Replica exchange Hybrid Monte Carlo simulations of the ammonia dodecamer and hexadecamer

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ABSTRACT

Several Hybrid Monte Carlo-replica exchange (HMC) simulations are carried out to obtain the classical thermodynamic behavior of the ammonia dodecamer and hexadecamer. We find evidence of solid to solid phase changes that we characterize using the structures of low lying minima. In a recent publication [40], we introduce a new integrator for clusters of rigid tops that works directly with non-Cartesian coordinates. This letter contains the first application of the integrator to enhance the efficiency of the Hybrid Monte Carlo simulation of clusters of rigid tops.

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1. Introduction

The chemical physics community has been interested in ammonia clusters [1–14] for well over a decade. Our own efforts have complemented the work of a number of experimental [3,8–12] and theoretical studies [5,13,14], aimed at elucidating the physical properties of these important systems. Recently, we have investigated the propensity for ammonia clusters (or clathrates) to serve as a hydrogen storage medium [1,2]. This would be a key development for the transportation industry since both the guest and the host can serve as fuel, and the energy storage to usage cycle could be made completely carbon free.

Our ongoing investigation [1,2] of the structure of the minima has extended the range of sizes for which we have data up to the $(NH_3)_{27}$ aggregate. In this range, there are only two clusters that are distinctly different in structure from the rest. For most, the building motif can be deduced from the results of our original minimization efforts [7]. The distorted cube shape of the octamer is the unit cell for the bulk ammonia ice structure, where every ammonia molecule in the bulk serves as a triple donor and triple acceptor of a hydrogen bond.

In finite hydrogen bonded systems, the structure of the global minimum is the result of opposing tendencies to minimize the surface tension while maximizing the number of hydrogen bonds that each molecule accepts and donates. For the dodecamer and the

hexadecamer this balance is achieved with the construction of a symmetric cage that could trap kinetically a hydrogen molecule inside, and that could perhaps serve as models for ammonia clathrates. Yet, the energy differences and the trend in evaporation energies obtained in our original investigation [7] seem to suggest that the thermodynamic behavior of these two intriguing systems should be quite different. The dodecamer, along with the octamer and the decamer, is a magic number, meaning it is a minimum point in the $E_n - E_{n-1}$ versus n plot, while nothing special can be said for the hexadecamer along these lines. Nevertheless, the gap between the global minimum and the next minimum is substantially larger for the hexadecamer than it is for the dodecamer [7]. These findings would suggest that these structures are particularly stable thermodynamically. Stability is a relative concept, evaporation energies yield information relative to evaporation events, whereas the presence of low lying minima yield information relative to melting or potentially solid–solid events. These events can be quantified with NVT ensemble simulations.

Thermodynamic simulations of the ammonia clusters using the polarizable potential energy model developed by Barral et al. [7] have been carried out for the dimer through the hendecamer [4]. Efforts to continue this investigation on larger clusters using the Metropolis algorithm [15–17] coupled with the parallel tempering strategy [18–23] have proved too inefficient to be practical. Unlike the regular Metropolis strategy which selects only a limited set of degrees of freedom at the time for each move, the Hybrid Monte Carlo (HMC) simulations [24–37] coupled with the replica exchange strategy (the dynamic equivalent of parallel tempering [18–23]) have been found more efficient for highly corrugated potential energy surfaces. All the degrees of freedom can be moved

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at once by using regular molecular dynamics, and at the end of an adjustable number of dynamic steps, the resulting configuration is accepted or rejected as with the regular Metropolis algorithm. The efficiency gain of HMC results from an arbitrary number of steps taken for each move improving the odds of overcoming energy barriers substantially.

One obstacle that we needed to overcome is that the polarizable model for the ammonia clusters is based on rigid ammonia molecules [7]. HMC simulations for rigid bodies are rare [36] because of the added complexities of propagating the dynamics [38,39] in curved spaces. We have made significant advances to this particular field in recent times [40–42]. In particular, we have proposed an integrator that works directly with non-Cartesian coordinates, and that does not require equations of constraints [38,39]. These are hard to write down for a molecule as simple as ammonia, and would be intractable for a relatively small oligomer. Instead, we use the parameters of continuous Lie groups (e.g. rotations) to define configurations, and we use the tools of differential geometry to integrate the resulting geodesic equations.

The goal of the present investigation is to use these latest developments to simulate the dodecamer and the hexadecamer of ammonia and to characterize insofar as possible the thermodynamic behaviors that they display. Our results are in Section 2. In Section 2.1 we provide a brief summary of the potential energy model for the ammonia clusters. The integration algorithm for the molecular dynamics in curved spaces is discussed in Section 2.2. Sections 2.3 and 2.4 contain our main results. Discussion and conclusions are in Section 3.

2. Methods and results

2.1. The potential

The potential energy surface (PES) for the ammonia clusters is a many-body rigid model [7] that includes point charges, dispersion and repulsion terms centered on all atoms, as well as a description of polarizability implemented using a single-step 'charge on spring' approach. The polarizability terms include many-body interactions while keeping the PES analytically differentiable. The function is obtained by optimizing the parameter set to match as closely as possible the computed energies to MP2/aug-cc-pVTZ energies for a relatively large set of selected configurations [7]. For finite temperature simulations we confine the clusters using the continuous version of the Lee–Barker–Abraham [43] potential V_{LB},

$$V_{LB} = V_0 \sum_{i=1}^{N} \left(\frac{|\mathbf{r}_{N_i} - \mathbf{r}_{cm}|}{R_0} \right)^{20}, \tag{1}$$

where V_0 is 1 Ha, $\mathbf{r}_{N_i}$ is the position of the nitrogen atom for the ith ammonia molecule, $\mathbf{r}_{cm}$ is the center of mass of the cluster, and R_0 is a parameter set to 18 bohr. This assures that the most important configurations can fit inside the Lee–Barker–Abraham sphere without having their energy, and thermodynamic properties impacted significantly [44,45]. The continuous version of the Lee–Barker–Abraham potential V_{LB} allows us to obtain an analytical gradient for the overall PES, which is needed for the dynamics.

2.2. The integration method

The algorithm we reproduce below has been developed and implemented in both classical and quantum simulations [40–42]. The method is based on the following set of update rules for the momenta associated with the degree of freedom μ at step k,

$$p_{\mu k} = \frac{1}{2}(g_{\mu\nu k} + g_{\mu\nu k+1})\gamma_k^\nu - \frac{\Delta t}{4} \partial_\mu g_{\sigma\nu k} \gamma_k^\sigma \gamma_k^\nu + \frac{\Delta t}{2} \partial_\mu \mathcal{V}_k, \tag{2}$$

and the update of the same at step $k+1$,

$$p_{\mu k+1} = \frac{1}{2}(g_{\mu\nu k} + g_{\mu\nu k+1})\gamma_k^\nu + \frac{\Delta t}{4} \partial_\mu g_{\sigma\nu k+1} \gamma_k^\sigma \gamma_k^\nu - \frac{\Delta t}{2} \partial_\mu \mathcal{V}_{k+1}, \tag{3}$$

In these equations,

$$\gamma_k^\mu = \frac{q_{k+1}^\mu - q_k^\mu}{\Delta t},$$

is the average velocity vector at time t_k, $\mathcal{V}_k$ is the overall potential energy at time t_k, and $g_{\mu\nu}$ is the metric tensor [40–42]. Each molecule of ammonia is represented with six degrees of freedom, three Cartesian-like coordinates for the location of the center of mass, and three stereographic projection coordinates for the orientations [4,6,40–42].

The steps to implement the methods are as follows. Eq. (2) is used to compute q_{k+1}. Eq. (2) is nonlinear in the vector γ_k, therefore we use a starting value for the updated positions, computed using the first order Euler–Cromer method applied to manifolds,

$$\begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{p} \end{pmatrix}_{t+\Delta t} = \begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{p} \end{pmatrix}_t + \Delta t \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}} \\ -\frac{\partial \mathcal{H}}{\partial \boldsymbol{q}} \end{pmatrix}. \tag{4}$$

The momenta $\mathbf{p}_t$ are sampled using the Cholesky decomposition of the correlation matrix (the metric tensor), and the Box–Muller algorithm together. The latter is used to generate Gaussian variables with zero mean, no correlation, and with unit variance. Then, the Cholesky decomposition of the correlation matrix is used to transform the resulting vector into the proper mass-weighted correlated momenta distribution [40].

We then evaluate the inverse of the matrix $g_k + g_{k+1}$ to find a corrected value for the updated positions, and rather than continuing until self-consistency is achieved, we use only one step. We find that this procedure is sufficient to suppress the serious energy drift that the Euler–Cromer propagator displays even when small steps are used. To overcome barriers in the PES during the HMC simulations, the dynamics have to be carried out with a sufficient number of steps and with large enough step size. The energy increase that results from a drifting integrator such as the Euler–Cromer in curved spaces prevents important configurations from being sampled by HMC, as they are rejected instead.

2.3. Constant volume heat capacity

The heat capacities of the dodecamer and the hexadecamer are graphed in Figure 1. The lines connecting the symbols are not actual data points, they are drawn to guide the eye. A total of 40 temperature points are selected using a nonlinear growth model

$$T_k = T_1 + (T_{\max} - T_1) \left(\frac{k-1}{N_w - 1} \right)^2, \tag{5}$$

so that the points are more closely spaced at the lowest temperatures. The parameters in Eq. (5) are the same for all our simulations; N_w is the number of walkers, set at 40, T_1 is the lowest temperature set at 0.5 K and $T_{\max}$ is 250 K. This temperature range was selected based on previous experience with ammonia clusters [6], and with the expectation that we may find cold temperature features in the thermodynamics. For each simulation, all 40 walkers are running simultaneously. The replica exchange algorithm is implemented by attempting configuration swaps between adjacent temperature walkers, with a frequency of one attempt every 10 moves. Configuration swaps are attempted approximately every 10 moves, and