Effect of solvation and confinement on the trans-gauche isomerization reaction in n-butane
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The effect of solvation and confinement on the conformational equilibria and kinetics of *n*-butane is examined using molecular dynamics simulations of the bulk and confined fluids and compared to appropriately chosen reference states. Clear evidence for a solvent shift of the preferred conformation in bulk *n*-butane is found. At a temperature of 292 K and a density of 6.05 nm$^{-3}$ a small solvent shift in favor of gauche is observed (similar to previously reported values), and the shift increases substantially with an increase in density to 8.28 nm$^{-3}$. The rate of torsional interconversion from the *trans* to the *gauche* state, calculated using the relaxation function method, was found to increase with increasing temperature and density. The rate constants $k_{TG}$ and $k_{GT}$ have an Arrhenius temperature dependence yielding activation energies significantly lower than the *trans*-gauche and *gauche*-trans barrier heights in the torsional potential for a free molecule, depending on the density. In the confined phase, we considered the same densities as simulated in the bulk phase, and for four different values of the physical pore width (~1.5–4.0 nm). At the high density, we find that the position of the *trans*-gauche equilibrium is displaced towards excess *trans* compared with the bulk phase, reflecting the confinement and interactions of the molecules with the pore wall. The isomerization rate is found to decrease with decreasing pore width. Again, we find that the kinetics obeys an Arrhenius rate law and the activation energy for the *trans*-gauche and *gauche*-trans interconversions is slightly smaller than that of the bulk fluid at the same density. © 2006 American Institute of Physics. [DOI: 10.1063/1.2363380]

I. INTRODUCTION

The importance of *n*-butane as an environmentally and commercially significant fluid is undeniable, and therefore the study of its behavior under a range of conditions is of considerable interest and has been the focus of many studies. From a more fundamental viewpoint, it is the simplest example of a hydrocarbon that exhibits the characteristic torsional flexibility typical of most large aliphatic hydrocarbons. Furthermore, the isomerization process is one of the simplest first order chemical processes, and the kinetics of the *trans*-gauche isomerization of bulk *n*-butane and *n*-butane in solution has been considered several times in the literature. This system is therefore ideal for investigative studies on the determination and behavior of rate constants, as well as the effects of thermodynamic state, solvation, and confinement on these properties.

Although a significant amount of data on this process is available, there is a need for more complete studies on the effects of solvation. With recent advances in simulation algorithms and speed of the current computing facilities, it is now possible to extend these early works to thoroughly analyze this process, and we will address this as part of the current paper. For example, we will reconsider the issue of whether or not solvation results in a shift in the conformation of *n*-butane towards *gauche* conformations, the temperature and density dependence of the rate constant, and the distribution of the conformers.

The kinetics of processes in fluids confined to microporous materials is important due to the wide range of applications of these materials in fields such as catalysis, separation of fluids, and their use as adsorbents. Clearly the behavior of fluids in porous materials, particularly nanoparticles, is expected to be different from that in the bulk phase. The fluid densities that are accessible in pores, the chemical composition of the wall, the size (or size distribution) of the pores, and their geometry will all play important roles in determining the structure and dynamics of the fluid, and thus the kinetics of any process that is occurring. Changes to the structure and behavior of the fluid are caused by the interactions of the fluid molecules with the pore wall and its confinement by the walls. Such systems are often very difficult to study experimentally since the measurement is likely to disturb the process being considered. In contrast, their small size makes them ideal candidates for molecular dynamics simulations. Recently, molecular dynamics simulations have been used to produce interesting results on the kinetics of chemical reactions and/or chemical reaction equilibria in
confined systems (see, for example, Refs. 8–13), emphasizing the utility of carrying out reactions in porous media, and the benefits of simulations in understanding the reaction process. It is anticipated that simulations will become an important resource for optimizing reaction conditions. Accurate determination of changes in the structure and behavior of the fluid in the pore environment as well as changes to its transport will be key factors in realistically modeling these processes.

A substantial amount of experimental and computational research has been carried out on the structure of chain molecules near surfaces and under confinement (for some examples, see Refs. 14–21, and references therein). Unbranched alkanes have been observed to prefer to lie flat and parallel to the surfaces, and scanning tunneling microscopy (STM) experiments of alkanes and haloalkanes on graphite show them adopting a trans conformation with the molecule lying flat on the graphite surface.22–24 This behavior is reproduced in molecular dynamics simulations, and branching is expected to result in rotation of the molecules away from the plane of the surface.16 Studies on confined alkanes show layering and ordering of chains at small confinements (see Ref. 25 and references therein). Yet despite the extensive interest and research in this area, there are many questions to resolve regarding the structure, dynamics, and kinetics of confined liquids at equilibrium and away from equilibrium.26

For these reasons, the main focus of this paper is to develop and assess a scheme for examination of changes in the rates of reaction for processes due to the confinement of fluids in pores and to use the results of molecular dynamics simulations to carefully probe properties of these nanoscale systems that have produced these changes. In particular, we consider the kinetics of isomerization of n-butane at equilibrium in slit pores. We also examine the changes in the isosteric heat of adsorption and discuss the relationships between structural properties and the rate constant of isomerization.

II. DETERMINATION OF RATE CONSTANTS

Whereas determination of many properties of fluids is straightforward, determination of rate constants is more complex. Transition state theory can give an estimate of the rate constant in some systems;6,7 however, it often provides a poor approximation in dense fluids. Therefore various methods have been developed for accurate calculation of rate constants in bulk systems (see Refs. 1 and 27–29 and references therein). These can be classed as equilibrium methods, which normally involve determination of the rate constant by time-correlation function expressions, and nonequilibrium methods where the rate constants are usually determined by monitoring the relaxation of a system from a perturbed state to its equilibrium.1

The correlation function methods were originally developed for the study of classical, unimolecular reactions where a reacting molecule was immersed in a liquid solvent. The reacting molecule is activated to its transition state, and then trajectories are determined by integrating forward and backward in time.5,30,31 This method has been known as the “reactive flux method.”

One difficulty with the application of the reactive flux method to systems involving many reacting molecules (e.g., concentrated solutions) is the preparation of the initial activated states so that a realistic initial distribution is obtained. This problem was addressed in Ref. 1 by perturbing the systems from equilibrium and monitoring their relaxation. An alternative approach was used by Brown and Clarke2,3 who used equilibrium simulations and considered a subset of particles that were in a particular state. This allowed pure, bulk fluid rate constants to be readily calculated, in addition to those of reacting molecules in a solvent. While this method was originally applied to bulk systems (a homogeneous fluid or a molecule in a liquid solvent), under some general conditions, it can be used to study confined systems and its application will therefore be discussed further in Sec. IV.

The original time-correlation function method has also been modified to give quantum forms (see Ref. 32 and references therein) and also so that the interactions between the reactant and the solvent are treated in an approximate manner using stochastic forces.33 These modifications extend the range of systems that can be treated accurately. In this work, the system is treated classically and the treatment of the surroundings is of importance and therefore the pore walls and surrounding molecules are modeled explicitly using molecular dynamics methods.

The system we consider displays interesting behavior in that butane has a small binding energy with an atomistic wall which will directly affect the isomerization process, and because confinement and restriction will also have a direct effect on this process. The trends observed are explained in terms of the structural and energetic properties of the system.

A. Macroscopic rate laws for isomerization kinetics

The united atom model of n-butane has a single torsional degree of freedom, α, with three minima: α = 0° (trans) and α = ±120° (gauche) (see Fig. 1). Here we classify the conformational states of the molecule as trans (T) gauche− (G⁻) and gauche+ (G⁺) defined by the values of the torsion angle in the range of −60° < α < +60°, −180° < α < −60°, and +60° < α < 180°, respectively. A state of dynamic equilib-
rium exists between these three conformational states and consequently one can define two separate rate constants describing the kinetics of conversion between these states,

\[ k_{TG}, \quad k_{GT} \]

\[ G^* \Leftrightarrow T \Leftrightarrow G^- \]

where \( k_{TG} \), for example, is the rate constant describing the conversion of a \textit{trans} isomer into one of the two equivalent \textit{gauche} states. Although this mechanism of isomerization is commonly assumed, it neglects the possible interconversion directly from \( G^- \) to \( G^* \). Brown and Clarke\(^2\)\(^,\)\(^3\) showed that this can be significant and needs to be considered in a complete treatment; however, its exclusion will not alter the results or conclusions of this paper which focus on the \textit{trans-gauche} isomerization, considering the population of \textit{trans} conformers in the system. Assuming the given mechanism and first order kinetics, the macroscopic rates of production of the fractions of each conformer can be written as

\[
\frac{dX_T(t)}{dt} = -2k_{TG}X_T(t) + k_{GT}[X_{G^-}(t) + X_{G^+}(t)], \quad (1)
\]

\[
\frac{dX_{G^-}(t)}{dt} = k_{TG}X_T(t) - k_{GT}X_{G^-}(t), \quad (2)
\]

\[
\frac{dX_{G^+}(t)}{dt} = k_{TG}X_T(t) - k_{GT}X_{G^+}(t), \quad (3)
\]

where \( X_T \), for instance, is the fraction of \textit{trans} conformers \((N_T/N)\) and the sum of \( X_T, X_{G^-}, \) and \( X_{G^+} \) is unity. Using this relation, one can eliminate the fractions of the two \textit{gauche} conformers from Eq. (1), giving upon simplifying

\[
\frac{dX_T(t)}{dt} = -kX_T(t) + k_{GT}. \quad (4)
\]

where the new rate constant \( k \) is given by

\[
k = 2k_{TG} + k_{GT}. \quad (5)
\]

The equilibrium fraction of \textit{trans} conformers is given by the steady-state solution of Eq. (4),

\[
X_{T,eq} = \frac{k_{GT}}{k}. \quad (6)
\]

Equation (4) can be solved for the instantaneous fraction of \textit{trans} conformers, giving

\[
X_T(t) = X_T(0)\exp(-kt) + \frac{k_{GT}}{k}(1 - \exp(-kt)). \quad (7)
\]

Making use of Eq. (6), we can simplify Eq. (7) to give

\[
\frac{X_T(t) - X_{T,eq}}{X_T(0) - X_{T,eq}} = \exp(-kt). \quad (8)
\]

Equation (8) shows that it is in principle possible to extract the rate constant \( k \) [and hence \( k_{GT} \) and \( k_{TG} \) using Eqs. (5) and (6) by following the decay of the fraction of \textit{trans} conformers with time].

Before using this model to predict rate constants, it must be ensured that the kinetics is consistent with the assumed macroscopic rate law.\(^2\) This is particularly important in the case of fluids in pores because the strong interactions with the walls in part of the system may result in different rate constants and mechanisms being observed in different regions of the pore.

### B. The Brown and Clarke direct method

Brown and Clarke\(^2\) introduced a straightforward and general method for studying chemical reaction kinetics in equilibrium systems. Using their direct method, they obtained rates for the isomerization reaction in liquid \( n \)-butane from equilibrium molecular dynamics simulations. The power of their method relies on the fact that there is no need to perturb the equilibrium distribution. Instead, one identifies subsets of molecules from the equilibrium distribution, which are all in the same conformational state at a particular time. One then calculates a relaxation function for this fraction of conformers and averages over many such subsystems.

Defining the relaxation function for molecules originally in a \textit{trans} state as\(^2\)

\[
R_{TT}(t) = \frac{\langle N_f(t_0, t_0 + t) \rangle}{N} = \langle H_f(\alpha_i(0))H_f(\alpha_i(t)) \rangle, \quad (9)
\]

where \( N_f(t_0, t_0 + t) \) is the number of molecules that are in the \textit{trans} conformational state at time \( t + t_0 \) from the set of molecules that were originally in this state at time \( t_0 \), \( N_f(t_0) \),

\[
N_f(t_0) = \sum_{i=1}^{N} H_f(\alpha_i(t_0)), \quad (10)
\]

and the characteristic function, \( H \), for the \textit{trans} state is

\[
H_f(\alpha_i) = \begin{cases} 1, & \text{if } \alpha_i < 60^\circ \\ 0, & \text{otherwise} \end{cases} \quad (11)
\]

The macroscopic law given in Eq. (8) can be written in terms of \( R_{TT} \) as

\[
\hat{R}_{TT}(t) = \frac{R_{TT}(t) - R_{TT}(\infty)}{R_{TT}(0) - R_{TT}(\infty)} = \frac{R_{TT}(t) - \langle X_T \rangle^2}{\langle X_T \rangle - \langle X_T \rangle^2} = \exp(-kt), \quad (12)
\]

where we have defined the normalized relaxation function \( \hat{R}_{TT}(t) \), and the final equality is only expected if the assumed macroscopic rate law is valid for the system studied. If this is the case, a plot of \( \ln \hat{R}_{TT} \) versus time will yield a straight line (after initial decay of transients), the slope of which is \(-k\). If the value of the equilibrium \textit{trans} fraction is also known, then Eqs. (5) and (6) can be used to determine \( k_{TG} \) and \( k_{GT} \). This method is efficient because it only requires a single equilibrium simulation to be carried out and is feasible provided the rate constants are not too small.

### III. DETAILS OF THE MODEL AND SIMULATIONS

We have conducted a series of bulk equilibrium molecular dynamics (EMD) simulations of \( n \)-butane as well as confined EMD simulations in which the butane molecules are sandwiched between two parallel atomic walls. The purpose of the bulk phase simulations was to enable the effect of
solvation to be studied by comparing the conformation equilibrium in the solvated phase with those of an ideal gas of \textit{n}-butane. The bulk phase simulations also provide a reference state for comparison with the confined butane.

\textbf{A. \textit{n}-butane model}

The model used for \textit{n}-butane is the same as the one introduced by Ryckaert and Bellemans\textsuperscript{34} (RB) in 1978, which is a four-site Lennard-Jones model incorporating a realistic torsional potential to provide internal flexibility. Since the introduction of the RB model, there have been many improvements made to models of linear alkanes, particularly with respect to the intermolecular potential. These improvements are meant to yield a better match between the model thermodynamic and transport properties and those of the real material. We have chosen to use the original model model thermodynamic and transport properties and those of particularly with respect to the intermolecular potential. These many improvements made to models of linear alkanes, par-

The RB model of \textit{n}-butane is one in which the four sites are treated as identical Lennard-Jones particles of mass equal to \(2.411 \times 10^{-26} \text{ kg}\) (1/4 the mass of the butane molecule). Distances between neighboring sites within a molecule are fixed at 0.153 nm, and bond valence angles are fixed at 109.47°. Rotation about the central C–C bond is restricted by a torsional potential of the form

\[
U_{\text{tors}} = \sum_{n=0}^{5} C_n (\cos \alpha)^n,
\]

where \(\alpha\) is the dihedral angle for a given molecule and \(C_n\) are potential parameters given by \(C_n/R=1.16 \times 10^{-3}, 1.462 \times 10^{-3}, -1.578 \times 10^{-3}, -0.368 \times 10^{-3}, 3.156 \times 10^{-3}, -3.788 \times 10^{-3}\) K. The RB torsional potential energy is plotted in Fig. I with the barrier heights marked.

Intermolecular interactions between sites on different molecules of butane were modeled using a spherically truncated Lennard-Jones potential with a cutoff radius of 2.5\(\sigma\). Each butane site has the same value of the Lennard-Jones parameters \(\sigma\) and \(\varepsilon\): \(\sigma=0.3923\) nm and \(\varepsilon/k_B=72\) K.

A fifth order Gear algorithm was used to integrate the following equations of motion for each united atom site \(\alpha\) on molecule \(i\):

\[
\dot{r}_{ia} = \frac{p_{ia}}{m},
\]

\[
\dot{p}_{ia} = F_{ia} + \sum_{n} M_{ian} \lambda_{ia} \hat{R}_{in} - \frac{1}{2} \xi \hat{p}_i,
\]

where \(\dot{r}_{ia}\) refers to the Cartesian position of a site, \(p_{ia}\) its momentum, \(m\) is the mass of a united atom, and \(F_{ia}\) is the total force (intramolecular and intermolecular) on a site (not including any constraint forces). The remaining two terms on the right-hand side (rhs) of Eq. (15) are, respectively, the holonomic and nonholonomic forces of constraint used to maintain the bond lengths and valence angles at their equilibrium values\textsuperscript{35} and to fix the translational temperature at the required value. These equations of motion were integrated with a reduced time step, \(\tau=(1/\sigma)\sqrt{\varepsilon/M}=0.0005\) (the code used to run these simulations works in reduced units) which is approximately 2 fs in real time units.

The term \(\sum_{n} M_{ian} \lambda_{ia} \hat{R}_{in}\) in Eq. (15) represents the total force of constraint on a site in a particular butane molecule resulting from nearest and second nearest neighbor distance constraints. The notation we have used is that used by Edberg \textit{et al.}\textsuperscript{36} in which \(M_{ian}\) is a selector matrix that activates the constraints appropriate to each of the sites on the molecule, \(\lambda_{ia}\) is a Gaussian constraint multiplier, and \(\hat{R}_{in}\) is a vector connecting a pair of sites involved in the \(n\)th constraint.

Integral feedback was used to counteract any numerical drift in the values of the constrained distances by adding the following terms to the equations of motion for the positions and momenta of the butane sites, respectively:

\[
-C M_{i} \hat{R}_{i} - d_{i} \hat{R}_{i},
\]

\[
-D M_{i} \hat{R}_{i} \hat{R}_{i},
\]

where \(\hat{R}_{i}\) is a unit vector directed along the \(n\)th constraint, and \(\hat{R}_{i}\) is the component of velocity along the \(n\)th constraint. The values of \(C\) and \(D\) used throughout this work are 10 and 15 reduced units, respectively. It should be noted that the benefit of using feedback equations in the form of Eqs. (16) and (17) is that the values of \(C\) and \(D\) given above should be transferable to any system, including molecules with disparate bond lengths.\textsuperscript{37}

For the bulk simulations only, a Gaussian thermostat was employed to fix the translational temperature by adding a term proportional to the center-of-mass momentum to the equations of motion [last term on the rhs of Eq. (15)]. In this term, \(\zeta\) is a Gaussian multiplier. As with the holonomic constraints, any drift in the value of the constrained temperature was nullified by adding a drift cancellation term to Eq. (15). This term has the form \(-\beta(T_M - T_0) \frac{1}{2} \hat{p}_i\), where \(\beta\) is taken to be 10 in reduced units, \(T_M\) is the instantaneous translational temperature, while \(T_0\) is the set point value of the temperature.

\textbf{B. Pore model}

Some of the simulations described in this paper involved butane molecules confined in slit-shaped pores. In these simulations, the model of butane is exactly the same as described in the previous section. The model of the slit pore used is briefly described below.

A slit-shaped pore model was constructed by stacking three layers of atoms parallel to each other and to the \(xy\) plane. These planes of atoms were separated from each other by a distance of \(\sigma\). The three layers taken together represent...
one wall. To form a slit pore, periodic boundaries were employed in all three Cartesian directions so that the first layer of the second wall is the periodic image of the outer layer of the first wall. This avoids the unnecessary use of two actual walls in the simulations, which would double the number of wall atoms required. The physical pore width is defined to be the distance between the center of masses of the two innermost wall layers.

Each layer of the wall consists of Lennard-Jones particles of identical mass and interaction parameters to the butane sites. These atoms are arranged in an fcc lattice with a surface number density of 3.25 nm$^{-2}$ in the spirit of the model introduced by Powles et al.\textsuperscript{38} The wall atoms interact with other wall atoms as well as with the sites on butane molecules. In order to prevent the wall atoms from drifting from their equilibrium lattice sites, we employ a harmonic restraining potential of the form

$$U_{\text{harm}}(r_i) = \frac{1}{2} k_s (r_i - r_{i,\text{eq}})^2,$$

where $k_s$ is the harmonic force constant and $r_{i,\text{eq}}$ is the equilibrium position of wall atom $i$. In addition to the harmonic restoring forces, Gaussian holonomic constraints were employed to maintain each wall center of mass at its zero time position in the confined direction. These constraints prevent the fluid from pushing back the walls and changing the pore volume (feedback terms to cancel numerical drift were found to be unnecessary for this type of constraint). This description provides a convenient model of a porous solid in which thermostating of the system is effected via conduction through the walls and no artificial wall scattering algorithms are required. In this work we have chosen the value of $k_s$ to be equal to 150 in reduced units. This value is sufficient to allow good thermal transfer between wall and fluid while preventing significant penetration of the wall by fluid molecules.

The dimensions of the slit pores were dependent on the particular simulation. We chose to model slit pores with four different values of the physical width, $H=4\sigma$, 6$\sigma$, 8$\sigma$, and 10$\sigma$. The lowest pore width that can be studied in this model is restricted by the size of the cutoff. Previous studies of atoms and small alkanes confined in slit pores similar to that which has been used in this work have shown large variations in liquid properties in going from a pore width of about 4$\sigma$ to one of about 10$\sigma$. A pore width range of 4–10$\sigma$ was therefore considered to be sufficiently wide to capture a reasonable change in isomerization kinetics. The walls were chosen to be square, i.e., $L_x=L_y$ in all our simulations. The value of $L_z$ used varied from 10$\sigma$ to 20$\sigma$ depending on the pore width employed. We carried out two sets of confined simulations at fixed fluid molecular number densities ($N/V$) of 6.05 and 8.28 nm$^{-3}$ (or $\rho = \rho_0\sigma^3 = 0.365$ and 0.5 reduced units, respectively). In order to maintain a fixed wall density and fixed fluid density across a range of pore widths, it was necessary to work with different numbers of fluid molecules in different simulations. The number of fluid molecules varied from $N=368$ to $N=504$ depending on the pore width used.

We have defined the density of the pore fluid in this work to be $\rho = N/(L_xL_yW)$, where $W$ is given by $H - \sigma$, and $H$ is the physical pore width.

The same Gear algorithm was used to integrate the equations of motion for the wall atoms as for fluid sites, with the same time step.

### C. Simulation parameters

All our simulations (bulk and confined) were conducted in a simulation cell of constant volume, constant particle number ($N=500$ for bulk simulations), and constant kinetic temperature. In the confined simulations we note that the walls are structured and the wall atoms can move, and therefore the volume of the fluid is not well defined and is not constant. For the bulk simulations, a Gaussian isokinetic thermostat\textsuperscript{35} was applied to the fluid molecules to maintain a constant kinetic temperature. For the confined simulations, the same thermostat was instead applied to the moving wall atoms to maintain a constant wall kinetic temperature.

One of the bulk simulations was carried out at the same thermodynamic state as that employed by Brown and Clarke.\textsuperscript{2} Several densities were then considered at the same fixed temperature of 291.6 K. The lowest density studied was 6.05 nm$^{-3}$, while the highest was 8.28 nm$^{-3}$. Similarly, several temperatures were scanned either side of 291.6 K at two fixed densities of 6.05 and 8.28 nm$^{-3}$. The lowest temperature studied was 150 K, while the highest was 500 K.

Due to the computational cost, only two densities were employed in the confined simulations (6.05 and 8.28 nm$^{-3}$). However, a wide range of temperatures was studied for each pore width at each of these two densities, ranging from 150 to 500 K and including 291.6 K. Bulk simulations were conducted for a total of $2 \times 10^6$ time steps while confined simulations were each conducted for a total of $20 \times 10^6$ (production) simulation steps [following equilibration runs of $(1-2) \times 10^6$ steps]. Equipartition of thermal energy between the wall and fluid was taken as a guide to the existence of an equilibrium state.

Starting configurations were generated using the following procedure. For bulk fluids, a fcc lattice of “sites” was generated corresponding to the desired molecular number density. The positions of these sites were then taken to be the positions of the centers of mass of the butane molecules. Cartesian laboratory frame coordinates for the sites were then obtained from the internal coordinates corresponding to molecules in a trans conformation plus a randomly generated orientation. The dynamics were then run using the truncated force method (TFM) of McKechnie et al.\textsuperscript{39} with automatic switchover to the standard Lennard-Jones force once the number of pair separations below a critical distance reached about 16. This algorithm works by employing a modified form of the Lennard-Jones potential such that a constant force is applied below some critical separation, which, in this work, was taken to be 0.85$\sigma$. For pore fluids, the initial center-of-mass positions were obtained by replicating layers of wall atoms to fill in the pore space. The TFM algorithm was applied to all interactions, not just the fluid-fluid ones. As an aside we note that TFM has proven to be very useful.
IV. RESULTS AND DISCUSSION

A. Bulk butane

1. trans population

The effect of the solvent on the percentage of trans conformers has been the subject of much interest in previous publications (e.g., Refs. 1, 2, 36, 41, and 42). We have therefore calculated the magnitude of this solvent shift in our simulations by comparing the fraction of trans conformers obtained from the simulations with the values predicted by statistical mechanics for an ideal gas of n-butane molecules. The latter value is obtained from

$$\langle X_T \rangle_{\text{ideal}} = \int_{-\pi/3}^{\pi/3} S^0(\alpha) d\alpha,$$  \hspace{1cm} (19)

where $X_T$ is the fraction of trans conformers, $\alpha$ is the dihedral angle (measured in radians), and $S^0(\alpha)$ is the probability of finding a butane molecule with a dihedral angle in the range $\alpha$ to $\alpha+d\alpha$ in the ideal gas state. The probability density, $S^0(\alpha)$, is given by

$$S^0(\alpha) = \frac{\left[g(\alpha)\right]^{1/2}}{\int_{-\pi/3}^{\pi/3} \left[g(\alpha)\right]^{1/2} \exp[\frac{-U(\alpha)/kT}{d\alpha}],$$  \hspace{1cm} (20)

where the factor $g(\alpha)$ originates from integrating out the momenta from the full phase space distribution function for a molecule subject to constraints (the kinetic energy for such a system is a function of both the generalised momenta and generalized positions). 46

For the RB model of n-butane, van Gunsteren has shown 45 that $g(\alpha)$ is given by the following polynomial expression:

$$g(\alpha) = \sum_{n=0}^{4} c_n f^n(\alpha),$$  \hspace{1cm} (21)

in which $f(\alpha)$ is given by

$$f(\alpha) = \left\{\frac{1}{2} - \frac{1}{2} \cos \theta\right\}^{1/2} (\cos \theta - (1 + \cos \theta) \cos \alpha),$$  \hspace{1cm} (22)

with $\theta$ the bond valence angle. The above result was obtained using a theory formulated by Fixman. 44 For this model of n-butane (all sites of equal mass and valence angles fixed at 109.47°), the coefficients, $c_n$, have the following values: $c_0=4.4448$, $c_1=-5.0801$, $c_2=-8.2222$, $c_3=0.54429$, and $c_4=1$.

Table I contains the values for the trans populations at various temperatures obtained from the simulations for the solvated phase, together with the values computed for an ideal gas of this model of n-butane [obtained via Eqs. (19)–(22)]. The deviation in trans fraction from that expected for an ideal gas may be termed the solvent effect or solvent shift. Calculated solvent shifts also appear in Table I. The variation of the trans fraction with temperature and density is plotted in Fig. 2. At the lower density the trans fraction in the liquid phase shows a small, but significant deviation from the ideal gas value; the magnitude of this deviation increases with increasing temperature. In both cases the trans fraction increases with decreasing temperature as more molecules adopt lower energy configurations. At the higher density, a similar qualitative dependence of trans fraction with temperature is observed. However, the data points are well below those of the ideal gas and low density curves, indicating large solvent shifts.

![FIG. 2. Plot of the fraction of trans conformers for bulk n-butane as a function of temperature at two different densities: $p=6.05$ nm$^{-3}$ (open circles) and 8.28 nm$^{-3}$ (filled circles). The solid line represents the ideal gas values calculated using statistical mechanics.](image-url)
The variation in the distribution with temperature is significant; the central peak is lowered substantially at 500 K compared with at 150 K, while the two gauche peaks broaden and increase in intensity. At infinite temperature, the barriers to internal rotation become insignificant such that there will be effectively free rotation about the central C–C bond in \( n \)-butane. An increase in density has the effect of lowering the height of the trans peak and increasing the height of the gauche peaks, again reflecting the preference for a compact structure.

2. Kinetics

The value of the composite rate constant, \( k [\text{defined in Eq. (5)}] \), was obtained in each of the simulations at the various temperatures and densities by taking the negative slope of the linear portion of a plot of \( \ln(\hat{R}_{TT}) \) versus time. Figure 5 shows a set of these plots for the \( \rho = 6.05 \) nm\(^{-3} \) density at various temperatures, clearly showing that all sets of data are well fitted with a linear function. The data show small deviations from linearity at long times due to statistical noise in the relaxation functions.

The rate constant \( k \) is plotted against temperature in Fig. 6 and against density in Fig. 7. From Fig. 6 it can be seen that \( k \) increases exponentially with increasing temperature, confirming its Arrhenius behavior. The exponential increase is greater at the higher density. In Fig. 7, it can be seen that at a fixed temperature (291.6 K), the rate constant, \( k \), increases with increasing density. The isomerization of
n-butane is a unimolecular process activated by collision with other molecules, and therefore as the density and collision rate increase, this increase is expected. It would be anticipated that if higher densities were considered, the rate constant would eventually plateau and then be reduced due to hindrance of the torsional motion of the molecule by nearby molecules, as predicted by Kramer’s theory.

Having determined the values for the overall rate constant $k$, the rate constants $k_{TG}$ and $k_{GT}$ were calculated using Eqs. (6) and (7). Arrhenius plots for these rate constants were constructed for the simulation data at densities of 6.05 and 8.28 nm$^{-3}$ and are shown in Fig. 8. The rate constants, activation energies, and preexponential factors obtained from linear least squares fits to the Arrhenius plotted data are given in Tables II and III. First, we can compare the value we have obtained for $k_{TG}$ at the Brown and Clarke state point ($T$=291.6 K, $\rho$=6.05 nm$^{-3}$) with values published in the literature. We obtain a value of $k_{TG}$=9.03±0.04 ns$^{-1}$. Brown and Clarke obtained a value of 8.8±0.4 ns$^{-1}$ while Ramírez and Laso obtain a value of 8.25 ns$^{-1}$ (no error bars quoted). Our results are in excellent agreement with those of Brown and Clarke and we are able to quote a value with considerably greater precision. Our result is somewhat higher than that obtained by Ramírez and Laso using transition path sampling (TPS). The reason for this discrepancy may be due to the lower average temperature simulated by these authors (275 K vs 291.6 K used in both this work and that of Brown and Clarke). Ramírez and Laso also note in their publication that the TPS method is not best suited to finding rate constants of systems such as liquid n-butane due to the computational expense compared to other methods such as the one we have employed in this work.

We find that the activation energy for the trans-gauche conversion is 11.57±0.14 kJ mol$^{-1}$ at $\rho$=6.05 nm$^{-3}$ and is 11.78±0.05 kJ mol$^{-1}$ at $\rho$=8.28 nm$^{-3}$. For the gauche-trans process, these values are, respectively, 8.75±0.06 and 9.17±0.07 kJ mol$^{-1}$. These activation energies should be compared with the barrier heights obtained from a Boltzmann inversion of the ideal gas distribution, evaluated with the RB torsional potential, in order to take into account the rigid bond length and bond angle constraints used in our model. An effective torsional potential is obtained via

$$U_{eff}(\alpha) = -k_B T \ln[S^0(\alpha)] + \text{const.}$$

This effective potential is shown in Fig. 9, with barrier heights of 16.2 kJ mol$^{-1}$ for trans-gauche isomerization and 12.6 kJ mol$^{-1}$ for gauche-trans isomerization. Differences between the RB barrier heights and the activation energies reflect solvent effects. Making the comparison, we see that the effective energy barrier that must be surmounted by a molecule in the trans state in order for it to change to either of the gauche conformational states is lowered by approximately 4.5 kJ mol$^{-1}$ at the low density and is 4.4 kJ mol$^{-1}$ at the high density. For the gauche-trans barrier height, lowering of 3.8 kJ mol$^{-1}$ is obtained at the low density, and 3.4 kJ mol$^{-1}$ at the highest density. Despite the large statistical uncertainty associated with the preexponential factor, we observe greater values for the higher density case. Comparing preexponential factors for the $G \rightarrow T$ and $T \rightarrow G$ changes,
we observe no significant change at low density but at the higher density, $A_{TG} > A_{GT}$.

Ramírez and Laso\textsuperscript{50} have also shown that their rate constant data obey an Arrhenius law and we have estimated the activation energy from their plot (Fig. 3 in their paper) obtaining a trans-gauche activation energy, $E_{aTG}$, of between approximately 10.2 and 11.4±0.8 kJ mol\textsuperscript{-1}, in broad agreement with our result.

The observation that the torsional kinetics obeys an Arrhenius rate law demonstrates that the isomerization reaction is an activated process; increasing the temperature increases the kinetic energy associated with the torsional motion, thereby giving the molecules a “push” over the energy barrier separating different conformational states. Solvation appears to lower the free energy barriers for conformational changes relative to the barriers in the ideal gas state, with the lower density fluid having the lower free energy barrier. The lowering of the free energy barrier can be determined by comparison of the ideal gas barriers with those shown in Table III, and has two contributions: an enthalpic contribution which stems from the fact that interactions between molecules raise the energy of the trans and gauche states, and an entropic contribution from molecular packing. Coupled with this is the frequency with which molecules encounter each other, and hence interact. The “collision” frequency will increase with increasing density. From our data we observe that an increase in density gives rise to an increase in the rate constant despite more favorable (lower) energy barriers at low density. This effect is the result of the collision frequency contribution to the rate dominating the activation energy term.

**B. Confined butane**

1. **Fluid structure**

The effect of confinement on the transverse density profile within the pore can be seen in Fig. 10 (6.05 nm\textsuperscript{-3}) and Fig. 11 (8.28 nm\textsuperscript{-3}). Here the local molecular fluid density is plotted against position in the pore (normalized by the half-width of the slits). The form of the density profile has been well documented in the literature (see, for example, Refs. 51–54) showing peaks that diminish in magnitude away from the walls, towards the middle of the slit, indicative of a layering effect. This layering effect is stronger at the higher mean adsorbate density (Fig. 11). There is a change in the number of liquid layers as the pore width changes. For example, in going from a width of 6$\sigma$ to 4$\sigma$, the number of liquid layers that can be accommodated drops from 4 to 3 at a mean density of 6.05 nm\textsuperscript{-3} and from 5 to 3 at a mean density of 8.28 nm\textsuperscript{-3}. The extent to which the fluid wets the wall is a function both of the slit width and the mean fluid density. As the slit width decreases, the degree of wetting decreases. For a given slit width, the local density is higher in the vicinity of the walls for the higher of the two global fluid densities. At the higher mean density one may conjecture that the molecules are able to pack more efficiently near the walls and these adsorbed layers then have a stronger layering effect on the fluid in the remaining pore volume. If the adsorbed molecules pack more tightly, there is space to fit an extra fluid layer in the remaining pore space compared with at the lower mean density, which explains the signifi-

**TABLE II. Rate constants at various temperatures for the two densities: $\rho$=6.05 nm\textsuperscript{-3} and $\rho$=8.28 nm\textsuperscript{-3}. The numbers in parentheses are the statistical uncertainty in the last digits (based on one standard error).**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ (ns\textsuperscript{-1})</th>
<th>$k_{TG}$ (ns\textsuperscript{-1})</th>
<th>$k_{GT}$ (ns\textsuperscript{-1})</th>
<th>$k$ (ns\textsuperscript{-1})</th>
<th>$k_{TG}$ (ns\textsuperscript{-1})</th>
<th>$k_{GT}$ (ns\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.21(2)</td>
<td>0.11(3)</td>
<td>0.99(3)</td>
<td>1.4986(7)</td>
<td>0.1755(5)</td>
<td>1.1476(1)</td>
</tr>
<tr>
<td>200</td>
<td>7.20(5)</td>
<td>0.94(1)</td>
<td>5.33(5)</td>
<td>11.70(3)</td>
<td>1.96(2)</td>
<td>7.78(1)</td>
</tr>
<tr>
<td>250</td>
<td>22.97(5)</td>
<td>3.92(2)</td>
<td>15.14(7)</td>
<td>38.36(6)</td>
<td>7.95(4)</td>
<td>22.46(2)</td>
</tr>
<tr>
<td>291.6</td>
<td>46.53(10)</td>
<td>9.03(4)</td>
<td>28.5(1)</td>
<td>73.42(55)</td>
<td>16.8(3)</td>
<td>39.9(2)</td>
</tr>
<tr>
<td>350</td>
<td>92.86(5)</td>
<td>20.40(8)</td>
<td>52.1(2)</td>
<td>152.7(8)</td>
<td>38.5(4)</td>
<td>75.7(3)</td>
</tr>
<tr>
<td>400</td>
<td>145.2(6)</td>
<td>34.49(8)</td>
<td>76.3(2)</td>
<td>245.2(6)</td>
<td>64.9(3)</td>
<td>115.3(2)</td>
</tr>
<tr>
<td>450</td>
<td>204.8(2)</td>
<td>50.9(1)</td>
<td>102.9(2)</td>
<td>356.9(8)</td>
<td>98.1(4)</td>
<td>160.7(3)</td>
</tr>
<tr>
<td>500</td>
<td>276.8(2)</td>
<td>71.5(2)</td>
<td>133.7(3)</td>
<td>471.2(3)</td>
<td>133.5(1)</td>
<td>204.2(1)</td>
</tr>
</tbody>
</table>

**TABLE III. Parameters obtained from Arrhenius plots of $k_{TG}$ and $k_{GT}$ at two different densities (preexponential factor $A$ and activation energy $E_a$). The numbers in parentheses are the statistical uncertainty in the last digits (based on one standard error).**

<table>
<thead>
<tr>
<th>$\rho$ (nm\textsuperscript{-3})</th>
<th>$A_{TG}$ (ns\textsuperscript{-1})</th>
<th>$E_{aTG}$ (kJ mol\textsuperscript{-1})</th>
<th>$A_{GT}$ (ns\textsuperscript{-1})</th>
<th>$E_{aGT}$ (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.05</td>
<td>1093(72)</td>
<td>11.57(14)</td>
<td>1060(29)</td>
<td>8.75(6)</td>
</tr>
<tr>
<td>8.28</td>
<td>2248(56)</td>
<td>11.78(5)</td>
<td>1825(58)</td>
<td>9.17(7)</td>
</tr>
</tbody>
</table>
cant difference between the high and low density systems for the 6σ slit pores.

Elsewhere in this article we made the point that our confined simulations were conducted at a similar fluid density to the bulk simulations. Ideally, a comparison made at equivalent pressures would be preferable but defining pressure in a confined system is not straightforward. An estimate of the pressure inside the pores can nevertheless be made by calculating the ratio of the component of the force acting normal to the inside walls, to the area of the wall. It is useful to compare the pressure estimated in this manner for a few confined simulations with that of a bulk fluid at the same temperature and density. At 291.6 K, the mean pressures calculated from the usual mechanical route are 398.73 and 712.3 bars for bulk fluids at densities of 6.05 and 8.23 nm$^{-3}$, respectively. Under confinement, the wall pressure is estimated to be 500 bars at $H=10\sigma$ and is 580 bars at $H=4\sigma$ for the low density case while it is 5454 bars at $H=10\sigma$ and is 2532 bars at $H=4\sigma$ for the high density case. All pressures quoted exclude long-range corrections due to the difficulty of including these in the confined systems.

It is of interest to see what effect the confinement has on the position of the trans-gauche equilibrium. Figure 12 shows a plot of percentage of trans conformers against temperature for an ideal gas of butane, bulk condensed phase butane at $\rho=6.05$ nm$^{-3}$, and confined butane at two different pore widths: $H=4\sigma$ and 10σ. Figure 13 is similar to Fig. 12 except that the data refer to the higher density of 8.28 nm$^{-3}$.

The data in Fig. 12 show that within the statistical uncertainty, confinement has a negligible effect on the position of the trans-gauche equilibrium in n-butane at a density of 6.05 nm$^{-3}$. The situation for the density of 8.28 nm$^{-3}$ is somewhat different. Figure 13 shows a significant confinement effect on the conformational equilibrium. The fraction of trans conformers is increased upon confinement relative to the bulk phase. Furthermore, the shift towards excess trans increases as the slit width decreases.

The effect of confinement on the equilibrium distribution of torsional angles is shown in Fig. 14. Confinement at the lowest slit width studied increases the height of the trans peak at the expense of the two gauche peaks, relative to a bulk fluid at the same density and temperature. This confine-
ment effect is exactly the opposite to what we observed from an increase in density in the bulk phase (see Fig. 4).

In order to further explore why confinement results in a greater proportion of molecules existing in the trans conformational state, we have calculated isosteric heats of adsorption and determined the local variation in the trans population at different pore widths. The isosteric heat is simply the difference between the enthalpy of the adsorbate in the gas phase and its partial molar enthalpy in the adsorbed phase, so more strongly adsorbed molecules will have higher isosteric heats. In the limit of zero loading, we can write

\[ q^0_{st} = k_B T - \langle U \rangle^0, \]  

(24)

where \( \langle U \rangle^0 \) is the mean potential energy of the adsorbate in the pore in the limit of zero loading. Equation (24) can then be used as a means for calculating \( q^0_{st} \) via the statistical mechanical expression

\[ q^0_{st} = k_B T - \frac{\int U(r, \psi) \exp[-\beta U(r, \psi)] dr d\psi}{\int \exp[-\beta U(r, \psi)] dr d\psi}, \]  

(25)

where \( \beta = 1/k_B T \), and \( \psi \) represents the Euler angles. In order to evaluate the multidimensional integrals in Eq. (25) we have used a Monte Carlo scheme in which a rigid molecule of \( n \)-butane is inserted into the slit pore at a random position and with a random orientation chosen from uniform distributions. The average potential energy and Boltzmann factor are then averaged over \( 500 \times 10^6 \) trial positions and orientations. The entire calculation is repeated for each of the torsion angles. For the purpose of these calculations we fixed the wall atom sites at their equilibrium positions. A more sophisticated calculation could take the movement of these into account.

The variation of isosteric heat with torsion angle and pore width is shown in Fig. 15. The data are plotted for a single temperature, \( T=200 \) K. The first point to note from Fig. 15 is that the isosteric heat of adsorption increases with decreasing pore width. This reflects the increasing overlap of

\[ \langle \chi_T \rangle \]  

for confined butane at a density of \( 8.28 \) nm\(^{-3} \) and a temperature of \( 500 \) K. Data for two pore widths are plotted: \( H=10\sigma \) (solid line) and \( H=4\sigma \) (broken line).

\[ q^0_{st} = k_B T - \frac{\int U(r, \psi) \exp[-\beta U(r, \psi)] dr d\psi}{\int \exp[-\beta U(r, \psi)] dr d\psi}, \]  

(25)

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\[ \langle \chi_T \rangle \]  

for confined butane at a density of \( 8.28 \) nm\(^{-3} \) and a temperature of \( 500 \) K. Data for two pore widths are plotted: \( H=10\sigma \) (solid line) and \( H=4\sigma \) (broken line).
the wall potentials as the slit width decreases, resulting in more attractive pores, and hence a more negative value for $\langle U \rangle$. The second point to note is the variation of the isosteric heat with torsion angle. At all pore widths, the isosteric heat is a minimum for an angle of 90°. However, for angles of 0° and 180°, the isosteric heat is a maximum. The height of these two maxima is different, with the 180° angle always giving rise to the higher $q_{st}^0$ value. Taken together, these results indicate an energetic preference for planar configurations of $n$-butane in the pore space (at zero loading) over nonplanar configurations. Furthermore, the more compact planar gauche configuration (with $\alpha=180^\circ$) is preferred to the planar trans configuration (with $\alpha=0^\circ$). The configuration that is most distorted from planar is the one corresponding to the lowest $q_{st}^0$ value, and hence the one least energetically favored. At higher temperatures, the same variation of $q_{st}^0$ with torsion angle is observed, but the difference in the two maximum values for $\alpha=0^\circ$ and $\alpha=180^\circ$ becomes smaller. The absolute value of $q_{st}^0$ tends to increase with increasing temperature, due mainly to the dominant contribution of $k_BT$ to $q_{st}^0$ [see Eq. (24)].

The variation of the local trans fraction is shown in Fig. 16 for two different pore widths ($H/\sigma=10,4$) at a density of 8.28 nm$^{-3}$ and a temperature of 500 K. These profiles were obtained by dividing the system into a number of parallel slabs of equal volume along the direction normal to the pore walls, and then accumulating the number of molecules in each slab at each time step that were in the trans conformational state. The final averages in each slab were then normalized by the local density in that slab. We used a total of 100 slabs in all our simulations. From the figure we observe an enhancement in the fraction of trans conformers near the pore walls relative to the fluid in the center of the pore. From the previous discussion on isosteric heats we know that the walls favor planar configurations of butane molecules in the limit of zero loading of the adsorbate. Any slight preference for the $\alpha=180^\circ$ form of butane over the $\alpha=0^\circ$ form will be offset by the greater steric hindrance present in the former. As the density of the adsorbate increases, packing effects will play a more significant role. If the first adsorbed layer contains a high proportion of trans conformers, as a result of the layering effect, a relatively high fraction of trans conformers will be maintained further away from the walls, but in absolute terms, will decrease as the effect of the wall potential diminishes with distance.
TABLE V. Rate constants, $k_{TG}$ (ns$^{-1}$), at various temperatures for four different slit widths at two densities: $\rho=6.05$ nm$^{-3}$ and $\rho=8.28$ nm$^{-3}$. The numbers in parentheses are the statistical uncertainty in the last digits (based on one standard error).

<table>
<thead>
<tr>
<th>$\rho$=6.05 nm$^{-3}$</th>
<th>$\rho$=8.28 nm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H/\sigma$</td>
<td>$k_{TG}$ (ns$^{-1}$)</td>
</tr>
<tr>
<td>4</td>
<td>0.109(1)</td>
</tr>
<tr>
<td>200</td>
<td>0.983(7)</td>
</tr>
<tr>
<td>250</td>
<td>3.82(2)</td>
</tr>
<tr>
<td>291.6</td>
<td>7.91(3)</td>
</tr>
<tr>
<td>350</td>
<td>17.86(4)</td>
</tr>
<tr>
<td>400</td>
<td>29.13(9)</td>
</tr>
<tr>
<td>450</td>
<td>45.68(8)</td>
</tr>
<tr>
<td>500</td>
<td>59.3(1)</td>
</tr>
</tbody>
</table>

2. Kinetics

We have measured the reaction rate for the trans-gauche isomerization in confined butane in an identical manner to the bulk treatment. The rate constant $k$ was extracted from plots of the normalized relaxation function, $\hat{R}_{TT}$ versus time. The exponential nature of the curve confirms that the kinetics is first order. Figure 17 shows an example of the relaxation function for n-butane under varying degrees of confinement at 500 K and at a density of $\rho=8.28$ nm$^{-3}$. The figure shows that the relaxation time for trans conformers increases with decreasing pore width. Table IV gives the value of the rate constant evaluated in Fig. 18 for the high density system at four different pore widths. The data follow an exponential change with temperature, indicative of an activated process. Figure 19 shows Arrhenius plots of the data shown in Fig. 18. Both sets of data can be fitted with straight lines confirming the Arrhenius temperature dependence of the rate constants. Taking the analysis a step further, we have calculated the more fundamental rate constants $k_{TG}$ and $k_{GT}$ in the same manner as was done for the bulk phase kinetics; the former set of rate constants is given in Table V. Again, a general trend emerges, in which $k_{TG}$ decreases with decreasing pore width, but increases with increasing temperature, the effect being weaker at the lower density.

Table VI contains the activation energies and preexponential factors obtained from the Arrhenius plots using the trans-gauche and gauche-trans rate constant data for two different densities and four different pore widths. Taking the statistical uncertainties into account we find no evidence of a trend in the values of the activation energies with pore width at the lower density, but there is a small, possibly insignificant decrease in the value of both activation energies as pore width decreases at the higher density. Extremely long simulation runs would be required to fully resolve this matter and are beyond the scope of the present investigation. The preexponential factors show some interesting trends. These factors generally increase as the fluid density increases. This merely indicates the greater collision frequency that will occur as the molecular crowding increases. As the slit width

TABLE VI. Preexponential factors $A$ and activation energies $E_A$ for four different slit widths at the two densities: $\rho=6.05$ nm$^{-3}$ and 8.28 nm$^{-3}$. The numbers in parentheses are the statistical uncertainty in the last digits (based on one standard error).

<table>
<thead>
<tr>
<th>$\rho=6.05$ nm$^{-3}$</th>
<th>$\rho=8.28$ nm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H/\sigma$</td>
<td>$A_{TG}$ (ns$^{-1}$)</td>
</tr>
<tr>
<td>4</td>
<td>855(27)</td>
</tr>
<tr>
<td>6</td>
<td>870(20)</td>
</tr>
<tr>
<td>8</td>
<td>990(55)</td>
</tr>
<tr>
<td>10</td>
<td>932(29)</td>
</tr>
<tr>
<td>Bulk</td>
<td>1093(72)</td>
</tr>
</tbody>
</table>
lowered for the high density fluid, the preexponential factors decrease with a significant drop between the 6σ and 4σ slit width cases. The value for the lowest slit width is also substantially lower than for the equivalent bulk fluid. For the lower density adsorbate, the change in the preexponential factor is fairly minimal by comparison.

We conclude this section by noting that the activation energies are lower under confinement than in the bulk phase; the effect being greater at the higher density. The observed lowering of the composite rate constant with decreasing pore width and relative to the bulk fluid at the same temperature and density indicates that although the barriers to internal rotation may be lowered under confinement this is outweighed by the greatly decreased collision rates.

V. CONCLUSIONS

Molecular dynamics simulations have been used to study the effect of solvation and confinement on the isomerization of n-butane under a range of thermodynamic conditions. We have studied conformational equilibria and isomerization kinetics of butane in the liquid and confined phases. The results of our study are interesting and should make a valuable contribution to the fields of statistical mechanics of liquids and chemical reactions including catalysis. We have used well-chosen reference states in order to isolate solvation and confinement effects; the ideal gas state serves as a reference for the bulk simulations while the bulk simulations in turn act as a reference state for the confined simulations. Furthermore, we have employed the method of Brown and Clarke for obtaining the rate constants for isomerization with low statistical noise, enabling us to study small changes in pore width on the rate constant for confined butane.2

It was found that the proportion of molecules adopting a gauche configuration in the bulk fluid increases with density. In the ideal gas at moderate temperatures, the trans configuration of the isolated molecule is preferred since it has a lower energy minimum. Only at very high temperatures (beyond the scope of this work), where almost free rotation can occur, is the gauche conformation preferred and this is simply due to the wider range of angles that are categorized as gauche. However, in the solvated state, as the density of the system increases the molecule is more likely to adopt a more compact gauche conformation due to the interactions between the molecules. This result agrees with earlier calculations by Chandler and Pratt using statistical mechanics,4 but with solvents. The rate constants are also found to increase with density, and this can be explained in terms of the reduced activation energies and the increased likelihood of collisions.

In the confined systems, density profiles, isothersmic heats of adsorption, conformational statistics, and rate constants have been determined. The proportion of trans conformations is larger than that in the bulk at the same average density and temperature due to an increased preference for planar molecules, especially near the walls. The activation energies for the isomerization process are smaller than in the bulk system, but the reaction rates are slower, presumably due to the reduced collision rate. Our study of the confining effects on isomerization kinetics represents the first simulations of this nature and will serve as a useful starting point for more in-depth studies of the effect of confinement on this type of “reaction.” The effect of varying the physical and chemical nature of the wall is one area that would appear very fruitful, especially with regard to heterogeneous catalysis. Studying the torsional kinetics in longer alkanes is also worth revisiting, especially with regard to cooperativity and confinement. In this work we assumed a reaction mechanism involving two rate constants. However, as shown by Brown and Clarke23 this does not fully explain the mechanism of isomerization since interconversion from G+ to G− is neglected. It would be interesting to consider the effects of solvation and confinement on kGG, and work in this direction is underway.

Finally, we note that the results obtained in this paper were obtained with model potentials for the n-butane molecules and slit pores that incorporate the key features of the system, while still being computationally efficient. It is also a model that has been adopted in other studies, and therefore allowed comparisons to be made. However, we note that it is not a highly accurate model of this physical system, and while the general trends observed are expected to be a good reflection of what will occur in a real system, the absolute numbers will not. Further studies will use this proven approach to examine more realistic models.

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Effect of solvation and confinement


40 Unpublished.