

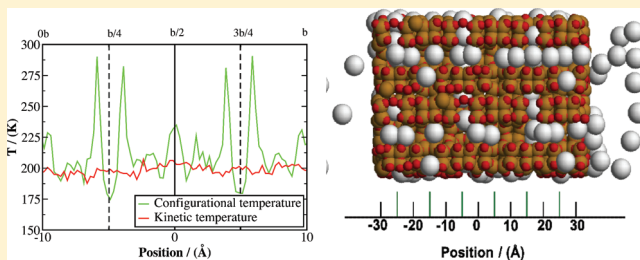
Temperature at Small Scales: A Lower Limit for a Thermodynamic Description

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ABSTRACT: We analyze the concept of equilibrium temperature in a set of interacting argon atoms, confined in a nanostructure, a zeolite with an intricate distribution of channels through which the atoms may move. The temperature is computed following two procedures: by averaging over the kinetic energy of the particles and over the forces acting on them. It is shown that for external surfaces and for regions which do not fall under the whole pattern of potential energy distribution, smaller than a quarter of a crystal unit cell, both temperatures, kinetic and configurational, show significant differences. The configurational temperature accounts for the different interactions on the particles in the different parts of the channels which makes them move in an energetically heterogeneous environment. The kinetic temperature is practically not affected by these inhomogeneities. The observed disparity between both temperatures disappears when averages are taken over larger regions of the zeolite. The size of these regions imposes a lower limit for a consistent thermodynamic description of a small-scale systems such as nanostructured materials, catalytic cells, and nano heat-exchangers.



INTRODUCTION

The current interest in the study of small-scale systems has raised questions as to the validity of thermodynamic concepts and functionalities, originally set forth in the study of large-scale systems,^{1,2} to treat processes taking place at small scales.^{2,3} In some cases, despite its reduced dimension, the system can be treated thermodynamically.⁴ This is the case of some proteins of nanometric size but still containing enough particles to emulate thermal processes occurring at large scales.⁵ However, in the race toward the progressive miniaturization of the systems, a fundamental question arises. Up to what sizes is a thermodynamic description valid?

The case of small-scale systems removed from equilibrium due to the intervention of external forces⁶ shares a similar problematic heightened by the fact that these external factors may increase the heterogeneity of the interactions even more.

This article aims to answer this fundamental question. We analyze the concept of temperature, whose consistency is a key ingredient to validate a thermodynamic description, at the molecular scales and elucidate under what conditions this quantity can univocally be defined. The example treated is an adsorbed phase, an ensemble of argon atoms confined in a zeolite.⁷ The peculiar form of the zeolite composed of a given distribution of channels oriented in the way indicated in Figure 1 introduces fluctuations of the interaction forces acting on each atom giving rise to an energetically heterogeneous environment in which the atoms move. We will show that under these conditions the kinetic temperature obtained from averages over

the kinetic energy of the particles through the equipartition law and the configurational temperature,^{8,9} inferred from averages of the forces, differ when averages are taken over very small regions, smaller than the crystal unit cell. The coincidence of both temperatures is regained at large sizes. This result thus establishes a lower limit for the consistency of the temperature concept and therefore for the validity of a thermodynamic description.

The paper is structured as follows. In the next section we describe the system and the simulation method. In the following sections, we introduce the concept of kinetic and configurational temperatures and we present results on the distributions of the interaction potential inside the pores and of both temperatures. Finally, in the Conclusion we summarize our main results.

SYSTEM AND SIMULATION METHODS

We consider a set of argon atoms confined in a siliceous (SiO₂) zeolite, silicalite, composed of pores with size of about 6 Å. The pores are built so as to shape two types of interconnected channels: straight channels and zigzag channels. Figure 1 shows the porous structure of a unit cell. The peculiar structure of the channel makes the strength of the interactions between the silicalite and the adsorbed molecules change dramatically over

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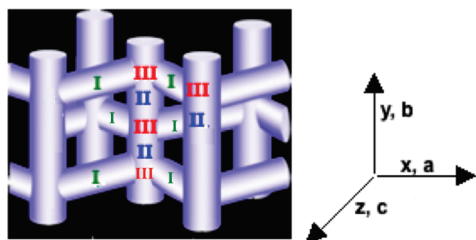


Figure 1. Picture showing the porous structure of a unit cell of silicalite. The intersections between the straight and zigzag channels are identified by the number III in red. The straight channels are orientated along the y direction, and the centers of the channels are denoted with the blue number II. The zigzag channels are orientated along the x and z directions, and their centers are indicated by the number I in green.

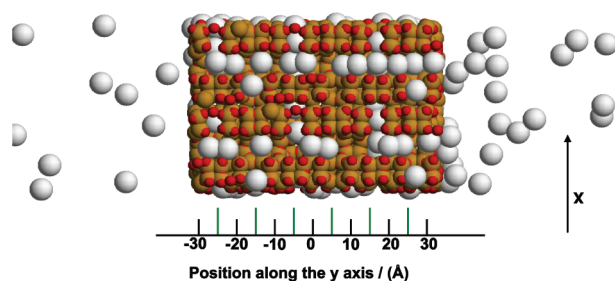


Figure 2. Instantaneous configuration at 200 K where gas atoms are in equilibrium with the adsorbed atoms both at the external surfaces and inside the micropores. The argon atoms are in gray, the silicon in yellow, and the oxygen in red. Atoms of the crystal are removed as to show the internal distribution of argon in the pores along the y axis. On the y axis the location of the centers of the intersection and the zigzag channels are shown using green lines while the centers of the straight channels correspond to the black tick marks.

very short distances even smaller than the size of the atoms themselves, see Figure 2. This fact induces important local variations of the density of the argon atoms in the nanopores. At large scales and under equilibrium conditions, these inhomogeneities are not statistically important and one can consistently define intensive quantities such as the temperature. Then the question arises: up to what sizes of the system are thermodynamic quantities well-defined?

Simulation Details. In the simulations, we consider an infinite membrane of silicalite, having an orthorhombic $Pnma$ structure,¹⁰ in contact with 240 argon atoms. The crystal is composed of 18 crystallographic unit cells containing 1728 atoms of silicon and 3456 atoms of oxygen. Its size is $(2a, 3b, 3c)$ with $(a), (b),$ and (c) being the crystallographic parameters: $a = 20.022 \text{ \AA}$, $b = 19.899 \text{ \AA}$, and $c = 13.383 \text{ \AA}$.¹⁰ By convention, (b) is oriented along the direction of the straight channels. In our analysis, we have used an orthonormal reference frame centered in the geometrical center of the crystal with the axis $x, y,$ and z oriented in the direction of $(a), (b),$ and $(c),$ respectively, Figure 1. Periodic boundary conditions are considered along the (a) and (c) directions at the limit of the crystal as to create an infinite membrane with external surfaces perpendicular to the (b) axis. Periodic boundary conditions are also applied in the (b) direction at a distance of 83.52135 \AA from the center of the zeolite, so that a gaseous phase is in contact with the external surface of the zeolite. On the basis of previous simulations,¹¹ we assumed that the presence of the external surface and of the gas

phase does not significantly affect the dynamics of the atoms adsorbed inside the pores.

The atoms of the silicalite interact via intra- and intermolecular potentials. Intra molecular potentials are stretching and bending potentials while truncated Lennard-Jones (LJ) potentials are used for the intermolecular part. These potentials have been described in ref 11. Interaction of argon atoms with the other atoms of the system are modeled with a truncated Lennard-Jones potential with parameters taken from ref 12. Lorentz–Berthelot mixing rules are used to get the LJ potential parameters of different type of atoms, the cutoff radius is set to $2.5 \sigma_{Si}$, with σ_{Si} the LJ parameter of silicon.

To integrate the equations of motion, we have used the well-known Verlet velocity algorithm with a time step of 1 fs. Trajectories of the argon atoms were generated in time lapses of 3 ns. In the first 2 ns, the system reaches the equilibrium state at the temperature of 200 K. To fix the value of the temperature, we used a simple thermostat based on the rescaling of the velocities of the atoms. During the last part of the trajectory which corresponds to the remaining time of 1 ns, the thermostat was switched off and microcanonical conditions were applied and data were taken under equilibrium conditions.

For each argon atoms, instantaneous values of different quantities were calculated along the trajectories and stored each 0.1 ps (100 time steps). The computed quantities are the interaction potential energy of the argon atoms with the zeolite, the velocity and the acceleration along the y direction, the derivative of the force with position, the square of the forces and the kinetic energy.

KINETIC AND CONFIGURATIONAL TEMPERATURES

In this work, the temperature of the argon atoms has been calculated by using two different definitions. The equipartition of the kinetic energy, K , of the adsorbed phase, was employed to calculate the kinetic temperature T_{kin}

$$T_{\text{kin}} = \frac{2}{3k_B} \langle K \rangle \quad (1)$$

with k_B the Boltzmann's constant; the bracket denotes here averages on atomic values of the corresponding quantity.

In this expression one assumes that each atom contributes three degrees of freedom (dof). This is not exact since the total linear and angular momenta are set to zero. The total number of dof of the system is then reduced by 6.¹² According to Todd et al.,¹³ the total dof in a given subvolume should reflect this global constraint. It means to change the number 3 in the above expression by $3 - 6/N_{\text{tot}}$ where N_{tot} is the total number of atoms. Since in our case $N_{\text{tot}} = 5424$, the error made when using the equipartition law in the form of eq 1 is much lower than 1% and therefore negligible.

It is also possible to calculate the temperature directly from the configuration of the system, from the distribution of forces acting on the particles.⁸ The so-called configurational temperature, T_{conf} , is a function of the interaction potential energy U of the atoms of the system, it establishes a relationship between the fluctuation of the forces and their spatial variations

$$T_{\text{conf}} = \frac{\langle (\nabla U)^2 \rangle}{\langle k_B \nabla^2 U \rangle} \quad (2)$$

The above expression was derived from the Yvon theorem (see eq 7.2.11 of ref 8) and was discussed in ref 14. This quantity has

been defined in the microcanonical and canonical ensembles in terms of the Hamiltonian of the system^{9,15,16} and has been applied to simulations of properties of liquids and colloids.^{14,17–22} It has been verified that when equilibrium is reached both temperatures are identical. For some out-of-equilibrium situations, the agreement is not so evident. For a discussion on this point see, for example, the articles by Ayton et al.,¹⁷ Delhommelle et al.,^{14,19} and Hoover et al.²³

Before going further it is important to notice that T_{conf} was derived using the total Hamiltonian of the system, which in our case includes zeolite and argon atoms. However, in ref 14 it was shown that the expression could also be used locally in sub-volumes of the total system, and in ref 20 expression 2 was employed for a colloidal suspension in an aqueous dispersion considering only the interaction between the colloidal particles and neglecting the interaction with the water molecules. In our case, the argon atoms form a thermodynamically consistent adsorbed phase⁷ that is described separately from the zeolite. The zeolite dynamics is weakly coupled to the argon dynamics. It is then possible to study the thermodynamic properties of such systems considering a rigid zeolite lattice.²⁴ The above expression of the configurational temperature could also be applied to this adsorbed phase in a structured microporous crystal.

In this study we will focus on equilibrium states of the systems. A total of 2 400 000 instantaneous values of K , $(\nabla U)^2$ and $\nabla^2 U$ are calculated for each argon atom separately and stored. The averages of these quantities are obtained by the following different protocols:

(a) The instantaneous data are sorted along the y axis and then averaged over 1000 values:

$$\langle X \rangle = \frac{\sum_{1;y \text{ increasing}}^{1000} X(y)}{1000}$$

where X is the computed quantity. This quantity is in general a function of time t , the position (x, y, z) and the specific atom i . Each value of $\langle X \rangle$ is associated to an average position

$$\langle y \rangle = \frac{\sum_{1;y \text{ increasing}}^{1000} y}{1000}$$

(b) The data of each atom are first averaged over 1 ps (10 instantaneous values)

$$X_m(i; t) = \frac{\sum_{nt=0}^9 X(i; t + 0.1 \times nt)}{10}$$

$$y_m(i; t) = \frac{\sum_{nt=0}^9 y(i; t + 0.1 \times nt)}{10}$$

then they are sorted along the y axis and averaged over 100 values

$$\langle X \rangle = \frac{\sum_{1;y_m \text{ increasing}}^{100} X_m(y_m)}{100}$$

$$\langle y \rangle = \frac{\sum_{1;y_m \text{ increasing}}^{100} y_m}{100}$$

(c) The data are sorted as a function of the interaction energy between the silicalite and the argon atoms, V_{ZAr} , and then

averaged over 1000 values

$$\langle X \rangle = \frac{\sum_{1;V_{\text{ZAr}} \text{ increasing}}^{1000} X(V_{\text{ZAr}})}{1000}$$

$$\langle V_{\text{ZAr}} \rangle = \frac{\sum_{1;V_{\text{ZAr}} \text{ increasing}}^{1000} V_{\text{ZAr}}}{1000}$$

(d) The data of each atom are first averaged over 1 ps (10 instantaneous values)

$$X_m(i; t) = \frac{\sum_{nt=0}^9 X(i; t + 0.1 \times nt)}{10}$$

$$V_m(i; t) = \frac{\sum_{nt=0}^9 V_{\text{ZAr}}(i; t + 0.1 \times nt)}{10}$$

then the data are sorted as a function of the interaction energy between the silicalite and the argon atoms and averaged over 100 values

$$\langle X \rangle = \frac{\sum_{1;V_m \text{ increasing}}^{100} X_m(V_m)}{100}$$

$$\langle V_{\text{ZAr}} \rangle = \frac{\sum_{1;V_m \text{ increasing}}^{100} V_m}{100}$$

The previous four protocols gave an identical statistical weight for each data corresponding to 1000 instantaneous values. Additional analysis were performed by averaging the data in control volumes and fixed intervals of energy.

(e) The data are sorted along the y axis and then averaged in control volumes or slabs perpendicular to the y direction of different thickness: $b/80$ (≈ 0.25 Å), $b/16$ (≈ 1.24 Å), $b/8$ (≈ 2.49 Å), and $b/4$ (≈ 4.97 Å), where b is the crystallographic axis. For a given slab, j , containing $N_{\text{inst}}(j)$ atoms the average quantity is given by

$$\langle X(j) \rangle = \frac{\sum_{k=1}^{N_{\text{inst}}(j)} X(k)}{N_{\text{inst}}(j)} \quad (3)$$

(f) The data are sorted as a function of the interaction energy between the silicalite and the argon atoms and then averaged by intervals of energy of 0.5 kJ/mol. Considering all the atoms, $N_{\text{inst}}(j)$, having an interaction energy within a given interval energy called j , the expression of the average quantity X reduces to eq 3.

Both kinetic and configurational temperatures are calculated after the different averaging protocols. For protocols a, b, and e, the values are sorted along the y axis only. A more refined study could have been performed by sorting in the x and z directions as well. This more general treatment would not substantially modify our conclusions, and so we have followed this simpler procedure.

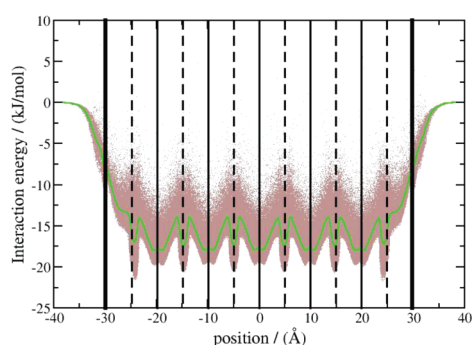


Figure 3. Instantaneous interaction potential energy between zeolite and argon as a function of the position along the y direction of argon particles inside the zeolite channels. The dashed lines give the crystallographic positions of the center of the zigzag channels while the solid lines are located at the center of the straight channels. The thick vertical lines are the crystallographic location of the crystal boundaries. The green line represents the average interaction energy along the y axis calculated with the averaging protocol (a).

RESULTS

In this section, we will present the results obtained by means of the six different averaging protocols introduced in the previous section.

Interaction Potential Energy. An instantaneous equilibrium configuration of the system is represented in Figure 2. The argon atoms are located in both the gas phase and the porous structure of the silicalite where they are distributed homogeneously (on average) in both the straight and zigzag channels and in their intersections. The averaged and instantaneous interaction energy between the zeolite and the argon atoms as a function of the position of the argon atoms along the y axis is shown in Figure 3. In the center of the graph, inside the crystal, the interaction energies are periodic with high and low energies. This periodicity is due to the crystal structure of the zeolite. In the channel intersections (red number III in Figure 1) where the free volume is higher than in the channels themselves argon atoms have the higher average energies, around -14 kJ/mol. Within the zigzag and the straight channels, on average the interaction energies of the argon atoms fall to -17.4 and -17.8 kJ/mol, respectively. It is important to notice that the variation of the energy can be very important on very short distances, of the order of one Å. The surface itself shows large variations of energy spread over larger distances, around 12 Å.

Results for the Kinetics and Configurational Temperatures. In the simulation performed, the global kinetic temperature of the zeolite and the argon was 198.0 K. For the argon atoms, kinetic and configurational temperatures differed by less than 2%; they were 198.4 and 201.6 K, respectively. These results confirm the agreement between the two different calculations of the temperature that were obtained by previous authors.^{14,17–19,22} Although the expression of T_{conf} was derived from the total Hamiltonian of the system, including argon and zeolite atoms, similar results for this quantity were obtained when considering in eq 2 only the atoms of the adsorbed phase, the argon atoms. In the rest of the paper, we will focus on the adsorbed phase.

The kinetic and configurational temperatures were calculated using the averaging protocol (e) with a control volume of about 0.25 Å. The results are presented in Figure 4. These show that, although the kinetic temperature is practically homogeneous along the sample, the configurational temperature exhibits large

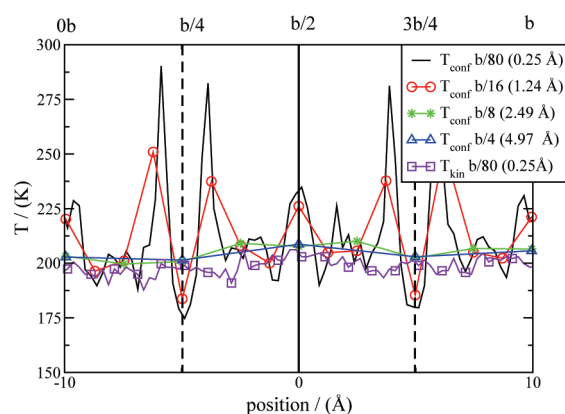


Figure 4. Configurational temperature of argon atoms inside the porous structure averaged in control volumes of different sizes along the y directions. The Figure represents the unit cell located at the center of the crystal with positions given in terms of the crystallographic parameter b . The control volumes are given in Å and in fractions of the parameter b . The kinetic temperature is given for the smallest control volume. The statistical error is smaller than 5% in each case. The periodicity of the temperature disappears when increasing the size of the control volume. The dashed lines give the crystallographic positions of the center of the zigzag channels while the solid line are located at the center of the straight channels.

local fluctuations ranging from 175 to 290 K. These variations are strongly correlated with the periodic structure of the zeolite: for the straight channel they have a W shape with a maximum value in the middle (225 K) and minima located at 1 to 2 Å from there (190 K), for the zigzag and intersection channel together, the shape is an inverse W with a minimum value (175 K) in the middle and maximum (290 K) for the closest wings. Using protocol (a) or (b), we obtained even sharper peaks and wells (150 to 300 K) for the configurational temperature, while the kinetic temperature remains constant.

The observed discrepancy between both temperatures contrasts with the agreement found in the literature,^{14,17–19,22} particularly in the case of a porous system in ref 14. To understand this situation, one has to notice that in ref 14 the system is a true fluid phase included in a mesoporous system, whereas we are dealing with a microporous system where argon atoms mainly interact with the zeolite atoms. In our case both temperatures give similar results only when averages are performed over control volumes of the size of a quarter of a crystalline cell as become clear in Figure 4, which shows results for larger control volumes.

Figure 5 shows T_{kin} and T_{conf} as a function of the interaction energies between the zeolite and the argon atoms for the averaging protocols (f). The difference between both temperatures observed in Figure 5 confirms the results of Figure 4. The kinetic temperature is practically homogeneous with a value of approximately 200 K in agreement with the global temperature, whereas the configurational temperature exhibits a strong dependence on the interaction energy. A similar behavior of T_{conf} was observed when this quantity is represented as a function of the force.

The configurational temperatures show large variations from around 50 K at low interaction energies to 600 K. It increases linearly within the channels below -14 kJ/mol and in the intersection with a higher slope. Additional simulations performed at 100 and 300 K exhibit exactly the same tendency, with

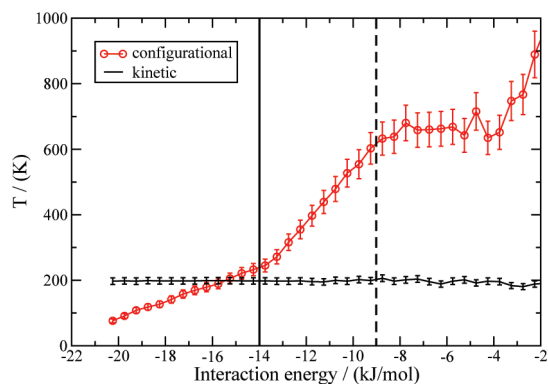


Figure 5. Configurational and kinetic temperature as a function of the interaction energy between argon atoms and the zeolite. The kinetic temperature is homogeneous while the configurational temperature increases with the interaction energy. The two vertical lines mainly separates the atoms located in the channels below -14 kJ/mol from those located in the intersections and on the external surface above -9 kJ/mol.

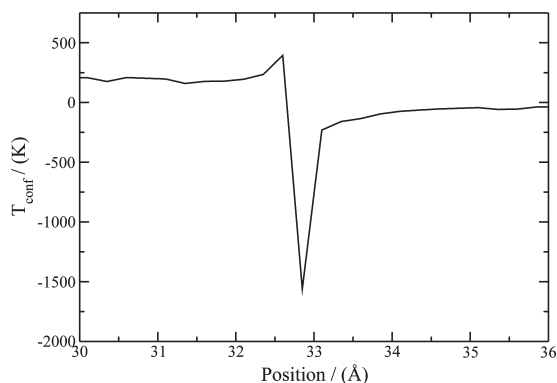


Figure 6. Configurational temperature of argon atoms at the external surface of the zeolite averaged in control volumes of thickness $b/80$ (0.25 Å) along the y directions. The crystal limit is located at the position 29.85 Å.

a minimum temperature around 50 K corresponding to the minimal value of the interaction energy. These results show that the local configurational temperature of physisorbed atoms or molecules in contact with a solid strongly depends on the energetic environment of the atoms.

For the external surface, above -9 kJ/mol, the differences between the two temperatures are still notable, contrary to what was observed for liquid–vapor interfaces²² and liquid in contact with a structured wall.¹⁴ For the zeolite, both temperatures are different due to the presence of nonhomogeneous forces on argon atoms resulting from the structure of the zeolite which is not the case for liquid interfaces.

The configurational temperature at the surface is plotted in Figure 6. It exhibits a discontinuous behavior with a negative value, in agreement with Grier et al.²⁰ At the surface, the number of argon atoms is small and they mainly interact with the zeolite. The second derivative of the Lennard-Jones potential interaction between the zeolite and the argon atoms $\langle \nabla^2 U \rangle$ is positive at short distances and negative for larger distances. It takes a zero value at a certain distance from the zeolite surface,²⁰ which leads to the discontinuity in the configuration temperature observed in

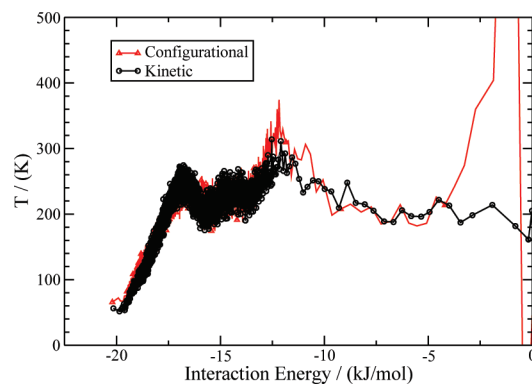


Figure 7. Kinetic and configurational temperatures, averaged according to protocol (d), as a function of the interaction energy between the zeolite and the argon atom.

Figure 6. For the liquid–vapor interface²² and in the case of the liquid in contact with a wall,¹⁴ the interactions between liquid atoms dominate the local dynamics of atoms, leading on average to a positive value of the second derivative of the potential interaction and to an homogeneous configurational temperature.

In the ideal case of atoms interacting with a surface (or under the action of an external force) but not between themselves, as the situation concerning us, the correction to the configurational temperature can be obtained as follows. In equilibrium, the local density $\rho(y)$ of the atoms is only a function of the distance y from the surface, and is given by

$$\rho(y) = \rho^{\text{gas}} \exp\left(-\frac{U(y)}{k_B T}\right) \quad (4)$$

where ρ^{gas} is the density of atoms in the gas phase and T the temperature of the system. By deriving two times the density with respect to the position, we obtain

$$\frac{k_B T}{\rho(y)} \left(\frac{\partial^2 \rho(y)}{\partial y^2} \right) = \frac{1}{k_B T} \left(\frac{\partial U(y)}{\partial y} \right)^2 - \left(\frac{\partial^2 U(y)}{\partial y^2} \right) \quad (5)$$

Using now eq 2 for the definition of T_{conf} one arrives at

$$\frac{T_{\text{conf}}}{T} = 1 + \frac{\frac{k_B T}{\rho(y)} \left(\frac{\partial^2 \rho(y)}{\partial y^2} \right)}{\left(\frac{\partial^2 U(y)}{\partial y^2} \right)} \quad (6)$$

This expression explains the jump observed in Figure 6 arising when the derivative of the force is small enough.

In Figure 7 the two temperatures are plotted as a function of the interaction energy following the averaging protocol (d). It includes a time averaging procedure (over 1 ps) and curiously gives similar results for both temperatures, with a pronounced increase of both temperatures below -17 kJ/mol, from 50 to 200 K, and a rather constant value for higher energies. This suggest that, for very low energies, argon atoms are really trapped locally in “deep” wells during times longer than 1 ps, whereas in the intersections or on the external surface they can more easily explore different energetic environments. It also means that the local external forces strongly affect the kinetic energy of individual argon atoms. This fact is observed when the kinetic energy is

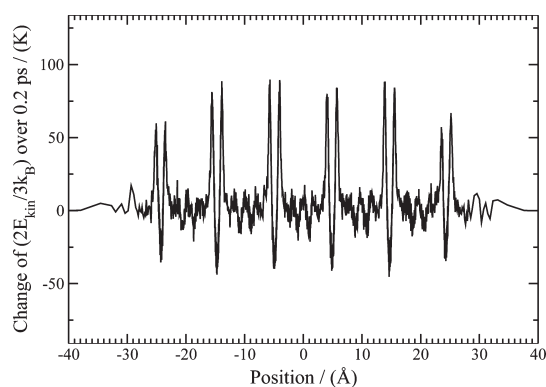


Figure 8. Average temperature variation over 0.2 ps as a function of the position along the y axis following protocol a.

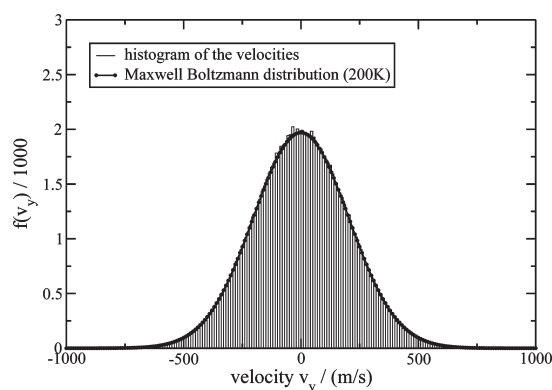


Figure 9. Distribution of the instantaneous velocities inside the zeolite pores compared with the Maxwell–Boltzmann's distribution.

averaged over time for each particle but not when instantaneous values are used according to protocols (c) or (f). This result is highlighted in Figure 8, where the changes of the kinetic temperatures over 0.2 ps are plotted as a function of the local position in the zeolite. Similarly to the T_{conf} profile in Figure 4, the figure shows the existence of high peaks and adjacent wells up to +90 and −40 K that follows the periodicity of the crystalline structure; however, as we will see, it does not affect the average velocity distribution.

In Figure 9 the distribution of the instantaneous velocities of the argon atom inside the zeolite is compared with the Maxwellian distribution. We obtained a very good agreement meaning that on the scale of the whole zeolite the distribution of the velocity is Maxwellian. We also plotted the distribution of velocities in control volumes larger or smaller than a quarter of a unit crystallographic cell always obtaining a Maxwellian distribution which means that the velocity distribution is independent of the external forces acting on the particles. The presence of large accelerations on short distances, cf. Figure 10, only influence the dynamical behavior of individual particles, as can be seen in Figure 8, but not the averaged behavior on many molecules.

For very short time scales, argon atoms inside the pores can be modeled by a particle in an one-dimensional harmonic potential. Using this model, by averaging over all positions and velocities of the particles compatible with a given value of the total energy one may easily verify that both temperatures are equivalent. On the contrary, if not all the possible configurations of the particle are taken into account in the averaging procedure, the kinetic and

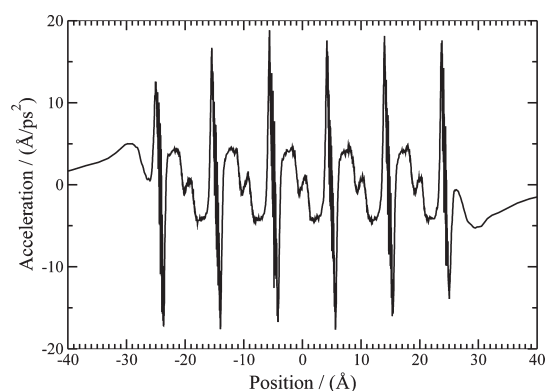


Figure 10. Acceleration distribution in the direction y (b) as a function of the position along the y axis following protocol a.

configurational temperature differ. Similarly, for the adsorbed phase, both temperatures coincide when they are calculated on a distribution of configurations energetically representative of that phase.

CONCLUSION

In this paper, we have analyzed the concept of equilibrium temperature of a substance confined in a nanostructure. We have considered in particular the case of an adsorbed molecular species, argon atoms, in a zeolite whose pores have molecular size, the silicalite. The intricate form of the nanostructure entails an inhomogeneous distribution of interaction energies between the particles themselves and with the structure.

We have performed equilibrium molecular dynamics simulations to show how the temperature of the adsorbed phase depends on the interactions and on the structure of the pores of the zeolite. Contrary to previous results from the literature, we have found that, for external surfaces and regions which do not fall under the whole pattern of potential energy distribution, the equilibrium kinetic and configurational temperatures are different. The probability distribution function corresponding to these regions, inside the pores, is not an equilibrium distribution, and therefore one cannot expect that equipartition of energy holds. When averages are performed on pertinent control volumes, the probability distribution of the configurations constitutes an equilibrium distribution and both temperatures coincide. In the case we have analyzed, because of symmetry reasons, the size of the volume corresponds to a quarter of a unit cell. The minimum size of the averaging region for which agreement between both temperatures is observed fixes a lower limit for a consistent definition of the temperature. This limit depends on the nature of the local interactions between the particles and therefore on the intimate structure of the system. The higher the heterogeneity in the interactions, the greater the region over which averages can be consistently performed to ensure the validity of a thermodynamic description. The analysis of such a limit is an important issue for the application of thermodynamics to processes taking place in systems such as nanostructured materials, catalytic cells and nano heat-exchangers, in which interactions forces are not homogeneously distributed.

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