Diffusion and transport coefficients in synthetic opals

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Opals are structures composed of close-packed spheres in the size range of nano to micrometers. They are sintered to create small necks at the points of contact. We have solved the diffusion problem in such structures. The relation between the diffusion coefficient and the thermal and electrical conductivity is used to estimate the transport coefficients of opal structures as a function of the neck size and the mean free path of the carriers. The theory presented is also applicable to the diffusion problem in other periodic structures.

I. NANOSTRUCTURED THERMOELECTRICS

A good thermoelectric material has low thermal conductivity κ, high electrical conductivity σ, and a high Seebeck coefficient, in order to maximize the thermoelectric figure of merit

$$Z = \frac{\sigma S^2}{\kappa}. \tag{1}$$

Z has units of inverse absolute temperature and is generally quoted as ZT. For more than 40 years, the search for better thermoelectrics has not provided a material with ZT significantly larger than one. ZT of about four would make thermoelectric coolers able to compete with gas-compression technology.

For many years, there has been a large effort to improve the efficiency of thermoelectric materials.[1,2] The search for better thermoelectrics can be classified by the material's length scale, with research done in the microscopic, mesoscopic, and macroscopic scale. In the microscopic scale, research has been done on chemical composition of candidate materials and alloys. The macroscopic range involves the design of the thermoelectric devices. So far, most of the effort has been done in these length scales. Only recently, with the improvement of different nanofabrication techniques, has the search for better thermoelectrics been done in the mesoscopic length scale. This includes the study of superlattices, quantum dots, and opals. It is interesting to mention an essential difference between this and the previously mentioned length scales. The theoretical tools needed to evaluate the improvements in the micro- and macrolength scales are fairly well established. Both the transport properties of compounds and alloys and the macroscopic equations for device modeling are well known. However, this is not the case in the mesoscopic scale. In many possible structures, we are still working on the basic theoretical framework to understand and plan new designs. A clear example of this is the discussion of the thermoelectric application of superlattices.[3] The purpose of the present work is to develop theoretical tools to evaluate the transport coefficients of one of these mesoscopic structures: synthetic opals.

Synthetic opals are nanostructured materials composed of close-packed spheres with a uniform radius a that can range from nanometers to micrometers. They are often made with glass spheres, but various techniques can be used to replace the glass spheres with almost any solid-state material. The opals are usually sintered so that the points of contact between neighboring spheres become small necks. Currents of electricity or heat can go from sphere to sphere through these necks. Here we calculate the electrical and thermal conductivity of such opal structures. We ask the question: How does the opal structure reduce the electrical and thermal conductivity? Assuming that the Seebeck coefficient will not be affected by the opal structure, if the thermal conductivity is reduced much more than the electrical conductivity, the opals could be useful thermoelectric materials.

Currently, there is an experimental group at AlliedSignal Corporation preparing and developing these structures to evaluate their potential as thermoelectrics. Our theory provides a theoretical tool to guide this evaluation and design.[4,5] The thermal conductivity of nanocomposites with regular structure have been studied by Bogomolov and collaborators and is reported in a series of publication starting from 1995.[6–11] The object of these studies has been a SiO_2 nanocomposite opal with first order voids completely filled with NaCl. Their results are analyzed with a theory for composite materials developed by Meredith and Tobias[12] on the basis of the original work of Lord Rayleigh.[13] The theory is based in the solution of the Laplace equation for a regular array of spheres embedded in a different medium. This theory cannot be applied to the case for which the spheres are touching each other, which is the focus of our present interest.

In Sec. II we relate the diffusion coefficient in the opal with the transport coefficients that are relevant for a thermoelectric analysis. The diffusion coefficient is evaluated with a random-walk model as explained in Sec. III and this model is analyzed and solved in Secs. IV and V. The results of applying this model to an fcc opal structure are discussed in Sec. VI.

II. TRANSPORT COEFFICIENTS AND DIFFUSION

Given a bulk material with thermal conductivity κ and electrical conductivity σ, we want to estimate the thermal and electrical conductivities, $\kappa^{(op)}$ and $\sigma^{(op)}$, of a synthetic opal made of spheres of this material. The origin and magnitude of the reduction in the transport coefficients depends on the mean free path of the carriers l compared with the diameter of the spheres d. If $l \ll d$, then the effect is due to a change in the boundary conditions, i.e., the thermal conductivity of the overall structure can be obtained by solving the Laplace equation in the opal geometry. If $l \approx d$, then the boundary scattering produced by the sphere surface and the necks becomes important. In addition to the geometrical effect, which is also present in this case, there is a reduction of the intrinsic conductivities due to the presence of the boundaries. In order to cover both situations with our model calculation, we will relate the transport coefficients to the diffusion coefficient of the opal and calculate this diffusion coefficient as a function of the mean free path and the opal geometric parameters, which are the diameter of the spheres d and the distance between its centers a.

The lattice thermal conductivity is proportional to the diffusion coefficient for phonons

$$\kappa = C D_{ph}, \tag{2}$$

where C is the specific heat of the material. Since we are mostly interested in semiconductors at room temperature, it is accurate to use Einstein's relation[14] to relate the mobility to the diffusion coefficient for electrical carriers,

$$\mu = \frac{e D_{el}}{k_B T}, \tag{3}$$

where e is the electron charge and k_B is the Boltzmann constant. Under these assumptions, neglecting the electronic contribution to the thermal conductivity and using $\sigma = ne\mu$, the thermoelectric figure of merit can be estimated as

$$Z = \frac{ne^2 S^2}{k_B T C} \frac{D_{el}}{D_{ph}}, \tag{4}$$

proportional to the ratio between the diffusion coefficient for electrons and the diffusion coefficient for phonons.

With Eqs. (2) and (3) in mind, to estimate the themoelectric figure of merit of opals we have to solve the diffusion problem in the opal structure for phonons and electrons. In this way, assuming that the Seebeck coefficient is not affected by the opal structure, we can estimate the figure of merit of the opal as

$$Z^{(op)} = \frac{ne^2 S^2}{k_B T C} \frac{D_{el}^{(op)}}{D_{ph}^{(op)}}, \tag{5}$$

where the superscript (op) identifies quantities related to the opal structure.

III. DIFFUSION COEFFICIENT AND RANDOM WALKS

Consider a particle moving with velocity v between collisions, each collision randomly changing the direction of the movement. In this situation the diffusion coefficient is given by

$$D = \lim_{t \to \infty} \frac{\langle r(t)^2 \rangle}{6t}, \tag{6}$$

where $\langle r(t)^2 \rangle$ is the mean-square displacement of the particle and t the total time of the random walk. This can be calculated by running a random walker that performs a step of length l at every time step of length τ. Chandrasekar[15] solved the diffusion problem of a random walker in an homogeneous media and obtained

$$\langle r^2 \rangle = l^2 N, \tag{7}$$

where N is the number of steps. By replacing this expression for $\langle r^2 \rangle$ in Eq. (6) for the diffusion coefficient, we obtain

$$D = \frac{1}{6} v l, \tag{8}$$

where v is the velocity of the random walker, i.e., the ratio l/τ.

The expression given in Eq. (7) for the mean-square displacement is only valid in a bulk material. If the carrier moves inside the spheres forming the opal structure, then we have to calculate $\langle r^2 \rangle$ in a different way in order to use Eq. (6) and obtain the diffusion coefficient of the opal $D^{(op)}$.

IV. DIFFUSION COEFFICIENT IN OPALS

We consider the carriers as classical particles performing a diffusive motion inside the material that forms the opal. The particle will move inside a sphere crossing from time to time the neck to a neighboring sphere. If the length of the jumps is smaller than the diameter of the spheres, the diffusion coefficient inside a sphere will be that of the bulk material with a microstructure corresponding to grains of the size of the spheres. The effective diffusion coefficient of the opal structure will be determined by the diffusion from sphere to sphere.

One method to evaluate this diffusion coefficient is the numerical simulation of the walker in the opal structure. However, if the diameter of the necks is small, as it is the case for the experimental situation, the walker will spend most of the time wandering inside a sphere and only sporadically crossing to the next sphere. As a consequence, most of the computer time will be lost in a diffusive movement inside the spheres and the diffusion coefficient calculation, which is essentially related with this motion from sphere to sphere, will become extremely expensive in computer time. A different method is needed.

Here we present such a method. The central idea is to integrate out the motion of the carrier inside a sphere while focusing attention on the motion from sphere to sphere. The diffusion in opals, with this picture in mind, is similar to the diffusion of a particle in a lattice, the lattice made up by the spheres. The standard theory of diffusion in a lattice is due to Chudley and Elliot.[16] However, their theory was for a particle diffusing from site to site without spending any time in the site. The diffusion in an opal is different and the theory must include the fact that there is a residence time within the

spheres. The opals are on a lattice, but the theory must include the diffusion within the spheres.

Define $\gamma_{ij}(t)$ as the probability per unit time that a particle departs through the neck i at time t if it entered the sphere through neck j at $t=0$. Define $f_i(\mathbf{R}_n,t)$ as the flux of particles departing a sphere centered at $\mathbf{R}_n$ through the neck labeled i at time t. Note that this quantity is *not* the net flux, which is the number of particles leaving minus the number entering. It is just the number leaving. The number entering the sphere through that neck is included as the flux leaving the neighboring sphere at $\mathbf{R}_n+\boldsymbol{\delta}_i$ through neck $\bar{i}$. Here we define the conjugate to neck i as $\bar{i}$. It is the label of the corresponding neck on the neighboring sphere. A neck i on one sphere is connected to $\bar{i}$ on the neighbor.

The rate equations for particle motion are

$$f_i(\mathbf{R}_n,t)=\sum_j \int_0^t dt'\,\gamma_{ij}(t-t')f_{\bar{j}}(\mathbf{R}_n+\boldsymbol{\delta}_j,t')+\delta_{i,1}\delta_n\delta(t). \tag{9}$$

The first term on the right is the outgoing flux due to all of the incoming particles at an earlier time. The last term on the right is the source term that starts the particle diffusion. The time integral can be eliminated by a Laplace transform

$$F_i(\mathbf{R}_n,p)=\int_0^\infty dt e^{-pt}f_i(\mathbf{R}_n,t),$$

$$\Gamma_{ij}(p)=\int_0^\infty dt e^{-pt}\gamma_{ij}(t). \tag{10}$$

After transforming Eq. (9), which describes the particle motion, it becomes

$$F_i(\mathbf{R}_n,p)=\sum_j \Gamma_{ij}(p)F_{\bar{j}}(\mathbf{R}_n+\boldsymbol{\delta}_j,p)+\delta_n. \tag{11}$$

The lattice properties are taken into account by taking a Fourier transform

$$G_i(\mathbf{k},p)=\sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_n}F_i(\mathbf{R}_n,p), \tag{12}$$

which leads to the final form of the equation of motion

$$G_i(\mathbf{k},p)=\sum_j \Gamma_{i\bar{j}}G_j(\mathbf{k},p)e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_j}+1, \tag{13}$$

where we have used $\boldsymbol{\delta}_j=-\boldsymbol{\delta}_{\bar{j}}$.

Equation (13) is a matrix equation that is solved for the functions $G_i(\mathbf{k},p)$. However, the diffusion properties are determined by the properties of the matrix

$$M_{ij}=\delta_{ij}-\Gamma_{i\bar{j}}\exp(-i\mathbf{k}\cdot\boldsymbol{\delta}_j). \tag{14}$$

The poles of G_i are determined by the zeros of the determinant of this matrix. In taking the inverse Laplace transform, the time dependence is given by the poles of G_i, which again are the zeros of $\det|M_{ij}|$. The smallest pole is defined as that with the smallest value of p. The long time behavior (diffusion) is determined by the smallest pole. We now discuss some properties of the matrix M, and the propagators γ that will be helpful in obtaining a form for the diffusion coefficient in opals $D^{(op)}$.

(i) If there is no absorption, then all of the particles which enter the sphere eventually must leave it sometime:

$$1=\sum_j \int_0^\infty \gamma_{ij}(t)=\sum_j \Gamma_{ij}(0). \tag{15}$$

Symmetry shows that this result is independent of i. If we define

$$\Gamma_T(p)=\sum_j \Gamma_{ij}(p), \tag{16}$$

the identity in Eq. (15) takes the form

$$\Gamma_T(0)=1. \tag{17}$$

(ii) If $\mathbf{k}=\mathbf{0}$ and $p=0$, then $\det|M|=0$. If $\mathbf{k}=\mathbf{0}$ each row of the matrix has the same elements, but in different order. As a consequence, the eigenvector ψ_0, which has all elements equal to one, has the feature that

$$M\psi_0=[1-\Gamma_T(p)]\psi_0. \tag{18}$$

Therefore at $p=0$ then $M\psi_0=0$. The vector ψ_0 has an eigenvalue of zero at $p=0$. Since the determinant is the product of the eigenvalues, this also means that the determinant of M_{ij} is zero in this case.

(iii) At $\mathbf{k}=\mathbf{0}$ $\det|M|$ has a factor $1-\Gamma_T(p)$. This is a direct consequence of the previous property.

All of the above results are at $\mathbf{k}=\mathbf{0}$. For diffusion one wants large values of $\mathbf{R}_n$, which means small values of $\mathbf{k}$. The expansion of the determinant at small p and small $k=|\mathbf{k}|$ has the general form

$$\det|M|=pu(p)U(p)+(ka)^2V(p), \tag{19}$$

where $U(p)$ and $V(p)$ are polynomials in the propagators $\Gamma_{i,j}(p)$, a is the nearest-neighbor distance, and $u(p)=[1-\Gamma_T(p)]/p$. As a result, the diffusion coefficient of the opal is given by

$$D^{(op)}=\frac{a^2}{u(0)}\frac{V(0)}{U(0)}, \tag{20}$$

where $u(0)$ is the limit of $u(p)$ for $p\to 0$.

These general results are illustrated for some relevant common lattices. For each particular lattice, the propagator $\Gamma_{i,j}$ depends only on the angle between necks i and j and we will use the notation Γ_θ, where θ is the angle between the normals to the neck surfaces.

A. Linear chain

We first present the simple case of the linear chain in order to illustrate the method. In this case, each sphere has two necks. We will define $\Gamma_0^{(lc)}(p)=\Gamma_{11}(p)=\Gamma_{22}(p)$ as the Laplace transform of the probability that the walker enters and leaves through the same neck, and $\Gamma_{180}^{(lc)}(p)=\Gamma_{12}(p)=\Gamma_{21}(p)$ corresponding to the probability of the walkers leaving the sphere through the opposite side. In this case the matrix M has the form

$$M^{(lc)}=\begin{bmatrix} 1-\Gamma_{180}^{(lc)}e^{ika} & -\Gamma_{0}^{(lc)}e^{-ika} \\ -\Gamma_{0}^{(lc)}e^{ika} & 1-\Gamma_{180}^{(lc)}e^{-ika} \end{bmatrix}. \tag{21}$$

The diffusion coefficient for this one-dimensional opal will be

$$D^{(op)}=\frac{a^2}{2u(0)}\frac{\Gamma_{180}^{(lc)}}{\Gamma_{0}^{(lc)}}. \tag{22}$$

B. Square lattice

In the case of the two-dimensional square lattice we have three different possibilities, the walker can go back through the same entry neck, can go out through one of the two necks that form an angle of 90° degrees with the incoming trajectory, or can leave the sphere through the opposite neck. The first possibility is represented by $\Gamma_{0}^{(sq)}(p)$, the second by $\Gamma_{90}^{(sq)}(p)$, and the last by $\Gamma_{180}^{(sq)}(p)$. In this case

$$\Gamma_{T}^{(sq)}(p)=\Gamma_{0}^{(sq)}(p)+2\Gamma_{90}^{(sq)}(p)+\Gamma_{180}^{(sq)}(p), \tag{23}$$

and the diffusion coefficient is given by

$$D^{(op)}=\frac{a^2}{4u(0)}\frac{\Gamma_{180}^{(sq)}+\Gamma_{90}^{(sq)}}{\Gamma_{90}^{(sq)}+\Gamma_{0}^{(sq)}}. \tag{24}$$

C. Simple cubic lattice

The simple cubic lattice has four necks at an angle of 90°, and as a consequence

$$\Gamma_{T}^{(sc)}(p)=\Gamma_{0}^{(sc)}(p)+4\Gamma_{90}^{(sc)}(p)+\Gamma_{180}^{(sc)}(p). \tag{25}$$

The diffusion coefficient is given by

$$D^{(op)}=\frac{a^2}{6u(0)}\frac{\Gamma_{180}^{(sq)}+2\Gamma_{90}^{(sq)}}{2\Gamma_{90}^{(sq)}+\Gamma_{0}^{(sq)}}. \tag{26}$$

D. Face centered cubic lattice

The fcc lattice corresponds to the close packing of spheres observed experimentally in opals. In the fcc lattice each sphere is connected through twelve necks to its nearest neighbors. Assume that we enter the sphere through neck 1. In the fcc lattice there are four necks with a normal forming an angle of 60° with the normal of neck 1, two at 90°, four at 120°, and one neck in the opposite side of neck 1 at 180°.

The result for the fcc lattice is

$$\Gamma_{T}^{(fcc)}(p)=\Gamma_{0}^{(fcc)}(p)+4\Gamma_{60}^{(fcc)}(p)+2\Gamma_{90}^{(fcc)}(p)+4\Gamma_{120}^{(fcc)}(p)+\Gamma_{180}^{(fcc)}(p) \tag{27}$$

and

$$D^{(op)}=\frac{\delta^2}{3u(0)}\frac{\Gamma_{60}^{(fcc)}(0)+\Gamma_{90}^{(fcc)}(0)+3\Gamma_{120}^{(fcc)}(0)+\Gamma_{180}^{(fcc)}(0)}{\Gamma_{0}^{(fcc)}(0)+3\Gamma_{60}^{(fcc)}(0)+\Gamma_{90}^{(fcc)}(0)+\Gamma_{120}^{(fcc)}(0)}. \tag{28}$$

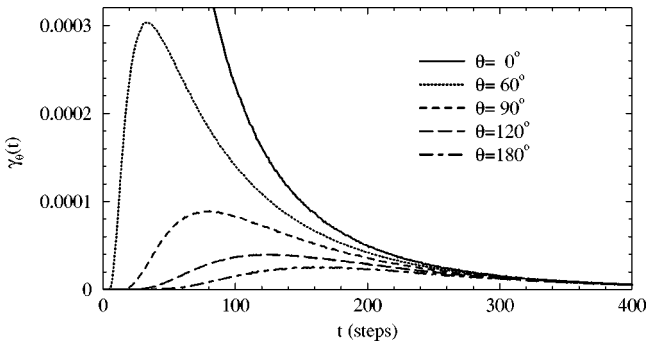

FIG. 1. Propagators as a function of time of a random walker inside an opal structure with diameter of the spheres d 5% larger than the intercenter spacing a. The mean free path $l=0.06a$.

The final stage of our calculation of the diffusion coefficient in opals is the determination of the particle propagators inside the sphere, $\gamma_{ij}(t)$, and this is the focus of the next section.

V. PROPAGATORS INSIDE THE SPHERES

The propagator inside the sphere, $\gamma_{ij}(t)$, was defined as the probability of a particle leaving through neck j at time t if it entered the sphere through neck i at $t=0$. We obtain these propagators by numerical simulation of the walker. A specific behavior of the walker when it hits the surface has to be specified to do the simulation. We found that the final result is not strongly dependent on the particular scattering at the surface as long as the particles are not absorbed. All the results shown here have been performed assuming that the walker starts a new random step after hitting the wall.

Since it is experimentally observed that the synthetic opal adopts a closed-packed arrangement of the spheres we will concentrate in the simulation of an fcc arrangement of spheres. In Fig. 1 we show the time dependence of the propagators for an opal in which the diameter of the spheres $d=1.05a$ and the step length of the walker $l=0.06a$. The propagator for leaving through the same neck of entry, $\gamma_0(t)$, is the only one that does not go to zero for $t\rightarrow 0$. There are many events in which the walker spends just a few steps inside the sphere and goes back through the same neck. To leave through another neck the walker needs at least a number of steps equal to the ratio between the shortest distance between these necks and the step length. Of course this contribution corresponds to events with very low probability in which the walker reaches the other neck in an almost ballistic way. All the propagators converge to the same exponential decay for long times. It is clear that after a long time of wandering inside the sphere, the walker looses all memory of the entry neck.

To calculate the diffusion coefficient we need the Laplace transform of these functions for $p=0$ that is the integral over all times, and the function u also evaluated at $p=0$. From its definition we see that

$$u(0)=-\left.\frac{d\Gamma_{T}(p)}{dp}\right|_{p=0}=\int_{0}^{\infty}t\,\gamma_{T}(t)dt. \tag{29}$$

Both integrals are very easy to obtain from the numerical simulation.

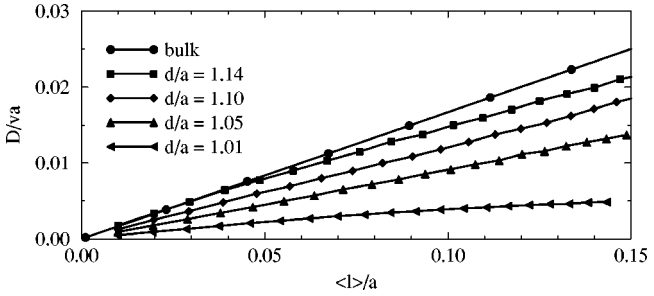

FIG. 2. Diffusion coefficient as a function of the mean free path for different diameters of the spheres. The diffusion coefficient is expressed in units of the velocity of the carriers times the lattice constant. The mean free path used for the plot is an average of the time step. The diffusion coefficient of the bulk material $D=vl/6$ is shown as a reference.

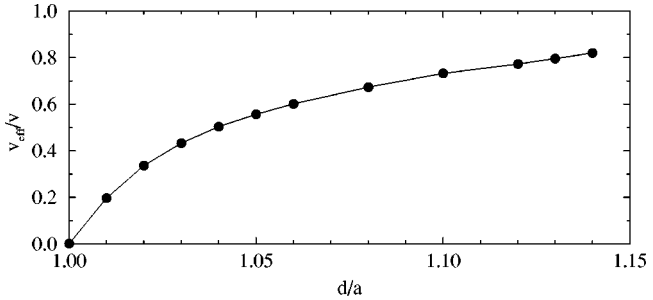

FIG. 3. Effective velocity as a function of the diameter of the spheres in the opal.

VI. DIFFUSION COEFFICIENT OF A FACE CENTERED CUBIC OPAL

We have used the theory described above to evaluate the diffusion coefficient of a fcc opal structure. Figure 2 shows the result as a function of the step length, for different sphere diameters. From the figure, the linear behavior of the diffusion coefficient with the step length is clear, at least when it is shorter than 15% the sphere diameter. The diffusion coefficient of the bulk material is shown as a reference.

The result that the diffusion coefficient of the opal is a linear function of the mean free path of the carriers is not promising for the opals as thermoelectric materials. This linearity implies that the ratio $D_{el}^{(op)}/D_{ph}^{(op)}$ will be approximately the same as the ratio D_{el}/D_{ph} and no increase of the thermoelectric figure of merit is to be expected.

The slope depends on the diameter of the spheres and defines an effective speed of the carrier. This dependence is shown in Fig. 3. This figure shows clearly that the diffusion coefficient goes to zero if the diameter of the spheres is smaller than the distance between the centers. This is because we assume a zero conductivity for the intersphere material. When the diameter is increased the effective velocity increases approaching that of the bulk material.

VII. SUMMARY AND CONCLUSIONS

We have developed a theory for diffusion of particles in an opal structure. With this theory, we calculate the diffusion coefficient of the opal as a function of the diffusion coefficient of the constituent material, the size of the spheres, and the necks between them. We apply this theory to some of the most common lattices and provide an explicit expression for the diffusion coefficient in each case.

The experimentally most relevant lattice is the fcc lattice. The application of this theory to a synthetic fcc opal structure shows that the diffusion coefficient is linear with the mean free path of the carriers. This result holds for mean free paths up to about 15% the diameter of the spheres. The effect of the opal structure is to reduce the effective speed of the carriers. We calculate the dependence of this effective velocity with the size of the spheres.

The linear dependence of the diffusion coefficient on the mean free path indicates that the overall reduction for electrons and phonons will be the same. Assuming that the Seebeck coefficient is not affected by the opal structure, we do not expect any increase in the thermoelectric figure of merit of opals compared with the bulk material. A major effect of the opal structure is expected in the case of a mean free path for phonons larger or of the order of the sphere diameter. However, this will correspond to a material that is a good thermal conductor in bulk and the reduction should overcome this unfavorable starting point.

As a final comment, there is an interesting property of all the expressions obtained for the diffusion coefficient in the different lattices, Eqs. (22), (24), (26), and (28). In all these cases, adding the numerator and denominator $\Gamma_T(0)$ is obtained, i.e., the sum is equal to 1. Even though this relation is very suggestive we could not find a good explanation for it. The theory developed in this work is applicable not only to synthetic opal structures but, can be used to solve the diffusion problem in any periodic structure in which the walker spends some time inside the unit cell.

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