p=32.0$.

lated and therefore the calculation of the density of states for $p \leq 1/16$ is trivial. In this region of concentration no significant change is seen for eigenvalues due to variation of wave vector \mathbf{k} as shown in Fig. 2-a). Figures 3-a) and 3-b) show the density of states for $p=1/8$ and $1/4$, respectively.^{*)}

ii) Intermediate concentration ($p=1/2, 1, 2, 4$).

As p increases the central peak, seen in Figs. 3-a) and 3-b), is reduced and shifted to higher energy region. Figures 4-a)-d) show the density of states for $p=1/2, 1, 2$ and 4 , respectively. Comparison of our results with M-T's indicates rather qualitative difference. The result of M-T seems to overemphasize the asymmetry of the density of states.

iii) High concentration cases ($p=8, 16, 32$).^{**)}

The density of states shows a remarkable asymmetry as seen in Figs. 5-a), b)

^{*)} Every figures of 3 to 5 is drawn such that the area of histograms is normalized to 1 when V_0 is equal to unity. Broken lines are of M-T's in Figs. 3-b) to 5-b).

^{**)} As one increases the value of p for fixed c the effective force range a^{-1} increases. One may therefore suspect that the approximation by the MEAPS for fixed c may become questionable for large p and the large \mathbf{k} -dependence for $p=32.0$ may be its reflection. However, for $p=32$ and $c=0.01$ by Eq. (2.8) the effective force range is $a^{-1}=3$, so that it is smaller than the length of the edge of the unit cell, which is equal to 10. Moreover, as p increases the sample-dependence of histograms is found to decrease. This fact together with the stability test suggests that the main feature of the obtained histogram is reliable even for large p .

and c) for $p=8, 16$ and 32 , respectively.

Agreement with M-T's is good in these cases. Every sample gives similar set of eigenvalues to lead to rapid convergence of ensemble averaging. The variation of eigenvalues with k becomes appreciable as shown in Fig. 2-c); in particular it is remarkable for lowest few eigenvalues.

§ 4. Discussion

In order to compare our result with Majlis's, we plot in Fig. 6 the integrated density of states as calculated by Majlis and by us. Although his calculation corresponds to $p=8.2$ while ours for $p=8.0$, general agreement is satisfactory. However, as enunciated in § 1 there is a systematic discrepancy; namely, for $0 \leq E/V_0 \leq 0.7$ $n(E; p)$ calculated by Majlis is larger than ours. This can be attributed to the size effect, since as shown in Table II in appendix his second moment of energy is estimated to have an error more than 17% when $p=8.0$. Therefore, Majlis's result gives somewhat higher density of states in the neighborhood of $E=0$ due to the size effect. It is to be noted from Table II that the error cannot be so much reduced with the increment of N , while our method is always free from this type of error.

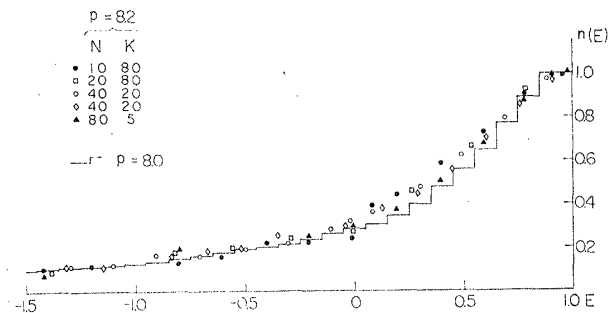


Fig. 6. The integrated density of states $n(E)$ for $p=8.0$ is drawn. Those by Majlis for $p=8.2$ are plotted, too.

In our calculation impurity sites are restricted on the fixed lattice points, while in the calculation of M-T and Majlis impurity sites can be any point in the space. This difference is negligible of course when $\alpha \ll 1$. Although this inequality is not necessarily well obeyed in our calculation, as shown in Fig. 1-b) the fact that the obtained histogram is rather insensitive to the change of both c and α for the fixed value of p lends support that the above difference is not serious for the results.

Apart from the above points the general agreement of our result with Majlis's gives confidence to the use of the MEAPS combined with the Monte Carlo method. We hope such an approach will disclose other salient features of aperiodic systems as well as enable us the calculation of more realistic models, where the approximative analytic approach is not free from ambiguity.

Acknowledgements

The authors are grateful to Professors T. Matsubara and Y. Toyozawa for their interest and for providing them with their unpublished table of numerical calculations. They are also indebted to Professor T. Yamamoto for constant

encouragement.

Numerical calculations were carried out with the aid of the HITAC 5020 in the Kyoto University Computing Center and of the HITAC 5020E in the Computer Center of the University of Tokyo.

Appendix

In general, the eigenvalues E_α ($\alpha = 1, 2, \dots, N$) of the $N \times N$ Hermitian matrix $\mathbf{H} = \{H_{mn}\}$ satisfy the following relations:

$$\bar{E} = \frac{1}{N} \sum_{\alpha} E_{\alpha} = \frac{1}{N} \sum_n H_{nn}, \quad (\text{A}\cdot 1)$$

$$\overline{E^2} = \frac{1}{N} \sum_{\alpha} E_{\alpha}^2 = \frac{1}{N} \sum_{n,m} H_{mn} H_{nm} = \frac{1}{N} \sum_{n,m} |H_{nm}|^2. \quad (\text{A}\cdot 2)$$

If we identify this matrix with the M-T Hamiltonian in the coordinate representation, we find by using Eqs. (1.1)-(1.4) in Eqs. (A.1) and (A.2) that

$$\bar{E} = 0 \quad (\text{A}\cdot 3)$$

and

$$\langle E^2 \rangle = \frac{1}{N} \int \dots \int \{V(\mathbf{R}-\mathbf{R}')\}^2 n(\mathbf{R}, \mathbf{R}') d\mathbf{R} d\mathbf{R}', \quad (\text{A}\cdot 4)$$

where $\langle \dots \rangle$ denotes the ensemble average over configurations of impurities, and $n(\mathbf{R}, \mathbf{R}')$ is the probability of finding a pair of impurities at the points \mathbf{R} and \mathbf{R}' per (unit volume)².

Now we consider an infinite simple cubic lattice with unit lattice constant and assume that the probability of finding an impurity at a given lattice point is equal to c independent of the configuration of impurities occupying other lattice points. Of course, impurities are assumed to be situated only on lattice points. Then, we have

$$\langle \overline{E^2} \rangle = c \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} V(n_1^2 + n_2^2 + n_3^2)^2. \quad (\text{A}\cdot 5)$$

According to the method described in § 2, the energy spectrum calculated by the MEAPS should give a value for $\langle \overline{E^2} \rangle$ as given by

$$\begin{aligned} \langle \overline{E^2} \rangle_{\text{MEAPS}} = & \lim_{L \rightarrow \infty} \frac{c}{M^3 L^3} \sum_{\mathbf{k}} \sum_{n_1=0}^{M-1} \sum_{n_2=0}^{M-1} \sum_{n_3=0}^{M-1} \left| \sum_{p_1=-L/2}^{L/2} \sum_{p_2=-L/2}^{L/2} \sum_{p_3=-L/2}^{L/2} \right. \\ & \times V(\sqrt{(n_1 + p_1 M)^2 + (n_2 + p_2 M)^2 + (n_3 + p_3 M)^2}) \exp\{i(\mathbf{k} \cdot \mathbf{p}) M\} \left. \right|^2, \end{aligned}$$

where M is the length of the cubic unit cell, \mathbf{k} and L are the same as in Eq. (2.4), and $\mathbf{p} = (p_1, p_2, p_3)$. Since we have

$$\frac{1}{L^3} \sum_{\mathbf{k}} \exp\{i\mathbf{k} \cdot (\mathbf{p} - \mathbf{p}')M\} = \delta_{\mathbf{p}, \mathbf{p}'},$$

we obtain

$$\langle \overline{E^2} \rangle_{\text{MEAPS}} = c \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} \{V(n_1^2 + n_2^2 + n_3^2)\}^2, \tag{A.7}$$

which is nothing but $\langle \overline{E^2} \rangle$ given in (A.5).

On the other hand, for a finite lattice with \overline{N}^3 lattice points $\langle \overline{E^2} \rangle$ becomes

$$\langle \overline{E^2} \rangle_{\overline{N}} = \frac{c}{\overline{N}^3} \sum_{n_1=1}^{\overline{N}} \cdots \sum_{m_3=1}^{\overline{N}} \{V(\sqrt{(n_1 - m_1)^2 + (n_2 - m_2)^2 + (n_3 - m_3)^2})\}^2. \tag{A.8}$$

In order to estimate the order of magnitude of the dependence of $\langle \overline{E^2} \rangle_{\overline{N}}$ on \overline{N} , we simply assume that

$$\begin{aligned} V(R) &= V_0 \quad \text{for } R < R_0, \\ &= 0 \quad \text{for } R > R_0. \end{aligned} \tag{A.9}$$

Then, on the right-hand side of (A.8) when

$$R_0 < n_\alpha < M - R_0 \tag{A.10}$$

($\alpha = 1, 2, 3$), (in the shaded region in Fig. 7), the summation over $\{m_\alpha\}$ approximately gives the contribution $(4\pi/3) V_0^2 R_0^3$. When at least one of the n_α 's fails to satisfy (A.10), the average of the summation over $\{m_\alpha\}$ for given $\{n_\alpha\}$ is less than

$$\frac{V_0^2}{R_0^2} \int_0^{R_0} dx \int_0^x \pi (R_0^2 - \rho^2) d\rho + \frac{2\pi}{3} R_0^3 V_0^2 = \frac{13}{12} \pi R_0^3 V_0^2. \tag{A.11}$$

Therefore, we obtain

$$\begin{aligned} \langle \overline{E^2} \rangle_{\overline{N}} &\lesssim c \frac{4\pi}{3} R_0^3 V_0^2 \left[\left(\frac{\overline{N} - 2R_0}{\overline{N}} \right)^3 + \frac{39}{48} \left\{ 1 - \left(\frac{\overline{N} - 2R_0}{\overline{N}} \right)^3 \right\} \right] \quad (\text{for } \overline{N} > 2R_0), \\ \langle \overline{E^2} \rangle_{\overline{N}} &\lesssim c \frac{13}{12} \pi R_0^3 V_0^2 \quad (\text{for } \overline{N} \leq 2R_0). \end{aligned} \tag{A.12}$$

If we put $c \cdot (4\pi/3) R_0^3 = p$ and let N be the number of impurities in the cube of volume \overline{N}^3 , then we have $N = c\overline{N}^3$, so that

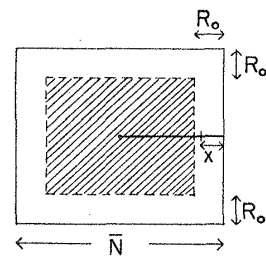


Fig. 7. We denote the number of lattice points by \overline{N} , the force range of $V(R)$ in Eq. (A.9) by R_0 and the variable x corresponds to x in Eq. (A.11). Size effect comes from the outside of the shaded region.

$$R_0/\bar{N} = (3p/(4\pi N))^{1/3}. \quad (\text{A}\cdot 13)$$

Using (A·12) and (A·13) we tabulate in Table II the upper bound of $\langle \bar{E}^2 \rangle_{\bar{N}} / \langle \bar{E}^2 \rangle_{\infty}$ for several values of p/N . This shows that even $N=80$ as was taken by Majlis is not necessarily large enough to neglect the surface effect.

Table II.

p/N	R_0/\bar{N}	Approximate upper bound of $\langle \bar{E}^2 \rangle_{\bar{N}} / \langle \bar{E}^2 \rangle_{\infty}$
0.01	0.134	0.88
0.1	0.288	0.83
1.0	0.62	0.81

References

- 1) H. Matsuda, Prog. Theor. Phys., Suppl. No. 36 (1966), 97.
- 2) H. Matsuda and N. Ogita, Prog. Theor. Phys. **38** (1967), 81.
- 3) P. Dean, Proc. Roy. Soc. **254** (1960), 507; **260** (1961), 263.
P. Dean and J. L. Martin, Proc. Roy. Soc. **259** (1960), 409.
P. Dean and M. D. Bacon, Proc. Roy. Soc. **283** (1965), 64.
J. Hori, Prog. Theor. Phys., Suppl. No. 23 (1962), 3.
- 4) S. F. Edwards, Phil. Mag. **3** (1958), 1020; **6** (1961), 617.
R. Klauder, Ann. of Phys. **14** (1961), 43.
F. Yonezawa, Prog. Theor. Phys. **31** (1964), 357.
F. Yonezawa and T. Matsubara, Prog. Theor. Phys. **35** (1966), 357, 759.
T. Matsubara and T. Kaneyoshi, Prog. Theor. Phys. **36** (1966), 695.
- 5) J. S. Langer, J. Math. Phys. **2** (1961), 584.
R. W. Davies and J. S. Langer, Phys. Rev. **131** (1963), 163.
- 6) T. Matsubara and Y. Toyozawa, Prog. Theor. Phys. **26** (1961), 739.
- 7) N. Majlis, Proc. Phys. Soc. **90** (1967), 811.