Molecular-dynamics calculation of the thermal conductivity of vitreous silica

Philippe Jund and Rémi Jullien
Laboratoire des Verres–Université Montpellier 2, Place Eugène Bataillon, Case 069, 34095 Montpellier, France
(Received 1 February 1999)

We use extensive classical molecular-dynamics simulations to calculate the thermal conductivity of a model silica glass. Apart from the potential parameters, this is done with no other adjustable quantity and the standard equations of heat transport are used directly in the simulation box. The calculations have been done between 10 and 1000 K and the results are in good agreement with the experimental data at temperatures above 20 K. The plateau observed around 10 K can be accounted for by correcting our results taking into account finite-size effects in a phenomenological way. [S0163-1829(99)00121-6]

I. INTRODUCTION

The thermal properties of glasses exhibit some specific and unusual features which have been well known for quite some time.[1] These features are apparent in the specific heat and the thermal conductivity but we would like to focus here on the thermal conductivity κ. The temperature dependence of $\kappa(T)$ can be separated in three distinct temperature domains:

(i) At very low temperature ($T \leqslant 1$ K) the thermal conductivity increases like T^2. This increase can be explained within the tunneling model[2] which was proposed almost 30 years ago.

(ii) At intermediate temperatures ($2 \leqslant T \leqslant 20$ K) the thermal conductivity exhibits a ''plateau'' for which several explanations have been given.[3] An extension of the tunneling model, the soft-potential model has been proposed and gives a coherent description of the plateau by introducing the concept of ''soft vibrations.'' [4,5]

(iii) At high temperature ($T \geqslant 30$ K), $\kappa(T)$ rises smoothly and seems to saturate to a limiting value κ_∞ unlike crystals where $\kappa(T) \sim 1/T$ at elevated temperature. Recently this second rise of the thermal conductivity has also been explained within the soft-potential model[6] which appears to be able to account for all the thermal anomalies of glasses over the whole temperature range.

Our aim here is not to propose a new or alternative explanation of the above-mentioned anomalies. The purpose is to perform a molecular-dynamics (MD) simulation on a model silica glass using a very widely used interaction potential [the so-called ''BKS'' (van Beest, Kramer, and van Santen) potential[7]] without any preconception of the model able to explain the thermal anomalies of silica. This means that we do not add or inject an *a priori* quantity in the potential to reproduce a specific model. We use the standard definition of the heat transport coefficients that we calculate directly in our simulation box. In fact we introduce artificially inside the system a ''hot'' and a ''cold'' plate which therefore induce a heat flux. This flux creates a temperature gradient and once the steady state has been reached we can determine the thermal conductivity. By using plates compatible with the periodic boundary conditions we are able to calculate the thermal conductivity directly during the simulations without any additional parameter. This technique has been inspired by earlier studies[8] in which the plates were treated like hard walls and has mainly been applied to the calculation of the thermal conductivity in one- or two-dimensional systems.[9,10] Nevertheless, very recently Oligschleger and Schön applied the same method in a study of heat transport phenomena in crystalline and glassy samples (mainly selenium).[11] In parallel to these studies which can be called *in situ*, other methods relying on the use of the density and heat flux correlation functions[12] or on the Kubo and Greenwood-Kubo formalism[13] have been developed in order to determine the thermal conductivity of solids. Our results for the thermal conductivity obtained with the BKS potential compare reasonably well with the experimental data. First of all, the order of magnitude is correct above 20 K and, at least in the range 20–400 K, a nice quantitative agreement is obtained. Furthermore, by taking care of finite-size corrections in a very simple phenomenological way, we are able to reproduce the plateau around 10 K. Of course, the very low-temperature T^2 behavior, which is known to be due to quantum effects, is out of the scope of such a classical calculation.

This paper is organized in the following way. In Sec. II we describe the *modus operandi* we have used to obtain the thermal conductivity. In Sec. III we present first the results obtained directly from the MD simulations. Then we show the effect of finite-size corrections on these results and discuss our findings. In Sec. IV we draw the major conclusions.

II. MODUS OPERANDI

Except the determination of $\kappa(T)$, the simulations are standard classical MD calculations on a microcanonical ensemble of 648 particles (216 SiO_2 molecules) interacting via the BKS potential. As in a previous study,[14] the particles are packed in a cubic box of edge length $L = 21.48$ Å (the density is approximately equal to 2.18 g/cm^3) on which periodic boundary conditions are applied to simulate a macroscopic sample. The equations of motion are integrated using a fourth-order Runge-Kutta algorithm with a time step Δt equal to 0.7 fs. The glassy samples are obtained after a quench from the liquid state ($T \approx 7000$ K) at a constant quenching rate of 2.3×10^{14} K/s.

The principle of the thermal conductivity determination is illustrated in Fig. 1. We consider two plates P_- and P_+

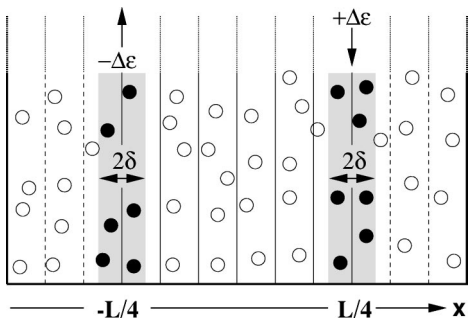

FIG. 1. Schematic representation of the method used to determine the thermal conductivity. More details can be found in the text.

perpendicular to the Ox axis and located at $x=-L/4$ and $x=+L/4$. These plates have a width 2δ along Ox and their surface is L^2. The positions of these plates permit to keep the periodic boundary conditions without introducing an asymmetry in the system. This has the advantage, compared to other studies[15] in which the introduction of the thermostatic plates breaks the symmetry, to use a relatively small number of particles. At each iteration the particles which are inside P_- and P_+ are determined and their number is, respectively, N_- and N_+. Once these particles are determined, a constant energy $\Delta\epsilon$ is subtracted from the energy of the particles inside P_- and added to the energy of the particles in P_+. By imposing the heat transfer in this manner we insure a constant heat flux per unit area J_x,[16] which is equal to $\Delta\epsilon/(2L^2\Delta t)$ (the factor 2 comes from the fact that the heat flux coming from the hot plate splits equally into two parts to reach the cold plate). The energy modification is done by rescaling the velocities of the particles inside the plates. Nevertheless, to avoid an artificial drift of the kinetic energy this has to be done with the total momentum of the plates being conserved. For a particle i inside P_- or P_+ the modified velocity is given at each iteration by

$$\mathbf{v}_i' = \mathbf{v}_G + \alpha(\mathbf{v}_i - \mathbf{v}_G) \tag{1}$$

where $\mathbf{v}_G$ is the velocity of the center of mass of the ensemble of particles in the plate and

$$\alpha = \sqrt{1 \pm \frac{\Delta\epsilon}{E_c^R}}, \tag{2}$$

depending on whether the particles are inside P_+ or P_-. The relative kinetic energy E_c^R is given by

$$E_c^R = \frac{1}{2}\sum_i m_i \mathbf{v}_i^2 - \frac{1}{2}\sum_i m_i \mathbf{v}_G^2. \tag{3}$$

Following the standard definition of the transport coefficients[16] the thermal conductivity is given by

$$\kappa = -\frac{J_x}{\partial T/\partial x}, \tag{4}$$

where $\partial T/\partial x$ is the temperature gradient along Ox. This formula, known as Fourier's law of heat flow, is only valid when a stable, linear temperature profile is obtained in the system. To calculate the gradient we divide the simulation box into N_s ''slices'' along Ox in which the temperature is calculated at each iteration. Due to the periodic boundary conditions we can concentrate only on the $N_s/2$ slices between $x=-L/4$ and $x=L/4$ and have a better determination of the temperature in these slices since by symmetry arguments these slices are equivalent to the $N_s/2$ slices located outside $[-L/4,L/4]$. We can therefore determine the temperature T_i $(i=1,...N_s/2)$ of each slice at each iteration. By averaging each T_i over a large number of iterations to kill the unavoidable large temperature fluctuations (due to the small average number of particles in each slice), we are able to determine after which simulation time τ the averaged profile of $T(x)$ can reasonably well be approximated by a straight line. After that time we estimate $T(x)$ using a first-order least-square fit of the averaged T_i's, the slope of which will give us the temperature gradient. At that point all the quantities necessary to calculate κ are determined.

Concerning the ''practical details'' of the simulation we have checked that the results are independent on the choice of $\Delta\epsilon$ and for the other quantities we have used a compromise between computer time and accuracy of the results. Here are the values used in our simulations: the width of the plates has been taken equal to $2\delta=1$ Å which means that approximately 30–40 atoms are inside the plates at each iteration. The temperature gradient has been determined on $N_s/2=$six slices, each slice containing approximately 100 particles. κ has been determined on samples which have been saved all along the quenching procedure and therefore have different temperatures T. To have the same treatment for each sample we have fixed $\Delta\epsilon$ to 1% of k_BT which appears to be a good choice. The temperature gradients obtained this way are small enough to insure the validity of Eq. (4). The most problematic choice is the simulation time τ. Indeed in order to reach the steady state one needs long MD runs. For us a typical run consists of 50 000 MD steps (35 ps) directly after the quench during which the average temperature is fixed and the heat transfer is switched on. Then we perform 450 000 supplemental steps (315 ps) with only the heat transfer but no other constraints during which the results are collected and averaged. After this time the temperature gradient should have converged and the value of κ should be constant. As we can see in Fig. 2, this can be considered to be qualitatively true for the samples above 10 K but certainly not for the low-temperature systems. In fact, at low temperature, longer runs [1 million steps (700 ps)] are necessary and still the convergence is not perfect [it is interesting to note that though our method converges slowly, it still converges faster than the calculation of $\kappa(t)$ given by a steady state experiment without a temperature gradient (Ref. 17, p. 61)]. It is also worth noticing that the characteristic sigmoidal shape of the temperature profile observed at 1 K is consistent to what is expected in the intermediate regime where only heat transport over a small distance close to the plates is effective. In the following, only the results above 8 K will be reported.

III. RESULTS

The results obtained for the thermal conductivity as a function of temperature in our model silica glass are reproduced in Fig. 3 and compared to experimental data collected

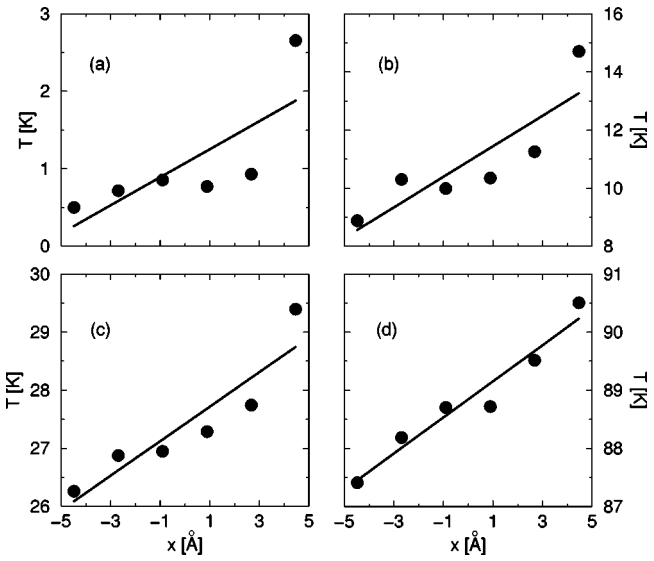

FIG. 2. Values of the temperature as a function of x in the slices located between $x=-L/4$ and $x=L/4$ for four different samples and the corresponding least square linear fit: (a) $T\approx 1$ K, (b) $T\approx 11$ K, (c) $T\approx 27$ K, and (d) $T\approx 89$ K.

between 1 and 100 K,[18] and up to 1000 K.[19] The first observation is that our simulations with the BKS potential give the correct order of magnitude over the whole temperature range (except at very low temperatures) with no adjustable parameters apart from the ''technical parameters'' described above and the constitutive potential parameters. At very high temperatures, say above 500 K, one observes a more marked saturation of $\kappa(T)$ than in the experiments. This might be explained by the fact that other contributions than the one described here can occur in the experiments at such high temperatures. It is known that the radiative contributions (photon transport) in particular increase quickly in this temperature range and can become of the order of the phonon

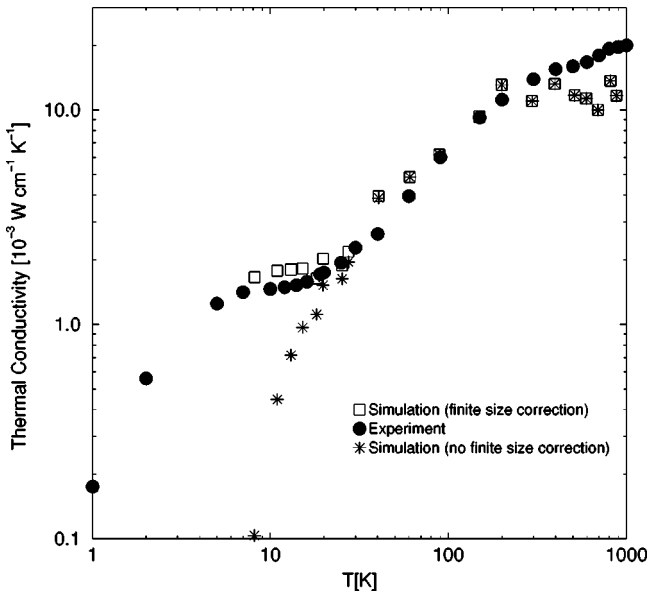

FIG. 3. Log-log plot of the thermal conductivity as a function of temperature in silica: ●: experiment; *: simulations; □: simulations with finite-size corrections.

contributions.[19] In a large intermediate range, 20–400 K, the agreement between the calculated and experimental values is very good. Indeed in the simulation κ also increases in this temperature range unlike what is found in crystalline samples. The major discrepancy between the simulation and the experiment can be seen between 8 and 20 K since we do not find the characteristic plateau in the thermal conductivity. In the following, we would like to argue that this discrepancy is essentially due to finite size effects.

In our cubic finite simulation box with periodic boundary conditions, the components of the **k** wave vectors take discrete values of the form $k_x=n_x 2\pi/L$, where n_x is a relative integer (and similarly for the other space directions), and one cannot find, in principle, propagative phonons with a frequency smaller than a lower cutoff ω_c which can be estimated by $2\pi v_T/L$, where v_T is the transverse sound velocity. Considering the experimental value $v_T=3.75\times 10^5$ cm/s for silica[20] this gives $\omega_c/2\pi\simeq 1.5$ THz [in practice, when diagonalizing the dynamical matrix in our low-temperature sample, we find, similarly to a previous work done on the same system[21], a slightly lower first nonzero frequency $\omega_o/2\pi\simeq 1.2$ THz, in agreement with the existence of an excess of modes (maybe nonpropagative), the so-called boson peak,[22] in this frequency range].[23] Therefore using the correspondence $\hbar\omega=3k_BT$ which gives the average phonon frequency ω of the phonons excited at temperature T, there are certainly not enough phonons excited at temperatures below $T_o\simeq 19$ K in our box to be able to reproduce the experimental curve correctly. In Fig. 3, the departure between our simulations and experiments is actually seen at a temperature of the order of 20 K, in good agreement with this analysis.

To try to put this argument on more quantitative grounds, let us assume that the thermal conductivity is given by the usual formula,[24]

$$\kappa=\frac{1}{3}Cv\ell, \tag{5}$$

where C is the heat capacity per unit volume, and v and ℓ the velocity and mean free path of the phonons, respectively. When applying such a formula to glasses one has to be careful because of localization effects. Obviously v and ℓ are the characteristics of the ''propagative'' phonons, i.e., those which really contribute to the transport phenomena. Consequently the heat capacity C to be considered should be only due to the contribution of these phonons and therefore (according to other authors[2,4]) should exhibit at low temperature the usual Debye behavior (the same as in crystals). If we assume also that the lack of phonons in our box, i.e., a wrong value of C, is the essential cause for the underestimated calculated value of κ, a very simple and crude way to take care of this is to multiply our simulation results by a corrective factor C_∞/C_b which can be estimated by taking for C_∞ and C_b the heat capacities calculated in the Debye approximation for an infinite system and a finite cubic box of edge L, respectively. To calculate this temperature-dependent factor we have used the standard formulas[24]

$$C_\infty=\frac{k_B}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\int_0^{\omega_D}\left(\frac{\hbar\omega/2k_BT}{\sinh(\hbar\omega/2k_BT)}\right)^2\omega^2 d\omega, \tag{6}$$

$$C_b = \frac{k_B}{L^3} \sum_p \sum_{\mathbf{k}} \left(\frac{\hbar v_p k / 2k_B T}{\sinh(\hbar v_p k / 2k_B T)} \right)^2 \quad (7)$$

with $\omega_D^3 = (N/L^3) 18\pi^2 (1/v_L^3 + 2/v_T^3)^{-1}$. In the expression of C_b the double sum runs over the three polarizations $p = L, T_1, T_2$ and over the first N $\mathbf{k}$ vectors (quantized as indicated above) of lowest norm $k = |\mathbf{k}|$. For N and L we have taken the simulation values $N = 648$ and $L = 21.48$ Å and for the sound velocities the experimental values $v_L = 5.9 \times 10^5$ cm/s and $v_{T_1} = v_{T_2} = 3.75 \times 10^5$ cm/s.[20] When correcting our numerical data this way, we obtain the open squares represented in Fig. 3 which turn out to be in very good agreement with the experimental results in the plateau region. Of course, our reasoning is very crude since it assumes that finite-size corrections affect only the heat-capacity contribution in the expression of κ [Eq. (5)] and that the harmonic approximation holds for the propagative phonons in that temperature range, however we think that the agreement with the data cannot be fortuitous.

It is unfortunate that we could not obtain more reliable results at temperatures lower than 8 K (due to the impossibility to reach the permanent regime). Anyway, after correction, these results would certainly give larger values for κ than the experiments since it is known that, at very low temperatures, the propagative phonons start to be scattered on the quantum two-level systems[2] and therefore should have a lower mean free path than the one obtained in a classical calculation like the one performed here.

IV. CONCLUSION

In conclusion, we have presented the results of an extensive classical molecular-dynamics simulation aimed to determine the thermal conductivity in a model silica glass. This determination has been done directly inside the MD scheme with the use of the standard equations governing the macroscopic transport coefficients and no preconceived model has been assumed. Moreover, it turns out that this method has considerable advantages (especially concerning the length of the simulations) compared to the standard methods usually implemented to calculate the transport coefficients.[17] The calculated values of the thermal conductivity are in good agreement with the experimental data at high temperature ($T > 20$ K) and by including finite-size corrections in a simple way we are able to reproduce the plateau in the thermal conductivity around 10 K, which has been the topic of several interpretations in the literature.[3] The agreement between the calculated and the experimental values of the thermal conductivity is even more striking when taking into account the ultrafast quenching rate used to generate our amorphous samples. This shows once more the good quality of the BKS potential which permits to reproduce the thermal anomalies of vitreous silica with no additional parameters.

Of course, our arguments on the finite-size effects should be tested in the future by running larger samples. Nevertheless, the simple phenomenological correction is so efficient that one can reasonably claim that the initial discrepancy between the calculated and experimental values of the thermal conductivity is indeed due to finite-size effects and not to a weakness of the method. Therefore we believe that this technique is a good way to calculate the thermal properties of materials directly inside molecular-dynamics simulations.

Most of the numerical calculations have been done on the IBM/SP2 computer at CNUSC (Center National Universitaire Sud de Calcul), Montpellier. We would like to thank Claire Levelut and Jacques Pelous for very interesting comments.

[1] R. Bruckner, J. Non-Cryst. Solids **5**, 123 (1970); R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971); D. G. Cahill and R. O. Pohl, *ibid.* **35**, 4067 (1987).
[2] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[3] J. E. Graebner, B. Golding, and L. C. Allen, Phys. Rev. B **34**, 5696 (1986); C. C. Yu and J. J. Freeman, *ibid.* **36**, 7620 (1987); E. Akkermans and R. Maynard, *ibid.* **32**, 7850 (1985); S. Alexander, O. Entin-Wohlman, and R. Orbach, *ibid.* **34**, 2726 (1986).
[4] V. G. Karpov, M. I. Klinger, and F. N. Ignat'ev, Zh. Éksp. Teor. Fiz. **84**, 760 (1983) [Sov. Phys. JETP **57**, 439 (1983)].
[5] M. A. Ill'in, V. G. Karpov, and D. A. Parshin, Zh. Éksp. Teor. Fiz. **92**, 291 (1987) [Sov. Phys. JETP **65**, 165 (1987)].
[6] L. Gil, M. A. Ramos, A. Bringer, and U. Buchenau, Phys. Rev. Lett. **70**, 182 (1993).
[7] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).
[8] A. Tenenbaum, G. Ciccotti, and R. Gallico, Phys. Rev. A **25**, 2778 (1982); R. D. Mountain and R. A. MacDonald, Phys. Rev. B **28**, 3022 (1983).
[9] A. Maeda and T. Munakata, Phys. Rev. E **52**, 234 (1995).
[10] J. Michalski, Phys. Rev. B **45**, 7054 (1992).
[11] C. Oligschleger and J. C. Schön, Phys. Rev. B **59**, 4125 (1999).
[12] A. J. C. Ladd, B. Moran, and W. G. Hoover, Phys. Rev. B **34**, 5058 (1986).
[13] P. B. Allen and J. L. Feldman, Phys. Rev. B **48**, 12 581 (1993); J. L. Feldman, M. D. Kluge, P. B. Allen, and F. Wooten, *ibid.* **48**, 12 589 (1993).
[14] P. Jund and R. Jullien, Philos. Mag. A **79**, 223 (1999).
[15] H. Kaburati and M. Machida, Phys. Lett. A **181**, 85 (1993).
[16] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).
[17] M. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1990).
[18] R. B. Stephens, Phys. Rev. B **8**, 2896 (1973).
[19] J. Zarzycki, *Les Verres et l'État Vitreux* (Masson, Paris, 1982), and references therein.
[20] F. Terki, C. Levelut, M. Boissier, and J. Pelous, Phys. Rev. B **53**, 2411 (1996).
[21] S. N. Taraskin and S. R. Elliott, Phys. Rev. B **55**, 117 (1997).
[22] G. Winterling, Phys. Rev. B **12**, 2432 (1975); F. L. Galeener, A. J. Leadbetter, and M. W. Stringfellow, *ibid.* **27**, 1052 (1983); U. Buchenau, H. M. Zhou, N. Nucker, K. S. Gilroy, and W. A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).
[23] We do find (like other authors; see Ref. 21) an excess of modes at low frequencies compared with the Debye formula when diago-

nalizing the dynamical matrix. However, the maximum of this excess of modes is located at a frequency of about 2 THz, i.e., almost twice the experimental value. We think that this discrepancy is simply due to finite-size effects: by reducing the lowest frequency ω_o one would shift this maximum excess of modes to lower frequencies.

[24] C. Kittel, *Introduction à la Physique de l'État Solide* (Dunod, Paris, 1970).