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1992 J. Phys.: Condens. Matter 4 1269

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Calculation of diffusion activation energies in covalent solids: application to vitreous silica

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Received 19 August 1991

Abstract. A general method is proposed for estimating activation energies of diffusion in (amorphous) covalent solids. The parameters involved are the shear modulus, the effective area associated with a bond and the size of diffusion saddle-point doorways associated with the critical percolation pathway for diffusion in the structure. Calculations of the effective force constant for dilating the diffusion doorways in a model of amorphous silica, made using the Keating potential, are in very good agreement with the behaviour predicted by the model, and calculated activation energies for diffusion are in good agreement with experimental values for diffusion of rare gases in vitreous silica.

1. Introduction

When ions or atoms diffuse through materials, very often they have to pass through 'doorway' restrictions in the structure when moving from one interstitial site to another. Energy may be needed in the diffusion process in order to expand these doorways, and the magnitude of this energy is consequently very important in determining the diffusional energetics, especially in non-metals where the effect of valence electrons is negligible. In this paper we give a simple, general method to estimate this doorway-expansion energy for covalent structures.

The present method deals with the *static* atomic structure: atoms are assumed to occupy fixed positions in space. The method can be applied to any structure, crystalline or amorphous, provided that the strain energy of the structure can be calculated as a function of the atomic positions, and that the atomic positions can be 'relaxed' to the lowest energy state using some method.

An example of the application of this method is given using the structure of amorphous silica, the canonical glass former. The Keating potential was used to represent the (strain) energy of the structure in terms of covalent bond-stretching and bending interactions. However, it should be stressed that the method is general, and it will work for any potential-energy scheme.

2. The method

The doorway restrictions, or diffusion saddle points, are found by a method which has been described previously (Chan and Elliott 1990, 1991). In brief, sets of three

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atom centres are chosen, and the position of the point lying in the plane defined by these three centres and equidistant from the 'surfaces' of the three atoms (defined say by the Van der Waals radius) is calculated. If there are no atomic surfaces nearer to this point than the three chosen atoms, this point is a diffusion saddle point. By inspecting all triads of atoms, all diffusion saddle points (doorways) in the structure should be identified.

The basic idea of the method is to relax the atomic structure while keeping a diffusing atom at the diffusion saddle point to keep the doorway expanded. Let P denote the saddle point, i.e. the point that is equidistant from the surfaces of, and lying in the plane defined by, the three atoms A, B and C comprising the doorway. The size of the doorway, r_d , is defined to be the distance from P to the atom surfaces, namely

$$r_d = PA - r_a = PB - r_b = PC - r_c \quad (1)$$

where r_a is the (Van der Waals) radius of atom A, etc.

Suppose an atom of size r_a is to be squeezed through the doorway. It will be assumed that it then exerts forces of magnitude F proportional to the size difference between it and the doorway radius

$$F \propto (r_a - r_d). \quad (2)$$

These forces act along the line from the diffusing atom to the centre of each of the three atoms A, B, C comprising the doorway. The *whole* structure is then energy-relaxed in the usual manner, using whatever method and whatever potential-energy scheme is appropriate. At each relaxation step, the door atoms will have to take up extra displacements proportional to the force F . Since the atoms move between relaxation steps, the position of the saddle point P needs to be recalculated at each step using the positions of the three door atoms. Care also needs to be taken to ensure if a fourth, or even a fifth, atom comes into contact with the diffusing atom at some stage during the relaxation process, it also experiences forces from the diffusing atom. The magnitudes of these forces are also given by expression (2) above, except that r_d is replaced by the distance between the centre of the diffusing atom and the surface of the (extra) atom in contact.

In the following, the (amorphous) structure under investigation was relaxed by displacing atoms by distances that are proportional to the forces that they experience (Gaskell and Tarrant 1980), including these extra doorway-related terms. In general, if a method like the conjugate-gradient method (Steinhardt *et al* 1974) is used to relax an atomic structure, there is no force term involved in the relaxation process. However, one can still give extra displacements to the three door atoms that are proportional to the force described above.

In addition to the extra energy necessary to overcome the doorway restriction, the force required was also calculated. This force was evaluated by freezing the configuration when the structure had been relaxed *with* the diffusing atom at the doorway saddle point, and then applying the usual force equations (derived from the Keating potential in the following section) in order to calculate the force experienced by the door atoms.

3. Details of the calculation

The Keating potential (Keating 1966) was used throughout the following investigation,

although the method is not restricted to this particular form of potential. The strain-related potential energy, V , of a structure in this representation is given by a sum of bond-stretching and bond-bending terms which, for the case of (amorphous) silica, can be written as

$$V = A \sum_{\text{bonds}} \frac{(r_{ij}^2 - r_0^2)^2}{r_0^2} + B \sum_{\text{Si angles}} \frac{(r_{ij} \cdot r_{ik} + r_0^2/3)^2}{r_0^2} + C \sum_{\text{O angles}} \frac{(r_{ji} \cdot r_{ji'} - r_0^2 \cos \theta_0)^2}{r_0^2} \quad (3)$$

In this equation, r_{ab} is the vector along the bond between atoms a and b . Subscripts i and i' represent Si atoms, while j and k represent oxygen atoms. The (average) equilibrium Si-O bond length is denoted r_0 , θ_0 is the average oxygen bond angle, and A , B and C are force constants.

The structural model used in the following calculation was generated by Feuston and Garofalini (1988) using molecular dynamics. The model consists of 216 'units' of SiO_2 in a cubic repeating box of length 21.403 Å; the average Si-O bond length is 1.619 Å and the mean oxygen bond angle is 154.2°. Before any calculations relating to the energetics of the doorways can be performed, the model needs first to be relaxed using the Keating potential (equation (3)) since this is the potential that we shall use and the model was not generated using this potential. The equilibrium bond length, r_0 , and the equilibrium oxygen bond angle, θ_0 , in equation (3) were taken to be equal to the mean values for the model given above.

In order to investigate the elastic behaviour of the doorways, each doorway in the structure was dilated by a set amount, i.e. the values $(r_a - r_d)$ were taken from a fixed set of values, ranging from as little as 0.02 Å to 0.2 Å. The value of 0.02 Å is actually less than the thermal vibration amplitude of the atoms, being about 0.08 Å for Si atoms and 0.13 Å for O atoms (Wright and Sinclair 1985), and hence does not have any *direct* physical meaning. However, use of such small values can help one get a complete picture of the behaviour of the static structure starting from zero dilation. The relationship between the (given) amount of dilation, the force needed for the dilation and the energy required for the dilation were studied.

In order to relate the calculated saddle-point energies to experimentally measurable quantities, the energies should be compared with the calculated shear modulus (see section 4 for a discussion of this point). The shear modulus for the (isotropic) model was calculated by rescaling the size of the repeating box of the continuous-boundary model and then calculating the stress on the faces of the repeating box. In each calculation, the box is scaled by the factors $1 + e$, 1 and $1 - e$ in the three orthogonal directions, where e is the chosen strain. The model is then relaxed with the Keating potential before the stress is calculated. There are three different ways of achieving this rescaling (namely different permutations of the scaling factors $(1 + e)$, 1 and $(1 - e)$ in the x , y and z directions). The value of calculated shear modulus reported below is the average of the results of these three rescalings.

4. Choice of force parameters in the Keating potential

Although the Keating potential has been widely used in the simulation of the structure of vitreous silica, there appears to be no preferred choice for the force-constant

parameters A , B and C in equation (3). Table 1 contains some values of these parameters as used in previous studies. It should be noted that, as far as the static structure (i.e. the positions of atoms) is concerned, it is only the relative ratios between A , B and C that matter; their absolute values do not affect the static structure. Hence, in the studies by Ching (1982) and Guttman and Rahman (1988), for example, only the ratios between the force-constant parameters are given.

Table 1. Values of force-constant parameters in the Keating potential used in studies of vitreous silica. Note that the exact potential equation used may be different in each case. The values in the table are derived by equating the corresponding energy term with the Keating expression and comparing first-order changes.

A (kg s^{-2})	B (kg s^{-2})	C (kg s^{-2})	Comment	Reference
69.75	53.25	22.87	fitted to vibrational spectrum	e
75	101.25	41.25	A fitted to vibrational spectrum	d
83.12	57.94	—	quantum-mechanical calculation on $\text{Si}(\text{OH})_4$ molecule	e
92.88	—	13.83	quantum-mechanical calculation on $(\text{OH})_3 \text{SiOSi}(\text{OH})_3$ molecule	f
—	—	13.72	quantum-mechanical calculation on $(\text{OH})_3 \text{SiOSi}(\text{OH})_3$ molecule	g
x	$0.17x$	$0.17x/3$	a	h
x	x	$1.2x$	a, b	i
75	55	20	b	j

^a In these studies, the absolute values of the force-constant parameters were unimportant since only the atom coordinates of the model were of interest.

^b More than one set of force-constant parameters were used in this study. The values quoted in the table are those quoted most frequently or the most suitable.

^c Gaskell and Tarrant (1980).

^d Robertson and Moss (1988).

^e Gibbs *et al* (1981).

^f Murakami and Sakka (1988).

^g Newton *et al* (1980).

^h Ching (1982).

ⁱ Guttman and Rahman (1988).

^j Present study.

In order to minimize the effect of using different force parameters, we shall compare the calculated values of the saddle-point energies with that of the shear modulus because the dilation of a spherical or cylindrical cavity in a homogeneous medium is related to the shear modulus (see next section). In fact, most previous estimations of the saddle-point energies in covalent (amorphous) solids have been made using macroscopic-based formulae involving the shear modulus.

In the present study, we have mainly used the representative values $A = 75 \text{ kg s}^{-2}$, $B = 55 \text{ kg s}^{-2}$ and $C = 20 \text{ kg s}^{-2}$ (see table 1), although two other sets of values have also been used and the results compared.

5. Relationship between the saddle-point dilation energy and the shear modulus

In previous theoretical studies of diffusion in (amorphous) solids, doorway dilation energies have been estimated using equations relating the energy to the shear modulus

G of the material concerned. In these estimations, the material was always treated as a *continuous* medium.

The energy to dilate a spherical cavity in such a continuous medium from radius r_d to r is

$$E = 8\pi G r_d (r - r_d)^2 \quad (4)$$

(Frenkel 1947). Hakim and Uhlmann (1971) suggested that the saddle-point energy should be estimated by considering the dilation of an elliptical cavity, instead of a spherical one; the corresponding energy is given by

$$E = 8\pi G r_d f(c/a)(r - r_d)^2 \quad (5)$$

where $f(c/a)$ is a factor depending on the ratio of the minor axis a to the major axis c of the ellipsoid; it is unity for a sphere. Shelby (1979) has taken $f(c/a)$ to be 0.32. There have also been efforts to model the diffusion saddle point by considering the dilation of a cylindrical cavity of circular cross-section in a continuous medium. The energy to dilate a cylindrical hole of depth w from radius r_d to r is given by (Sokolnikoff 1983)

$$E = \pi G w (r - r_d)^2. \quad (6)$$

McElfresh and Howitt (1986) take w to be half of the average jump distance λ travelled by the diffusing species, assuming that the strain is sinusoidally distributed between the two sites defining λ , hence

$$E = \pi G \frac{\lambda}{2} (r - r_d)^2. \quad (7)$$

6. Results

It has been found previously (Chan and Elliott 1991) that there are on average 9.09 diffusion saddle-point doorways per SiO_2 unit in the model of vitreous silica constructed by Feuston and Garofalini (1988). For each doorway, relaxations were carried out, using at first the set of force-constant parameters $A = 75 \text{ kg s}^{-2}$, $B = 55 \text{ kg s}^{-2}$ and $C = 20 \text{ kg s}^{-2}$, for dilations of 0.02 \AA , 0.05 \AA , 0.1 \AA and 0.2 \AA . It should be noted that the dilation of the doorway after relaxation of the structure is not exactly the same as that introduced *during* the relaxation since, at the end of the relaxation, the dilation force is balanced by the restoring force of the structure, and the dilation force would be zero if the dilation were to be equal to the one introduced.

The population distributions of the force acting on each doorway atom at the end of the relaxations for the different dilations introduced are given in figure 1. It can be seen that the distributions are very similar in shape and are not very wide. Comparing the distributions of the four values of dilation, it can be seen that the forces have an approximately linear relationship with the amount of dilation. Thus one may write

$$F = kx \quad (8)$$

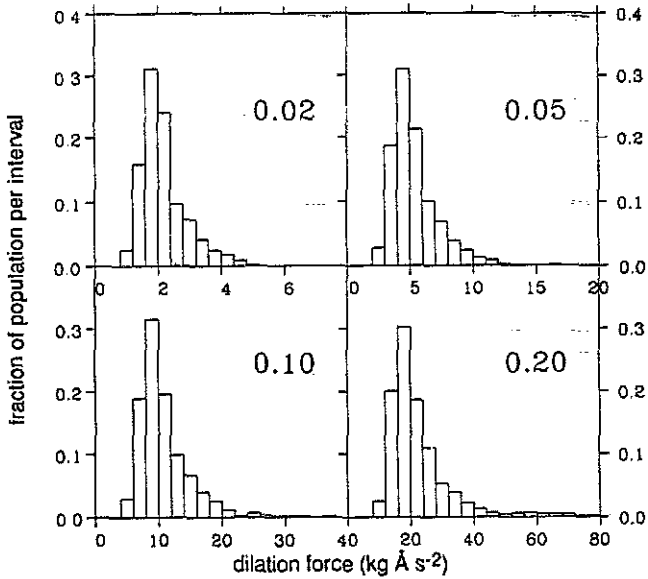


Figure 1. Population distributions of the door-dilation force acting on each doorway atom at the end of the relaxation; the values of dilation used (in Å) are shown for each figure.

where F is the force required for a dilation $x = r - r_d$, and k is a constant. The average values of $k = F/x$ for the different doorways were found to be 114.7, 113.4, 115.4 and 120.6 kg s^{-2} for dilations of 0.02, 0.05, 0.1 and 0.2 Å, respectively. The larger value of k for the introduced dilation of 0.2 Å may be due to the need to displace a nearby fourth atom for some doorways or it may also be due to the onset of anharmonicity for the Keating potential at large displacements.

Since the force on each door atom associated with a dilation is proportional to the dilation (figure 1), the energy involved in the displacement of each door atom in dilating the doorway would be $kx^2/2$, and so the total dilation energy should be

$$E = \frac{3}{2}kx^2 \quad (9)$$

if there is no fourth atom nearby which becomes associated with the diffusion doorway. Figure 2 gives the population distribution of the saddle-point energies of the doorways; again, the distributions are not wide. The average energies after relaxation for the introduced dilations of 0.02, 0.05, 0.1 and 0.2 Å were found to be 0.36, 2.32, 9.74 and 43.15 eV, respectively, which are indeed approximately proportional to the square of the amount of dilation. If the value of the constant k is calculated from the dilation energy E and the actual dilation x at the end of the relaxation, and assuming that equation (9) is valid, values of k equal to 107.9, 109.6, 116.0 and 130.2 kg s^{-2} , respectively, are obtained. These are comparable with the values of k as obtained from the dilation force. Again, it should be noted that the value of k increases somewhat for the larger dilations.

The calculated values of shear modulus, G , obtained by the method described in section 3, are given in table 2, together with the experimental literature value (Mazurin *et al* 1983). It can be seen that the value of the force-constant parameter B affects the magnitude of the calculated value of G more than does C , but the dominant factor is expected to be the bond-stretching force constant (although the effect of varying A was not investigated). However, the *absolute* magnitude of the

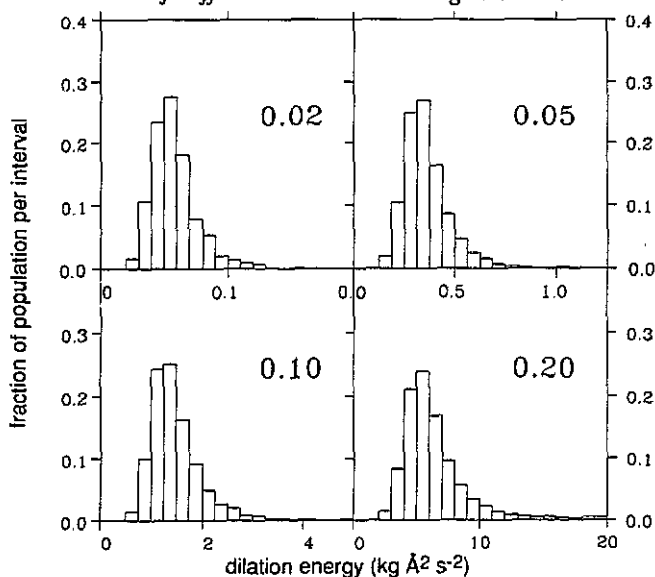


Figure 2. Population distributions of the door-dilation energies of the doorways; the values of dilation used (in Å) are shown for each figure.

values of G calculated using these force-constant values is appreciably larger than the experimental value. Due to the associated uncertainty in the values of the force constants, we therefore choose in the following to discuss the results normalized to the shear modulus calculated for the model with the same values of force constants.

Table 2. Values of shear modulus, G , calculated for the Feuston-Garofalini model. A , B and C are force-constant parameters for the Keating potential.

G (GPa)	A (kg s ⁻²)	B (kg s ⁻²)	C (kg s ⁻²)
86	75	55	20
105	75	75	20
89.4	75	55	40
31.3 ^a	—	—	—

^a Experimental value taken from Mazurin *et al.* (1983).

7. Interpretation of the diffusion saddle-point energies

The dilation of a diffusion saddle-point doorway at the microscopic level is indeed similar to the dilation of a cylindrical hole of circular cross-section in a homogeneous medium. However, as described in section 5, knowledge of the depth, w , of the hole is necessary before one can use the formula for the energy of dilation (equation 6). The crucial point is then what to take as the depth of the hole.

An expression for the depth, w , can be obtained by considering the effect of pressurizing a material at the atomic level. During pressurization, the forces act on the surface atoms through the bonds into the bulk of the material. Hence, each bond can be regarded as receiving the force due to the stress on a certain effective area, S . This effective area can be taken to be the reciprocal of the number of bonds cut

by a plane per unit area of the plane which cuts through the material. As shown in the appendix, the effective area, S , is given generally by the expression

$$S = \frac{2}{b\rho_0} \quad (10)$$

where ρ_0 is the number of bonds per unit volume, and b is the average bond length. For the case of the Feuston-Garofalini (1988) model for $v\text{-SiO}_2$, $S = 14 \text{ \AA}^2$.

For a diffusion doorway (in silica) which is surrounded by three (oxygen) atoms, there are six associated bonds which transmit the force to the bulk of the material. Hence, if one is to draw a parallel with the dilation of a cylindrical hole in a continuous medium, it is reasonable to take a depth w such that the area of the circular, cylindrical tube corresponding to the hole in the continuous medium has a value six times the effective area of a bond, i.e. w should be given generally by the expression

$$2\pi r_d w = 6S. \quad (11)$$

Here, r_d is the radius of the cylindrical tube and can be taken as the distance from the diffusion saddle point to the centres of the door atoms, since the force acts through the atom onto the bonds. For the case of the Feuston-Garofalini model for $v\text{-SiO}_2$, we have previously found (Chan and Elliott 1991) that this radius has the value $r_d \approx 2.2 \text{ \AA}$. Thus, from equation (11), the average depth of the 'cylindrical hole' associated with the diffusion saddle-point doorway is $w \approx 6.1 \text{ \AA}$ for the Feuston-Garofalini model. McElfresh and Howitt (1986) estimated this length to be 1.7 \AA , but associated this with half a typical atomic jump distance; we believe our method for estimating w to be more generally applicable and to have greater physical significance.

The elastic energy required to dilate a cylindrical hole in a homogeneous medium is given by equation (6) and, substituting the relation for w , the depth of the cylindrical hole, from equation (11), yields

$$E = \frac{3SGx^2}{r_d} \quad (12)$$

where x is the dilation ($r - r_d$). Note that, in equation (12), the activation energy is independent of the depth of the hole (i.e. the atomic jump distance) and in this respect is at variance with the McElfresh-Howitt (1986) relation (equation 7). Comparing equation (12) with equation (9), the elastic energy involved in displacing the three door atoms, it is apparent that in this picture the force constant, k , can be written as

$$k = \frac{2SG}{r_d}. \quad (13)$$

Thus a plot of k (or equivalently F/x , where F is the force required to dilate a hole by a displacement x) versus $1/r_d$ (the inverse of the radius of the cylindrical hole) should yield a straight line with a gradient equal to $2SG$.

Figure 3 shows such plots for three different choices of force-constant parameters in the Keating potential (table 2), for an applied dilation of 0.1 \AA , for all diffusion doorways in the Feuston-Garofalini model.

It can be seen that, with the exception of a cluster of points at a value of $1/r_d \approx 0.55 \text{ \AA}^{-1}$ which will be discussed subsequently, in general the points do

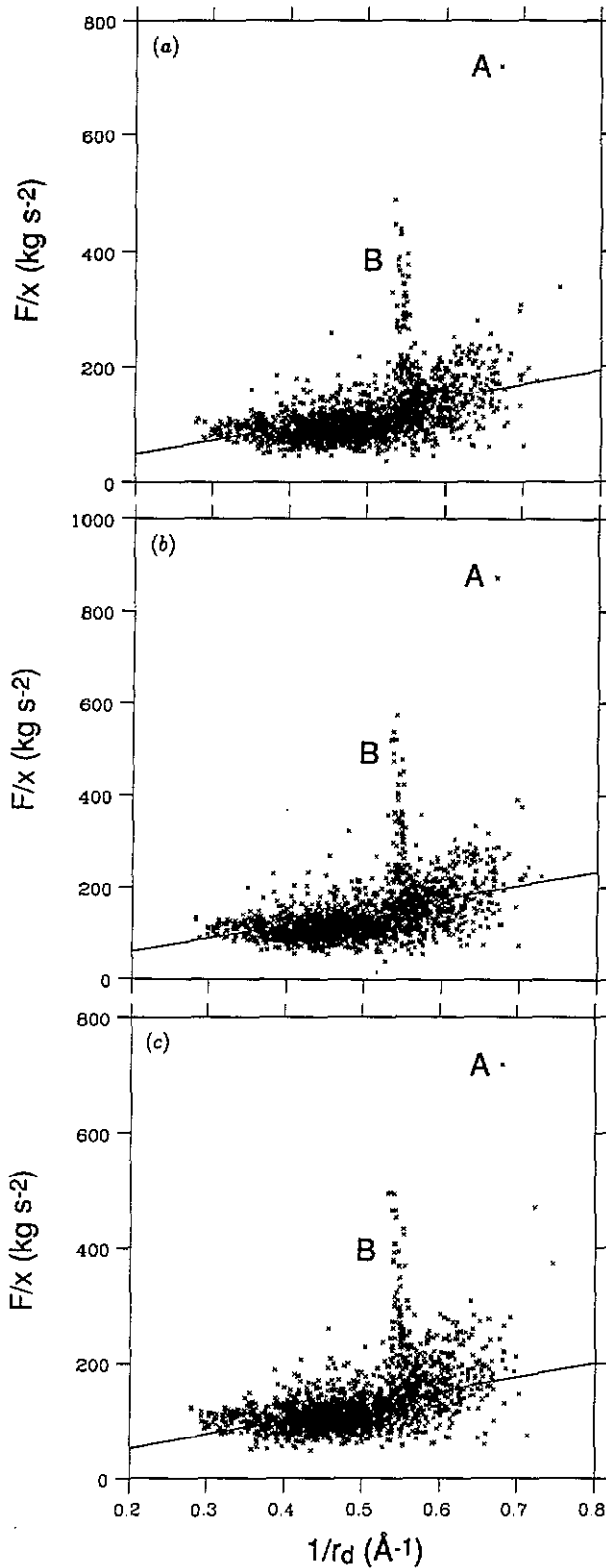


Figure 3. Dilation force divided by the magnitude of the dilatation (0.1 \AA) plotted versus the reciprocal of the doorway size (distance from the saddle point to the centre of a doorway atom). The straight line has a slope of $2SG$ (see text), where G is the calculated shear modulus (see table 2). Different force-constant parameters in the Keating potential have been used in each case: (a) $A = 75 \text{ kg s}^{-2}$, $B = 55 \text{ kg s}^{-2}$, $C = 20 \text{ kg s}^{-2}$; (b) $A = 75 \text{ kg s}^{-2}$, $B = 75 \text{ kg s}^{-2}$, $C = 20 \text{ kg s}^{-2}$; (c) $A = 75 \text{ kg s}^{-2}$, $B = 55 \text{ kg s}^{-2}$, $C = 40 \text{ kg s}^{-2}$.

indeed tend to fall on a straight line, as predicted. Moreover, the straight lines also shown in figures 3(a)–(c) are *not* best fits to the data points but are theoretical lines having slopes equal to $2SG$ (cf equation 13), where G in each case is the value of shear modulus calculated for the particular choice of force-constant parameters (see table 2). It can be seen that the data points in general cluster rather closely about these straight lines, lending strong support to our model for the interpretation of diffusion saddle-point energies.

Nevertheless it is evident from figure 3 that the values of $k = F/x$ for some diffusion doorways deviate systematically from the linear behaviour expected theoretically. These points, marked A and B in the figure, have been analysed further to ascertain the reason for their anomalous behaviour, i.e. why are these doorways stiffer than others with comparable door radii?

It has been found that most of these anomalous points correspond to doorways associated with very small rings in the structure. For example, the most anomalous point, A, corresponds to the single three-membered ring (in terms of oxygen atoms) in the structure of the Feuston–Garofalini model. The band of anomalous points labelled B in figure 3, lying at a value of $1/r_d \approx 0.55$, contains 42 points with values of $k = F/x \geq 250 \text{ kg s}^{-2}$. Three of these have been found to be related to anomalously coordinated oxygen atoms (in the Feuston–Garofalini model there are 2 three-fold and 2 one-fold coordinated oxygen atoms). Of the remaining 39 anomalous points in the band B, 29 are associated with four-membered rings in the structure (i.e. the 3 atoms forming the doors comprise a subset of the four oxygen atoms in the four-rings). There are a total of 48 four-rings in the model, and 114 of the total number of 2011 doorways in the model are associated with four-rings. Therefore, generally there is a strong correlation between anomalously stiff doorways and small (in this case, predominantly four-membered) rings.

For the majority of (larger) rings, the stiffness of the doorways corresponds well to the theoretical expression, equation (13). Therefore our approach offers the prospect of a completely general method for estimating values of effective force constants associated with the dilation of doorways during atomic diffusion principally using experimentally based data, namely S and G ; in the absence of detailed calculations for an appropriate structural model, r_d would have to be estimated, but it is very likely to fall within a relatively narrow range of values (cf figure 3).

From our previous analysis of the void distribution of structures of $v\text{-SiO}_2$ (Chan and Elliott 1991), we have found that (at least for the case of the Feuston–Garofalini model) the doorway radius associated with the critical percolation pathway is $r_d^p = 2.41 \text{ \AA}$. It can be seen from figure 3 that the distribution of values of force-constant values, k , at the inverse of the value, namely $1/r_d^p = 0.42 \text{ \AA}^{-1}$, is rather narrow, i.e. k_p is rather well defined. Hence our method can be used to estimate effective diffusion energies, through k_p and equation 9, since these are most likely to be determined by those diffusion saddle-point doorways on the critical percolation pathway.

Thus, from equation (12), and taking the *experimental* value of $G = 31.3 \text{ GPa}$ (table 2), and $S = 14 \text{ \AA}^2$ with $r_d = r_d^p = 2.41 \text{ \AA}$ (for the Feuston–Garofalini model), we obtain for the diffusion activation energy

$$E_{\text{diff}} = (54.6 \text{ kg s}^{-2})x^2. \quad (14)$$

Now

$$x = r_a - r_p$$

where r_a is the radius of the diffusing atom and the percolation radius is given by $r_p = r_d^P - r_{ox}$, where r_{ox} is the (Van der Waals) radius of the oxygen atom and has a value $\approx 1.5 \text{ \AA}$ (Chan and Elliott 1991); thus, $x = (r_a + r_{ox}) - r_d^P$. Table 3 gives values of diffusion activation energies estimated in this way for various representative values of $R = r_a + r_{ox}$. Also given in table 3 are experimental values for the activation energies of diffusion of a variety of rare-gas atoms in vitreous silica; agreement between experimental and theoretical values is reasonable, considering the uncertainties in the estimations of atomic radii, for example.

Table 3. Theoretical and experimental values for activation energies of diffusion in vitreous silica. The sum of the atomic radii is $R = r_a + r_{ox}$, where r_a is the radius of the diffusing atom. The radius of the oxygen atom, r_{ox} , is taken as 1.5 \AA in obtaining the values of R^{exp} . The experimental activation energies are taken from McElfresh and Howitt (1986).

$R \text{ (\AA)}$	$E^{calc} \text{ (eV)}$	Atom	$R^{exp} \text{ (\AA)}$	$E^{exp} \text{ (eV)}$
2.5	0.03	He	2.5	0.29
2.6	0.12	Ne	2.7	0.49
2.7	0.29	H ₂	2.75	0.45
2.8	0.52	Ar	3.1	1.24
3.0	1.19			

8. Conclusions

We have developed a simple, general classical model for estimating activation energies of diffusion in (amorphous) solids in terms of three parameters, namely the shear modulus, the effective area associated with a bond and the size of diffusion saddle-point doorways associated with the critical percolation pathway for diffusion in the structure. The first two parameters can be obtained experimentally whilst the last can be estimated (and has been found for the case of vitreous silica (v-SiO₂) from a theoretical analysis of a structural model). Calculations of the effective force constant for dilating all the saddle-point doorways in this model of v-SiO₂, made using the Keating potential, are in very good agreement with the behaviour predicted by the model. Furthermore, theoretical estimates for the activation energy of diffusion are in good agreement with experimental values for diffusion of rare gases in vitreous silica.

Acknowledgments

We are grateful to Professor S H Garofalini for providing the coordinates of the model of vitreous silica used in this study. SLC is grateful to the EC for financial support.

Appendix.

We derive here an expression for the average area, S , associated with a bond in a (non-crystalline) structure (equation 10 in the text).

The average area per bond can be evaluated by considering the areal number of bonds, distributed homogeneously, intersecting an arbitrary plane cutting through the structure. The number of bonds of length b , intersecting a plane of area A , is $Ab \cos \theta \rho(\theta)$, where θ is the angle between the normal to the plane and the bond direction, and $\rho(\theta)$ is the density of bonds in this orientation, given by

$$\rho(\theta) = 2 \frac{2\pi \sin \theta}{4\pi} \rho_0 = \rho_0 \sin \theta$$

where ρ_0 is the total number of bonds per unit volume. Thus, the total number of bonds intersecting the plane is given by

$$\int_0^{\pi/2} Ab \cos \theta \rho(\theta) d\theta = \int_0^{\pi/2} Ab \rho_0 \sin \theta \cos \theta d\theta = \frac{Ab\rho_0}{2}.$$

Hence, the average area associated with each bond is given by

$$S = \frac{2}{b\rho_0}.$$

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