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## Calculation of the formation and migration energies for a vacancy in anthracene crystals

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**Abstract.** The formation energy of a molecular vacancy in a crystal of anthracene was calculated using the atom–atom potential method. This energy was found to be 93% of the packing energy of a regular lattice. The relaxation of molecules surrounding the vacancy was very small and anisotropic. The migration of an anthracene molecule from one site to another vacant site was also studied in two directions. The calculated value of the self-diffusion energy for the [010] jump was 125% of the regular lattice energy, whereas that for the [001] jump was 138%.

### 1. Introduction

The disturbance of a crystal structure in the vicinity of a vacancy was first calculated by Craig and Markey (1979) for naphthalene and anthracene using the atom–atom potential method (Silinsh 1980, Pertsin and Kitaigorodsky 1987). The model used consisted of a cluster of 20 molecules, which were the nearest neighbours to a vacant site. The cluster had no outer rigid layer. Lattice relaxations found in this model were so small that no molecule was displaced by more than 0.01 nm from its perfect-crystal site. The gain in packing energy due to a relaxation was estimated to be 2–4% of the packing energy of the regular lattice. Mokichev and Pakhamov (1982) estimated this gain to be 1.4% in a naphthalene crystal.

Recently, Dautant and Bonpant (1986) calculated the formation and migration energies for a vacancy in a naphthalene crystal. The model for the formation energy consisted of the inner layer of the 12 nearest-neighbouring molecules, which were allowed to relax, and the outer rigid layer. The energy variation due to relaxation was estimated to be 4.4% of the packing energy of the regular lattice. The molecular arrangements for the migration were composed of a diffusing molecule, the four nearest-neighbouring molecules, and the outer rigid layer.

In this paper we will report calculations of the formation and migration energies for a vacancy in an anthracene crystal. The two-layer cluster model was adopted to estimate these energies. Both the methods of static energy minimisation and molecular dynamics were used to evaluate the formation energy of the vacancy. To estimate the migration energy only the static method was adopted. We have examined in detail the influence on the energy of the size of the inner layer and of the magnitude of the cut-off radius for the interaction between atoms. In order to calculate the relaxation energy numerically

with high accuracy, we will introduce several kinds of cut-off radii as Mokichev and Pakhamov (1982) did. We were able to perform these numerical calculations with the aid of a supercomputer. Supercomputers HITAC S810 and S820 were used in this work.

## 2. The potential function and the regular lattice

It is assumed that the potential energy of interaction between any two molecules in a crystal is given by a sum over the atom-atom pair interactions. In the present calculation the functional form of the pairwise-additive atom-atom potentials is the Buckingham function

$$\phi_{ij}(r_{ij}) = -A_{ij}/r_{ij}^6 + B_{ij} \exp(-C_{ij}r_{ij}) \quad (2.1)$$

where  $r_{ij}$  is the distance between non-bonded atoms and  $A$ ,  $B$  and  $C$  are empirically determined parameters. For  $A$ ,  $B$  and  $C$  we used the values presented by Williams (1966) in set IV, (Craig and Markey 1979, Dautant and Bonpant 1986). All molecules are assumed rigid, i.e. intramolecular vibrations are assumed to be negligible. Atomic position coordinates for an anthracene molecule were taken from the neutron diffraction experiments (at  $T = 16$  K) by Chaplot *et al* (1982).

We begin by constructing the regular lattice, which is stable under the given potential parameters. An anthracene crystal is monoclinic (space group  $P2_1/a$ ) with two molecules (A and B) in a unit cell. The potential energy per molecule of this regular lattice is expressed by seven variables:

$$E_L = E_L(a, b, c, \beta, \theta, \varphi, \psi) \quad (2.2)$$

where  $a$ ,  $b$  and  $c$  represent the unit lengths of three axes of the crystal,  $\beta$  is the angle between the  $a$  and  $c$  axes,  $\theta$ ,  $\varphi$  and  $\psi$  are the Euler angles of a molecule of type A. The Euler angles ( $\theta$ ,  $\varphi$ ,  $\psi$ ) of a molecule are taken to be those present in rotation from the state where the molecular plane is parallel to the  $ab$  plane of the crystal and the long molecular axis is parallel to the  $a$  axis. We minimise  $E_L(\{x_j\})$  by means of the Newton minimisation method. In order to calculate with high accuracy and make good use of a supercomputer, instead of differentiating numerically we introduce differential functions  $\{\partial E_L/\partial x_j\}$ ,  $\{\partial^2 E_L/\partial x_i \partial x_j\}$  and then calculate them numerically. The energy  $E_L$  is given by

$$E_L = \frac{1}{2} \sum_{lpq} \phi_{pq}(r_{kp,lq}) \quad (2.3)$$

where  $\phi_{pq}(r_{kp,lq})$  represents the interaction energy between the  $p$ th atom in the  $k$ th molecule and the  $q$ th atom in the  $l$ th molecule. The vector  $r_{kp,lq}$  is given as

$$r_{kp,lq} = r_k - r_l + \mathbf{T}(\Theta_k)\mathbf{a}_p - \mathbf{T}(\Theta_l)\mathbf{a}_q \quad (2.4)$$

where  $r_k$  and  $r_l$  represent the positions of the centres of mass of the  $k$ th molecule and the  $l$ th molecule, respectively;  $\mathbf{T}(\Theta_k)$  and  $\mathbf{T}(\Theta_l)$  are transfer matrices for those molecules; the Euler angles ( $\theta$ ,  $\varphi$ ,  $\psi$ ) are abbreviated to  $\Theta$ ;  $\mathbf{a}_p$  and  $\mathbf{a}_q$  are the vectors that indicate the relative positions of the  $p$ th atom and the  $q$ th atom with respect to the centres of mass of those molecules, respectively. By calculating differential functions numerically, the Newton minimisation scheme is repeated until the energy has converged. Typically, seven or eight repetitions are necessary to achieve a converged value with errors within  $1 \times 10^{-5}$  kJ mol $^{-1}$ .

**Table 1.** Cohesion energy  $|E_L|$  of the regular lattice at various values of  $r_L$ ;  $r_L$  is the cut-off radius that is used when a stable lattice is calculated using the Newton minimisation scheme;  $r_{ESL}$  is that which is used when the energy is summed.

	$ E_L $ (kJ mol <sup>-1</sup> )			
	$r_L = 0.8$ nm	1.6 nm	2.4 nm	3.2 nm
$r_{ESL} = r_L$	94.97	104.52	105.49	105.73
$r_{ESL} = \infty$	105.89	105.90	105.91	105.91

Table 1 shows the influence on the energy of the cut-off radius for interaction between atoms. We denote by  $r_L$  the cut-off radius that is used in the Newton method and by  $r_{ESL}$  that which is employed in the energy summation (Mokichev and Pakhamov 1982). The calculations were performed for  $r_L = 0.8, 1.6, 2.4$  and  $3.2$  nm. The energy values for  $r_{ESL} = \infty$  were calculated using a continuum approximation at the range  $r > r_L$ . It is revealed that the calculated values of  $E_L$  depend very weakly on  $r_L$  but strongly on  $r_{ESL}$ . Therefore we use a large value of  $r_{ESL}$  in order to determine the energy  $E_L$  with high accuracy. Under the potential parameters mentioned above, the potential energy  $E_L$  of the regular lattice was estimated as  $-105.9$  kJ mol<sup>-1</sup>.

The experimental value of the enthalpy of sublimation ( $\Delta H$ ) given by Malaspina *et al* (1973) is  $100.5$  kJ mol<sup>-1</sup>. Using the law of equipartition of thermal energy we get the following approximate expression (Pertsin and Kitaigorodsky 1987):

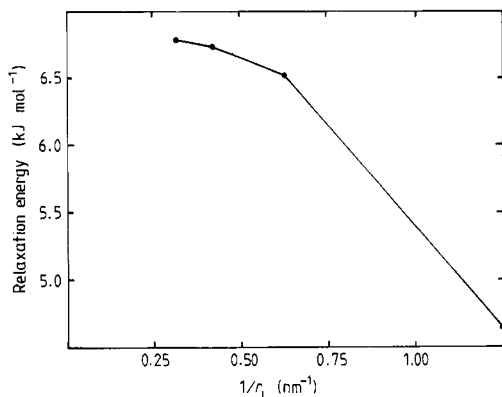
$$|E_L| \approx \Delta H + 2RT \quad (2.5)$$

where  $R$  denotes the gas constant. From (2.5) we obtain the value of  $107$  kJ mol<sup>-1</sup> for  $|E_L|$ , which is almost identical to our calculated value. The evaluated lattice constants were  $a = 0.812$  nm,  $b = 0.595$  nm,  $c = 1.117$  nm,  $\beta = 2.15$ ,  $\theta = 1.18$ ,  $\varphi = 1.13$  and  $\psi = 1.91$ . The experimental values obtained by Chaplot *et al* (1982) are  $a = 0.837$  nm,  $b = 0.600$  nm,  $c = 1.112$  nm,  $\beta = 2.19$ ,  $\theta = 1.14$ ,  $\varphi = 1.10$  and  $\psi = 1.93$ . The calculated values agree approximately with these experimental values, except the unit length of the  $a$  axis.

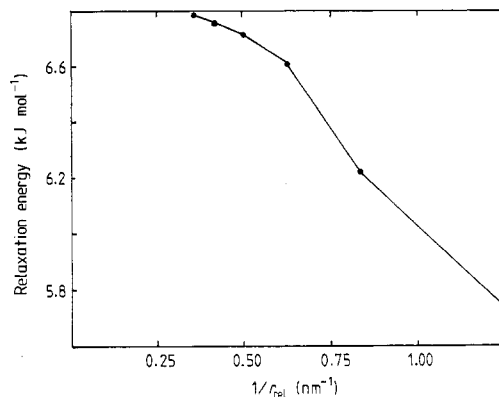
### 3. Formation energy and equilibrium configuration of a vacancy

To estimate the formation energy of a vacancy we have used the methods of static energy minimisation and molecular dynamics. It was confirmed that both methods gave the same result. Since the static method converged more rapidly than the molecular dynamics method, the former was adopted to determine parameters, as will be explained in the following.

After constructing a stable regular lattice of sufficient size, in order to create a vacancy we remove one molecule from the centre site  $(0, 0, 0)$  and put it on the kink site on the surface. The system now has an interaction energy just  $|E_L|$  higher than that before removing the molecule. Our model to deal with the relaxation of molecules around the vacancy consists of two layers. One is the outer rigid layer. The other is the inner layer, which consists of the molecules of which at least one atom is included by the sphere of radius  $r_{rel}$  with centre at the vacancy site. The positions and orientations of the molecules in the inner layer are allowed to relax to minimise the potential energy. We



**Figure 1.** Relaxation energy versus  $1/r_L$ ;  $r_L$  is the cut-off radius that is used when the outer rigid regular lattice is constructed.



**Figure 2.** Relaxation energy versus  $1/r_{\text{rel}}$ ;  $r_{\text{rel}}$  denotes the radius of the inner relaxable layer.

apply the Newton minimisation method separately to individual molecules and move all molecules simultaneously. We calculate numerically differential functions using a cut-off radius  $r_{\text{NM}}$ . Typically, 70 or 80 repetitions are necessary to achieve a converged value with errors within  $1 \times 10^{-4}$  kJ mol $^{-1}$ . When we sum the energy variation  $E_{\text{rel}}$  due to the relaxation using the cut-off radius  $r_{\text{ES}}$ , displacements of molecules are much smaller than the  $r_{\text{ES}}$ . Therefore the approximation  $\phi = \phi(r_{\text{ES}})$  for  $r > r_{\text{ES}}$  is better than the complete cut-off  $\phi = 0$ :

$$E_{\text{rel}} = E_{\text{rel}}(\text{complete cut-off}) - \sum_{\alpha} [N_{\alpha}(\text{initial}) - N_{\alpha}(\text{final})] \phi_{\alpha}(r_{\text{ES}})$$

where  $[N_{\alpha}(\text{initial}) - N_{\alpha}(\text{final})]$  is the difference in numbers of  $\alpha$  pairs ( $\alpha = \text{C-C}, \text{C-H}, \text{H-H}$ ) between the initial and final states. Because of this correction, the calculated values of  $E_{\text{rel}}$  begin to increase monotonically with the repetition of the Newton method.

In the numerical calculations we have introduced four parameters,  $r_L$ ,  $r_{\text{rel}}$ ,  $r_{\text{NM}}$  and  $r_{\text{ES}}$ . We examined the influence of these parameters on the relaxation energy  $E_{\text{rel}}$ . Figure 1 shows that the energy  $E_{\text{rel}}$  is strongly dependent on the cut-off radius  $r_L$  that is used when the stable regular lattice in the outer rigid layer is constructed. The relaxation energies were calculated using  $r_L = 0.8, 1.6, 2.4$  and  $3.2$  nm. Other parameters used were  $r_{\text{rel}} = 2.8$  nm (562 molecules in the inner layer),  $r_{\text{NM}} = 1.0$  nm and  $r_{\text{ES}} = 1.4$  nm. We can get the energy  $E_{\text{rel}}$  with errors within 5% through the use of  $r_L > 2$  nm, which is about twice as large as the distance (0.93 nm) between the *ab* planes.

To examine the  $r_{\text{rel}}$  dependence of  $E_{\text{rel}}$ , the relaxation energy  $E_{\text{rel}}$  was calculated using  $r_{\text{rel}} = 0.8$  nm (24 molecules), 1.2 nm (56), 1.6 nm (120), 2.0 nm (222), 2.4 nm (354) and 2.8 nm (562). Figure 2 shows that the size of the inner relaxable layer also has a strong influence on  $E_{\text{rel}}$ . Other parameters used were  $r_L = 3.2$  nm,  $r_{\text{NM}} = 1.0$  nm and  $r_{\text{ES}} = 1.4$  nm. We can get  $E_{\text{rel}}$  with errors within 5% through the use of an inner layer that contains more than 200 molecules.

Contrary to the above, the relaxation energy  $E_{\text{rel}}$  depended on the cut-off radii  $r_{\text{NM}}$  and  $r_{\text{ES}}$  only to a small extent. To examine the  $r_{\text{NM}}$  dependence of  $E_{\text{rel}}$ , the relaxation energies  $E_{\text{rel}}$  were calculated using  $r_{\text{NM}} = 0.8, 1.0, 1.2$  and  $1.4$  nm (table 2). Other parameters used were  $r_L = 3.2$  nm,  $r_{\text{rel}} = 2.8$  nm and  $r_{\text{ES}} = 1.4$  nm. When relaxing the molecules in the inner layer by means of the Newton method, it is enough to use a

**Table 2.** Relaxation energies  $E_{\text{rel}}$  for various cut-off radii  $r_{\text{NM}}$ ;  $r_{\text{NM}}$  is the cut-off radius that is used when the molecules in the inner layer are relaxed using the Newton minimisation method.

$r_{\text{NM}}$ (nm)	0.8	1.0	1.2	1.4
$E_{\text{rel}}$ (kJ mol <sup>-1</sup> )	6.728	6.756	6.758	6.758

**Table 3.** Relaxation energies  $E_{\text{rel}}$  for various cut-off radii  $r_{\text{ES}}$ ;  $r_{\text{ES}}$  is the cut-off radius that is used when the energy is summed.

$r_{\text{ES}}$ (nm)	0.8	1.0	1.2	1.4	1.6	1.8	2.0
$E_{\text{rel}}$ (kJ mol <sup>-1</sup> )	6.994	6.856	6.792	6.785	6.781	6.780	6.780

**Table 4.** Difference between molecular coordinates in the crystallite with the vacancy and those in the ideal crystallite.

Site	$\Delta x'$ (nm)	$\Delta y$ (nm)	$\Delta z$ (nm)	$\Delta \theta$ (deg)	$\Delta \varphi$ (deg)	$\Delta \psi$ (deg)
-0.5, 0.5, 0	0.011	-0.006	0.003	-0.16	2.75	2.52
0.5, 0.5, 0	0.001	-0.006	-0.001	0.03	-1.00	-0.61
0, 1, 0	0.003	-0.007	0.011	-1.70	4.31	-2.23
1, 0, 0	-0.003	-0.001	0.0	0.01	-0.52	0.20
-1, 1, 0	0.001	-0.002	0.0	-0.18	0.02	-0.19
1, 1, 0	-0.001	-0.002	-0.001	-0.08	-0.01	0.14
0.5, -0.5, 1	0.0	-0.002	0.001	-0.08	-0.76	0.59
0.5, 0.5, 1	-0.002	0.001	-0.002	-0.92	0.15	-0.55
0, 1, 1	0.002	-0.001	-0.002	-0.51	-0.10	-0.29
1, -1, 1	-0.001	0.003	-0.002	0.56	-0.11	0.15

relatively small cut-off radius  $r_{\text{NM}}$ . Through the use of the cut-off radius  $r_{\text{NM}}$  of 1.0 nm we can get  $E_{\text{rel}}$  to errors within 0.5%.

To estimate the  $r_{\text{ES}}$  dependence of  $E_{\text{rel}}$ , the relaxation energies  $E_{\text{rel}}$  were calculated using cut-off radii  $r_{\text{ES}} = 0.8\text{--}2.0$  nm (table 3). Other parameters used were  $r_{\text{L}} = 3.2$  nm,  $r_{\text{rel}} = 2.8$  nm and  $r_{\text{NM}} = 1.0$  nm. We can also use a relatively small cut-off radius  $r_{\text{ES}}$  to sum the relaxation energy  $E_{\text{rel}}$ . It seems that these results are in contrast with those of the  $r_{\text{ESL}}$  which is used when the energy  $E_{\text{L}}$  of the regular lattice is summed. This is due to the fact that a small displacement of the remote molecules brings about only a slight change in the relaxation energy  $E_{\text{rel}}$ . Through the use of the cut-off radius of 1.4 nm we can get  $E_{\text{rel}}$  to within an error of 0.2%.

The value of  $E_{\text{rel}} = 7.0$  kJ mol<sup>-1</sup> was obtained using the above estimation. The formation energy  $E_{\text{f}}$  of the vacancy is given by

$$E_{\text{f}} = |E_{\text{L}}| - E_{\text{rel}} = 98.9 \text{ kJ mol}^{-1}.$$

The displacements due to the relaxation are small and extremely anisotropic. The inversion symmetry with respect to the vacancy site is retained after the relaxation. Table 4 shows differences between molecular coordinates in the crystallite with the vacancy and those in the ideal crystallite. This calculation was performed using parameters

$r_L = 3.2$  nm,  $r_{rel} = 2.8$  nm (562 molecules),  $r_{NM} = 1.0$  nm and  $r_{ES} = 1.4$  nm. The results showed that the maximum displacement of the centres of mass of molecules was only 0.013 nm. Displacements of molecules on the site  $(-\frac{1}{2}, \frac{1}{2}, 0)$  and  $(0, 1, 0)$  are relatively large. Those on the site  $(\frac{1}{2}, \frac{1}{2}, 0)$  are small in spite of the fact that this site is the nearest neighbour of the vacancy. All molecules around the vacancy deviate to make the vacancy cavity small.

#### 4. Activation energies for molecular migrations

We present the migration energy calculations in two different crystallographic directions: [001] and [010]. First a stable regular lattice of sufficient size is constructed and one molecule at the site  $(I_V, J_V, K_V)$  is removed. We have a sphere with a radius  $r_{rel}$ , the centre of which is at the middle point of the vacancy site and the site  $(I_M, J_M, K_M)$  of the molecule to be moved. The relaxable inner layer consists of the molecules of which at least one atom is included by that sphere. The molecules in the inner layer are relaxed to get initial equilibrium configurations. After that the molecule at the site  $(I_M, J_M, K_M)$  is moved step by step to the vacancy site. The final position of the migrating molecule deviates from the initial vacancy position by the displacement by which the molecule at the site  $(2I_V - I_M, 2J_V - J_M, 2K_V - K_M)$  deviates from the regular lattice site in the initial relaxation. We express the total displacement of the migrating molecule by the migration vector  $\mathbf{a}_M$ . To indicate the displacements of the migrating molecule we introduce the coordinates  $(X_1, X_2, X_3)$  with respect to the new axes  $\mathbf{e}_1, \mathbf{e}_2$  and  $\mathbf{e}_3$ :  $\mathbf{e}_1 \parallel \mathbf{a}_M$  and  $\mathbf{e}_2, \mathbf{e}_3 \perp \mathbf{a}_M$ . At each step the migrating molecule is forced to move by the following displacements:

$$\Delta X_1 = a_M / N_{step} \quad (4.1)$$

where  $N_{step}$  is the total number of steps, and

$$\Delta X_i = - \sum_{j=2}^6 (\mathbf{F}^{-1})_{ij} (\partial E_M / \partial X_j + \Delta X_1 \partial^2 E_M / \partial X_1 \partial X_j) \quad \text{for } i = 2-6 \quad (4.2)$$

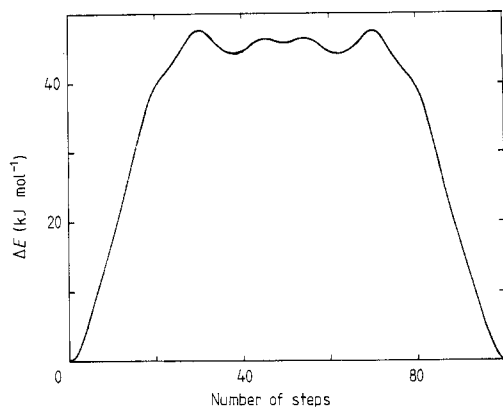
where the  $(5 \times 5)$  matrix  $\mathbf{F}$  is defined as

$$(\mathbf{F})_{ij} = \partial^2 E_M / \partial X_i \partial X_j$$

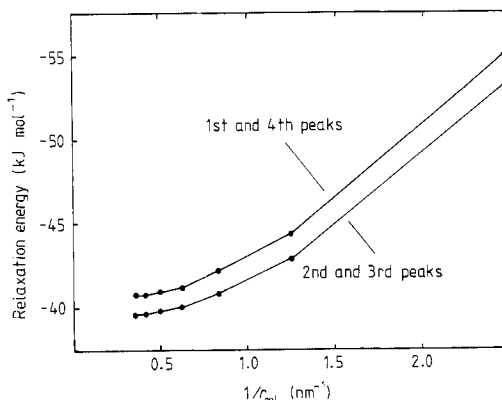
and  $E_M$  is the energy of the migrating molecule and  $X_4, X_5$  and  $X_6$  denote  $\theta_M, \varphi_M$  and  $\psi_M$  respectively. The equation (4.2) is used so as to avoid the collision between the migrating molecule and other molecules. The coordinates  $X_2$  to  $X_6$  are relaxed together with other molecules in the inner layer. When the matrix  $(\partial^2 E_M / \partial X_i \partial X_j)$  had negative eigenvalues at the saddle point in the [010] migration, the Davidson method was used instead of the Newton method. These calculations were performed using the parameters  $r_L = 3.2$  nm,  $r_{NM} = 0.8$  nm and  $r_{ES} = 1.4$  nm.

##### 4.1. [001] jump

In this case the diffusing molecule of type A situated at  $(0, 0, 1)$  passes to the vacancy site  $(0, 0, 0)$ . The migration vector  $\mathbf{a}_M = (0.607, 0.002, -0.932)$  was nearly equal to the translation vector  $-\mathbf{c} = (0.611, 0, -0.935)$  of the lattice. The total number of steps was chosen to be 100. The calculation was performed for the model where the molecular number in the inner layer was 359 ( $r_{rel} = 2.4$  nm). The migrating molecule moved almost



**Figure 3.** Variation of the potential energy versus number of steps in the [001] jump.



**Figure 4.** Peak values of the relaxation energy versus  $1/r_{\text{rel}}$  in the [001] jump;  $r_{\text{rel}}$  denotes the radius of the inner relaxable layer.

in a straight line between the initial and final sites, while the surrounding molecules relaxed. Figure 3 shows that the energy change  $\Delta E$  is symmetrical with regard to the crystallographic inversion centre situated at  $(0, 0, \frac{1}{2})$ . It possesses four peaks ( $\Delta E = 47.5, 46.4, 46.4$  and  $47.5 \text{ kJ mol}^{-1}$ ) and three valleys ( $\Delta E = 44.1, 45.6$  and  $44.1 \text{ kJ mol}^{-1}$ ). In the calculation in naphthalene two peaks were obtained in this direction by Dautant and Bonpant (1986).

Whether the energy minima obtained above were absolute minima or only local minima was investigated only at the 50th step, as follows. To search for energy minima that had the possibility to become absolute minima in the relaxable model, an unrelaxable model was examined in which the centre of mass of the migrating molecule was situated at  $(0, 0, \frac{1}{2})$  and the Euler angles were changed step by step ( $\Delta\theta = 0.05$ ,  $\Delta\varphi = 0.1$  and  $\Delta\psi = 0.1$ ). There were only three states with minimum energies within  $16 \text{ kJ mol}^{-1}$  of the minimum energy corresponding to the state obtained in the above calculations, that could be derived from it by a rotation about the molecular axes and were essentially the same as it. Therefore it seems that the energy of this state will also be the absolute minimum in the relaxable model. At other steps, even if the energy minima obtained in our calculation were not absolute minima, the former would be very close to the latter.

To examine whether the size of the inner layer used above was sufficient, the calculations mentioned above were repeated using parameters  $r_{\text{rel}} = 0.4 \text{ nm}$  (five molecules) to  $2.8 \text{ nm}$  (543 molecules). Figure 4 shows the peak values of the relaxation energies. Since the peak values of the energies remain nearly constant at  $r_{\text{rel}} = 2.4 \text{ nm}$ , the size used above is almost sufficient. The maximum peak value  $\bar{E}_{\text{rel}}$  of the relaxation energy was estimated to be  $-40.5 \text{ kJ mol}^{-1}$ . If only this jump was efficient, the diffusion observed in this direction would have the following activation energy  $E_{\text{dif}}$ :

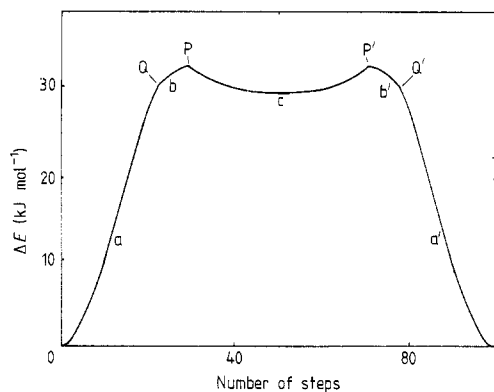
$$E_{\text{dif}} = |E_{\text{L}}| - \bar{E}_{\text{rel}} = 146.4 \text{ kJ mol}^{-1}$$

and a migration energy  $E_{\text{mig}}$ :

$$E_{\text{mig}} = E_{\text{dif}} - E_{\text{f}} = 47.5 \text{ kJ mol}^{-1}.$$

We also examined the case where the outer rigid layer had lattice constants that were calculated using a cut-off radius  $r_{\text{L}} = 0.8 \text{ nm}$ . This energy was found to be smaller by  $3 \text{ kJ mol}^{-1}$ .





**Figure 5.** Variation of the potential energy versus number of steps in the [0 1 0] jump. The energy variation curve consists of five branches, a, b, c, b' and a'.

#### 4.2. [010] jump

In this case the diffusing molecule of type A situated at (0, 1, 0) passes to the vacancy situated at (0, 0, 0). The migration vector  $\mathbf{a}_M = (-0.006, -0.581, -0.021)$  was nearly equal to the translation vector  $-\mathbf{b} = (0, -0.595, 0)$  of the lattice. In the course of migration in this direction, there were several energy minima, which were close together. To search for minima that had the possibility of becoming the absolute minima in the relaxable model, at several steps near the energy peak an unrelaxable model was examined in which the position of the centre of mass of the migrating molecules was changed step by step in a plane perpendicular to the migration vector and Euler angles of states with low energy were sought. The calculations in the relaxable model ( $r_{\text{rel}} = 2.4$  nm, 363 molecules) were performed using these states as initial states at suitable steps. Figure 5 shows that an energy variation  $\Delta E$  is symmetrical with regard to the centre and has five branches, a, b, c, b' and a'. The positions and Euler angles of the migrating molecule changed a little when this system transferred from one branch to the other branch at the cross-over points of Q, P, P' and Q'. However the height of the energy barrier from the a branch to the b branch at the point Q was very low in the unrelaxable model and that from the b branch to the c branch at the point P was lower than  $0.02$  kJ mol $^{-1}$ . Therefore it seems that these barriers also will be low in this relaxable model. The energy variation reaches the maximum value  $\Delta E = 33.5$  kJ mol $^{-1}$  at the point P and decreases by  $3.2$  kJ mol $^{-1}$  at the centre. The path of the centre of mass of the migrating molecule was symmetrical with regard to the site  $(0, \frac{1}{2}, 0)$  and the deviation of it from the b axis was small:  $\max(\Delta x) = 0.025$  nm,  $\max(\Delta z) = 0.020$  nm.

Near the middle point of migration there was one branch whose energy was lower than that of the c branch. However an energy barrier from the c branch to this branch at points from P to P' was considerably higher than the peak P, because the angle  $\psi$  of the migrating molecule corresponding to this branch differed by about  $80^\circ$  from that corresponding to the c branch. Therefore this state will have no influence on the height of the peak.

The maximum peak value  $\bar{E}_{\text{rel}}$  of the relaxation energy was estimated to be  $-26.8$  kJ mol $^{-1}$ . If only this jump was taken into account, the observed diffusion in this direction would have the following activation energy:

$$E_{\text{dif}} = |E_L| - \bar{E}_{\text{rel}} = 132.7 \text{ kJ mol}^{-1}$$

and a migration energy:

$$E_{\text{mig}} = 33.5 \text{ kJ mol}^{-1}.$$

## 5. Discussion

The vacancy formation energy and the activation energies of self-diffusion have been estimated using the atom-atom potential method. It was found that the lattice constants of the outer rigid layer and the size of the inner layer had a strong influence on the quantitative calculations. The relaxation energy in vacancy formation amounted to only 6.6% of the regular lattice energy. This ratio is, however, a little larger than that in the calculations for naphthalene (1.4–4.4%). The maximum displacement of the centres of mass of the molecules around the vacancy was less than 0.013 nm, and the displacements were extremely anisotropic. In organic molecular systems (Craig and Markey 1979, Koehler 1980, Mokichev and Pakhamov 1982, Dautant and Bonpunt 1986), the molecular cage around a vacancy is quite stable against collapse. It seems that this may come from the very interlocking form of the packing. This is confirmed by the fact that the potential energy has several peaks in the course of migration.

The experimental values of activation energy for self-diffusion perpendicular to the *ab* plane are 177 kJ mol<sup>-1</sup> (Sherwood and Thomson 1960), 92 kJ mol<sup>-1</sup> (Lee *et al* 1965), 84 kJ mol<sup>-1</sup> (Reucroft *et al* 1966) and 202 kJ mol<sup>-1</sup> (Burns and Sherwood 1972). Those in the direction [010] are 100 kJ mol<sup>-1</sup> (Lee *et al* 1965) and 84 kJ mol<sup>-1</sup> (Reucroft *et al* 1966). Except for these tracer methods, McGhie *et al* (1969) obtained the value of 210 kJ mol<sup>-1</sup> using the radical recombination method. This lack of quantitative agreement may arise from the effect of impurities, or the differing degrees of crystallinity of the sample used (Hood and Sherwood 1966). Our calculated values using the monovacancy mechanism are between the higher experimental values of about 200 kJ mol<sup>-1</sup> and lower values of about 100 kJ mol<sup>-1</sup>. If the experimental values of about 200 kJ mol<sup>-1</sup> were reliable, it would be necessary to examine other mechanisms such as self-diffusion by the divacancy mechanism in silicon (Casey and Pearson 1975). The calculated values of migration energy are 32% ([010]) and 45% ([001]) of the regular lattice energy, which are a little larger than those in naphthalene (30% and 41%) (Dautant and Bonpunt 1986). These ratios are relatively small compared with those in rare-gas solids (Chadwick and Sherwood 1975).

We also attempted the calculations of diffusion in the directions [110] and [1 $\bar{1}$ 0]. However the migration of the diffusing molecule in these directions is more difficult than that in the [010] and [001] directions because the rotation of the diffusing molecule is prevented by the surrounding molecules due to the interlocking form of the packing.

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