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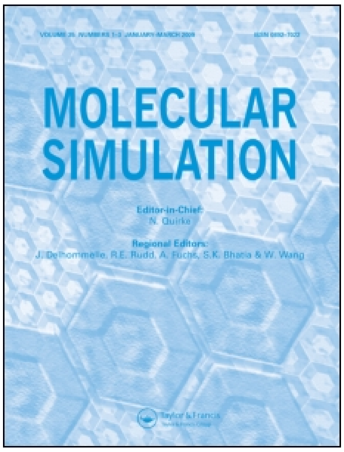

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MECHANISMS FOR STABILISING WATER CLATHRATES

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Molecular dynamics computer simulations are used to examine various possible mechanisms for stabilising water clathrates. It is found that the attractive interactions between guest and host molecules are not sufficient to explain the clathrate's stability; nor is there any significant dynamic coupling between the guest and host molecules in the clathrate. Instead, it appears that the repulsive guest-host interactions provide the mechanical stability of the clathrate, and that they are even sufficient to define its structure. Some of the thermodynamic implications of these observations are discussed.

KEY WORDS: Gas hydrates, water clathrates, cell theory.

1. INTRODUCTION

Water clathrates are formed by the inclusion of small, nonpolar molecules (guests) into an open, tetrahedral lattice of water molecules (the host); several different types of water lattice are known, but all of them are regular crystalline networks. Since the most common types of guest are gaseous under standard conditions, they are often referred to as gas hydrates.

There are a number of important applications that motivate the study of these clathrates. For example, they are able to form in gas pipelines, causing blockages and pressure drops. Further, there are vast quantities of methane contained in naturally occuring methane hydrate deposits [1], and these may become an important source of methane. The latter point also has environmental implications, as the sheer size of these deposits may make them an important positive feed-back mechanism for global warming: global warming may destabilise these deposits, thus releasing more methane (which is a "green-house gas") into the atmosphere. In all three of these examples, what is needed is an accurate knowledge of the conditions under which gas hydrates will form, and this will only follow from an understanding of the interactions that stabilise them.

Gas hydrates also exhibit properties that make them something of a scientific curiosity. In particular, they possess a surprisingly high concentration of "insoluble" compounds in water (*e.g.* mole fractions of methane in water of more than 0.1), and they represent a system in which the mixing of water with nonpolar molecules actually stabilises the water-water interactions. Both of these properties seem to challenge our conventional notion of the effect of hydrophobic forces, and so it is again important to understand why these clathrates form, and what is the mechanism of their stability.

Over the past 30 years, attempts to explain the stability of gas hydrates have been based on the cell theory proposed by van der Waals and Platteeuw [2]; however this approach has been only partially successful, even when implemented semi-empirically [3–6]. Recent computer simulation studies [7, 8] suggest that the underlying assumptions of the cell theory are either insufficient or inappropriate for gas hydrates. It therefore seems timely to widen the discussion, and rather than just seeking to amend the cell theory, to reassess all the possible mechanisms that might lead to gas hydrate stability. Three such mechanisms will be considered in the next section. The simulation methods used to examine these mechanisms will then be described in section 3, while the results and implications of the simulations will be addressed in sections 4–6.

2. POSSIBLE MECHANISMS

Broadly speaking, there are three types of interaction that might stabilise a gas hydrate: (i) the attractive guest-host interactions, (ii) the repulsive guest-host interactions (excluded volume effects), and (iii) a dynamic coupling between host lattice vibrations and the rattling motion of the guest in its cage.

The first of these is the most natural starting point for any discussion of stability, and it is this approach that is embodied in the cell theory [2]. Since the guest molecules are at best only weakly polar, it is clear that the strongest interactions will be those between the water molecules themselves; hence the behaviour of the water lattice (mechanical stability, dynamics etc.) will be determined by the water-water interactions, although they will be slightly perturbed by the guest-host interactions. This may be pictured in terms of a free energy surface: the empty hydrate lattice represents a local minimum on the free energy surface, and the guest-host interactions cause slight changes in the character (*i.e.* depth or shape) of this free-energy well. In its simplest form, the perturbation will merely lower the energy of the clathrate, *i.e.* change the depth but not the shape of the free-energy well. If enough of the cavities are occupied then the free-energy well will become the global minimum, thus making the clathrate thermodynamically stable. Higher order perturbations (*i.e.* changes in the shape of the well) could, in principle, be included; however such perturbations will be complicated many-body interactions that depend on the nature of the guest and even on the arrangement of occupied cavities in the clathrate, and as such they are likely to become rapidly intractable.

The second mechanism takes account of the hard-core repulsive part of guest-host interactions, but without neglecting the attractive contribution. The effect of these repulsive forces is to create an excluded volume for the water molecules that disrupts some of the vibrations of the host lattice, in particular restricting the amplitude of any unstable lattice modes – the water molecules are simply not given enough room in which to move. Thus not only are the guest molecules encaged by the water molecules, but the water molecules are also trapped by the guest molecules. In this way, the repulsive guest-host interactions provide substantial resistance to any rearrangement of the water lattice, and so generate the mechanical stability of the system. There are two important consequences of this mutual trapping that should be mentioned: (i) it implies that the bulk gas hydrate will be kinetically stabilised, so that any phase change or degredation of the hydrate crystal can only occur on its surface, and (ii) it implies that the hydrate will be impervious to both water and guest molecules. The latter point is just the macroscopic consequence of microscopic caging.

It is clear that these kinetic effects cannot supplant thermodynamic considerations;

however, as will be shown below, they can change the thermodynamic questions that need to be addressed. The resulting model can best be explained by describing the formation of a hydrate (*H*) at the interface between bulk water (*W*) and bulk guest (*G*) phases. (Note that it is only at the *G*/*W* interface that water and guest molecules will mix at a concentration that is suitable for clathrate formation). The first step in this process is nucleation – the formation of a thin layer of *H* at the *G*/*W* interface – and this will only occur if the interfacial layer of *H* is in equilibrium with both *W* and *G*. However, the very formation of *H* creates an impervious barrier between *W* and *G*, and so prevents the possibility of any further equilibration between *W* and *G* directly. If, for example, there is an excess of water in *G*, the hydrate crystal will prevent it from condensing in *W*. It must therefore condense either as more hydrate, or nucleate a new *W* phase; in the latter case, this will merely create a new *G*/*W* interface under conditions that favour the formation of a thin film of hydrate. Thus either way, the water will condense as *H* and not as *W*. An entirely analogous argument results if there is excess guest in *W*.

The crucial point about this argument is that it is only at the nucleation step that *W* and *G* can combine to give *H*, or conversely, that *H* can degrade to give *W* and *G* directly. Once the hydrate has formed *W* and *G* will no longer be in contact, and so the movement of molecules between these two phases can only take place through *H* (*i.e.* by hydrate forming on one interface and "melting" on the other); thus the water and guest molecules cannot move between *W* and *G* independently, but only in the same ratio that is found in the clathrate. An important consequence of this is that the chemical potential of the separate molecules need not be the same in all three phases (which is the condition for a true three-phase equilibrium). Instead, it is only required that the free energy of *H* be lower than that of the concentrated aqueous guest solution that would result from "melting" at the *W*/*H* interface, or the wet guest phase that would result at the *G*/*H* interface. This condition is far less stringent than requiring that the hydrate structure be the global free energy minimum.

The continued growth of the *H* phase involves the formation of bulk gas hydrate, and this should be an easier process than the creation of the interfacial film: if the free energy of molecules in the bulk were not lower than that of molecules on the surface, then the hydrate would form as large convoluted surfaces rather than as three dimensional crystals. Thus the most restrictive step in this model must be the nucleation stage, and the conditions for hydrate formation should be determined by the conditions for a three-phase equilibrium between bulk water, bulk guest, and an *interfacial* layer of hydrate. We note that the behaviour of this interfacial hydrate is likely to be quite different from the behaviour of the bulk hydrate considered in the first mechanism.

It is worth stressing that this mechanism does not contradict the first mechanism, it merely changes the thermodynamic conditions needed for stability: the free energy of the gas hydrate need no longer be the global minimum, but only lower than the free energy of any viable degredation products. In the process, it also shifts the focus of any theory away from the bulk properties and onto the surface properties.

The third mechanism may be thought of as a resonance effect. If the characteristic frequencies of translation of the guest molecule within its cage are similar to those of any host lattice vibrations then there may be a mode coupling between the two motions; such a mode coupling would lower the energy of the clathrate, and hence increase its stability. In this case, one might expect the properties of the clathrate to depend on quantities such as the mass of the guest molecule or its size relative to that of the cavity it occupies.

3. SIMULATION DETAILS

The simulation procedure has been described in detail elsewhere [9], and so only a brief outline of it is reproduced here. Molecular dynamics simulations were used to study the properties of a type I gas hydrate. This structure is characterised by a host lattice of $Pm3n$ symmetry, with the unit cell containing 46 water molecules and two different types of cavity (6 large and 2 small). All simulations were performed in the (N, V, T) ensemble and modelled a single unit cell containing up to 8 guest molecules; periodic boundary conditions were used to mimic an infinite crystal. A couple of simulations were repeated using 8 unit cells in order to check for system size effects, but these yielded no significant difference.

As with our earlier simulations [7, 9] water-water interactions were described with the simple point charge model (*SPC*) [10] and a one-site Lennard-Jones model of methane (M) was used for the guest. Long range electrostatic interactions were evaluated with a Ewald summation, while all other interactions were truncated when the molecular centre of mass separation was half the length of the simulation box. In addition to the reference methane guest, we also considered a purely attractive guest (A) and a purely repulsive guest (R), where A and R were the result of partitioning the methane potential into its attractive and repulsive parts (*i.e.* according to the Weakes/Chandler/Andersen decomposition [11]); note that this method creates a 'harder' repulsive guest than the r^{-12} potential used in our earlier work [7]. For a purely attractive guest there are, of course, no repulsive forces to create a cage, and the guest would therefore be free to diffuse through the hydrate. To counter this effect, the attractive guests were bound to the centre of their cavities with an external harmonic restoring force; the relevant force constant was chosen to ensure that the characteristic frequencies of the attractive guest's motion were comparable with those of a methane guest. A summary of the intermolecular parameters is given in Table 1, while the different model hydrates considered in this paper are listed in Table 2.

Equations of motion and rigid water molecule constraints were implemented with

Table 1 Intermolecular potential parameters

Lennard-Jones interaction	$U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$	
Repulsive potential	$V_r(r) = U(r),$ $= -\varepsilon,$	$r < 2^{1/6}\sigma$ $r > 2^{1/6}\sigma$
Attractive potential.	$V_a(r) = -\varepsilon,$ $= U(r),$	$r < 2^{1/6}\sigma$ $r > 2^{1/6}\sigma$

atom	σ (Å)	ε/k (K)
O–O	3.16	78.18
CH4–0	3.33	91.71
CH4–H	3.25	50.81
CH4–CH4	3.64	164.2

electrostatic parameters for water:

charge on O atom	$= -0.82$ a.u.	O–H bond length	$= 1.0$ Å
charge on H atoms	$= +0.41$ a.u.	-H–O–H	= 109° 28′

Force constant for harmonic binding force:
$B/k = 2400\,\mathrm{K}^{-1}\,\text{Å}^{-2}$

Where k is Boltzmann's constant.

Table 2 Summary of the simulations performed[a]

Simulation	*Guest*	*Occupancy*
*M*8	methane	all cavities
*M*1	methane	one large cavity in the unit cell
*M*0	—	none
*R*1	repulsive	one large cavity in the unit cell
*A*1	attractive	one large cavity in the unit cell
$H^{1/2}$	light methane (mass = 8 u)	one large cavity in the unit cell
H^{2}	heavy methane (mass = 32 u)	one large cavity in the unit cell
H^{10}	heavy methane (mass = 160 u)	one large cavity in the unit cell
MS	methane (stationary)	one large cavity in the unit cell
RS	repulsive (stationary)	one large cavity in the unit cell
AS	attractiave (stationary)	one large cavity in the unit cell

[a] All simulation used type I gas hydrate host lattice of water molecules with a cell parameter a = 11.88 Å, and temperature T = 200 K

the velocity-Verlet [12] and the RATTLE [13] algorithms respectively. A timestep of 5 fs was used throughout, which gave energy conservation (in constant energy simulations) of ~ 0.01% of kT. All simulations were started from the observed crystal structure [14] with random (thermal) velocities and were allowed to equilibrate for 10 ps before recording a further 30 ps for analysis. Results were then obtained by averaging over two independent trajectories. (Note that the results of section 4 were obtained by analysing 20 ps of one simulation).

Radial distribution functions were calculated from every 20th configuration, and every 50th step was used as a time origin for calculating the time-dependent properties (*i.e.* mean square displacements and time correlation functions). Unless otherwise stated, all simulations were performed at a temperature of 200 K, and with a unit cell of length 11.88 Å - the cell parameter being chosen to give a partial pressure of ~ 0 for the host lattice in the singly occupied simulations (*i.e.* with 1 guest molecule per unit cell).

4. VARIATIONS IN OCCUPANCY

As mentioned in section 2, the first stability mechanism is based on the idea that the guest molecules will only slightly perturb the behaviour of the water lattice. In particular, if this perturbation approach is to be tractable, the guest should not change the behaviour of the water lattice itself, but merely provide a favourable guest-host interaction energy that lowers the energy of the clathrate system. A good way to test for this is to vary the number of cavities in the host lattice that are occupied by guest molecules (the occupancy) and see whether this affects the behaviour of the host lattice. The effect of variations in occupancy has been discussed in detail elsewhere [7], but for completeness, a summary of the pertinent results will be given in this section.

Hydrate lattices with three different levels of occupancy were considered: (i) a methane molecule in each of the eight cavities in the unit cell (*M*8), (ii) a methane molecule in one of the large cavities from each unit cell (*M*1), and (iii) a host lattice with no guests included (*M*0). It was found that there were important differences between the properties of these three systems, with small but significant variations between $M8$ and $M1$, but a completely different behaviour for $M0$. For example, the potential energy arising from water-water interactions, U_{ww}, was found to be consistently lower in $M8$ than it was in $M1$: by $0.23 \pm 0.07\,\mathrm{kJ\,mol^{-1}}$ at a temperature of 200 K, and $0.58 \pm 0.13\,\mathrm{kJ\,mol^{-1}}$ at 270 K. These values might seem small, but they are of similar magnitude to empirical estimates obtained with the cell theory for the free energy difference between the hydrate water lattice and ice (1.2–$1.3\,\mathrm{kJ\,mol^{-1}}$ at 273 K [4,15]) and so could lead to large uncertainties in resulting predictions of clathrate stability. For $M0$, however, it was not possible to calculate an equilibrium value for U_{ww} since the energy of the hydrate steadily decreased throughout each simulation. This suggests that the empty hydrate lattice is completely unstable, and spontaneously rearranges to a lower energy configuration even on a picosecond timescale.

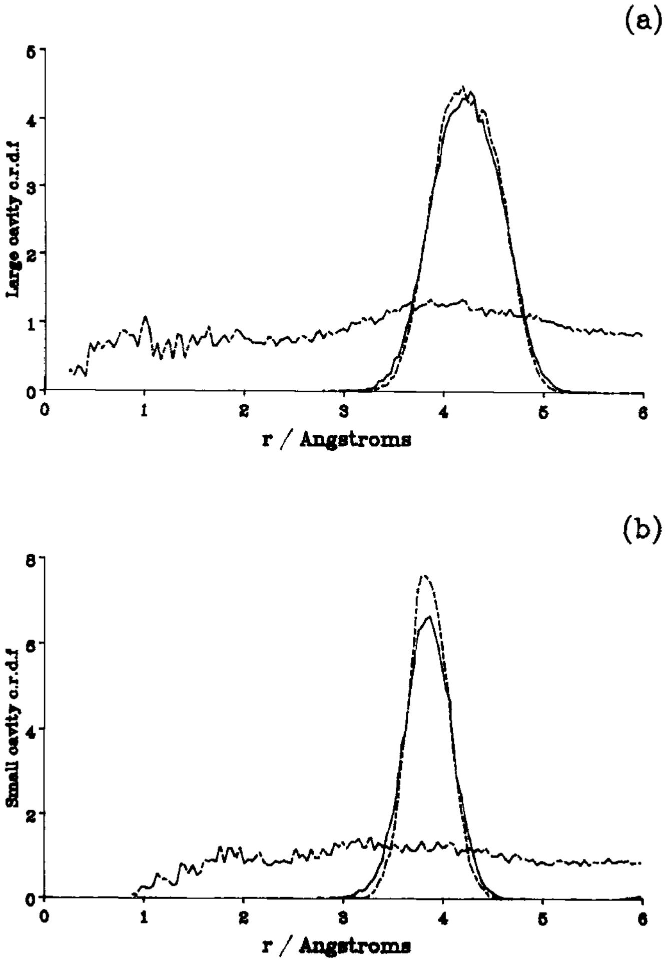

Figure 1 Radial distribution of oxygen atoms about the centre of (a) the large cavities, and (b) the small cavities: ----, $M8$; ——, $M1$; — — —, $M0$

The decay of the empty hydrate can be confirmed by looking at various other structural properties of the host lattice. Just two such properties will be mentioned here. The first is the radial distribution of the water's oxygen atoms about the centre of the cavities in the hydrate crystal (cavity radial distribution function, or c.r.d.f.). Since these sites will define cavities only when the long-range spacial order of the hydrate crystal lattice is present, the c.r.d.f. should be particularly sensitive to any changes in the hydrate structure. From the c.r.d.f.'s depicted in Figure 1, it is clear that the host lattice structure has broken down in *M*0. For *M*8 and *M*1 these functions show a large void surrounded by a dense 'wall' of water molecules, indicating that the cavity structure characteristic of a type I hydrate is quite stable for the duration of the simulations; the cavity structure is better defined in *M*8, but the behaviour of the two systems is quite similar. For *M*0, however, the c.r.d.f. is broad and structureless, indicating an almost isotropic distribution of water molecules and suggesting an amorphous or liquid-like phase.

The other function to be considered is the mean square displacement (m.s.d.) of the oxygen atoms in the host lattice. These functions are depicted in Figure 2, and they reinforce the conclusions drawn from the c.r.d.f.'s. Both *M*8 and *M*1 show an upper bound for the displacement of the oxygen atoms (and hence also of the water molecules), thus showing that the water molecules are indeed tied to their lattice sites and that the crystal structure is stable. The small differences that do exist indicate that the water molecules are more tightly bound in *M*8 than in *M*1. This behaviour is again in stark contrast with that of *M*0, for which the water molecules are clearly unbounded. Instead of being confined to well defined spacial positions as would occur in a crystalline structure, the water molecules appear to be diffusing through the *M*0 system.

The conclusion to be drawn from this discussion is that behaviour of the host lattice does depend on the presence or absence of guest molecules, with quantitative differences between *M*8 and *M*1, but qualitative differences between occupied and unoccupied hydrates. Indeed, the dramatic nature of the distinctions between *M*1 and *M*0 implies that the behaviour of the host lattice must be fundamentally affected by the guests, with the mechanical stability of the clathrate being intimately related to the guest-host

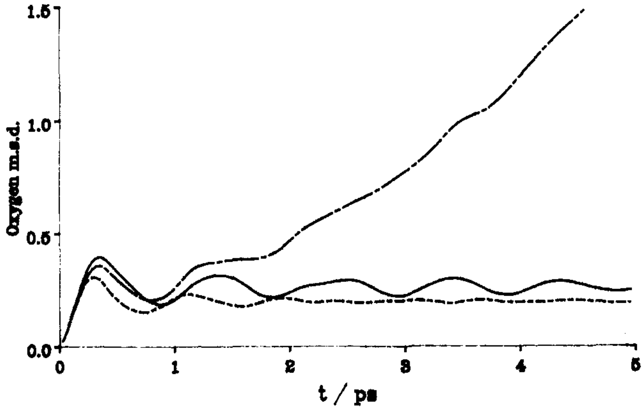

Figure 2 Mean square displacement (in Å^2) of oxygen atoms in the host lattice: ----, *M*8; ——, *M*1; – – –, *M*0.

interactions (note that mechanical stability is a prerequisite for thermodynamic stability). This has important consequences for the first mechanism discussed in section 2, since it implies that the host lattice is not a good reference system for any perturbation approach.

5. THE NATURE OF THE GUEST: REPULSIVE AND ATTRACTIVE INTERACTIONS

We turn now to the question of whether the host lattice is sensitive to the nature of the guest, and if so, what property of the guest molecule is most significant. In particular, we will be concerned with the relative importance of repulsive and attractive guest-host interactions. This question is directly relevant to the applicability of the second mechanism discussed in section 2, but might also be expected to have a

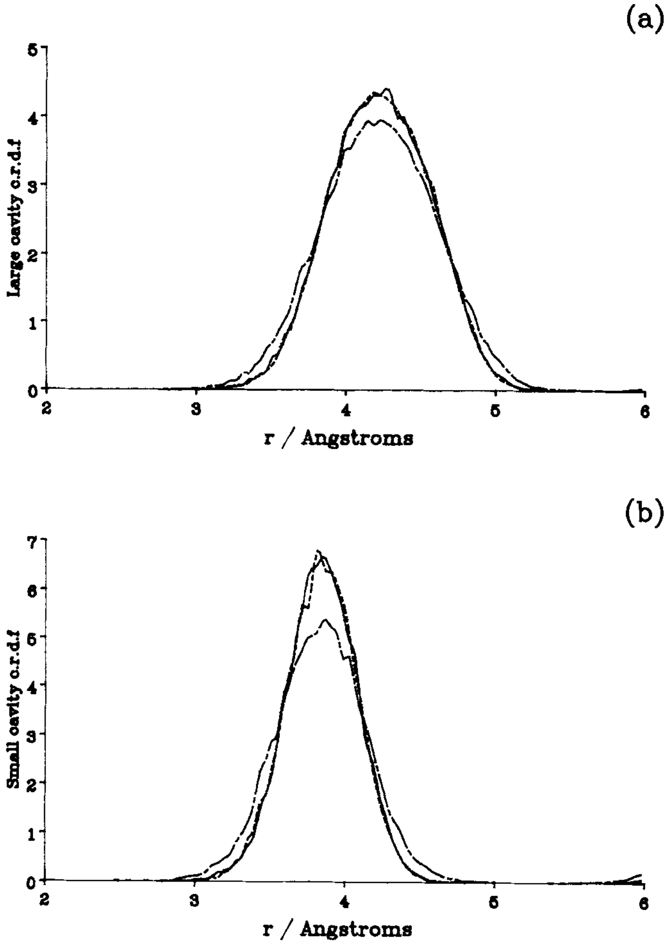

Figure 3 Radial distribution of oxygen atoms about the centre of (a) the large cavities, and (b) the small cavities: ——, *M*1; ----, *R*1; — — —, *A*1.

bearing on the effect properties such as molecular size and polarizability have on hydrate formation.

The easiest way to compare these two interactions is to completely separate them, and so we have considered hypothetical gas hydrates in which the guest molecules are either completely attractive or completely repulsive; the potentials for these hypothetical guests were described in section 3 and Table 1. In addition, since the inclusion of the first guest molecule appears to have the biggest effect on the host lattice, it is likely that differences arising from the nature of the guest will be seen most clearly in a singly occupied hydrate (*i.e.* one guest per unit cell). Two further sets of simulations have therefore been performed: a hydrate with one attractive guest per unit cell (*A*1), and a hydrate with one repulsive guest per unit cell (*R*1).

C.r.d.f.'s for M1, R1 and A1 are shown in Figure 3. On a timescale of tens of picoseconds, all three systems exhibit the well defined cavities that characterise a stable gas hydrate. This suggests that both attractive and repulsive interactions can modify the behaviour of the water molecules sufficiently to make the hydrate at least metastable. However, whilst the attractive hydrate is stable, it still exhibits less structure than *M*1 (the peak for *M*1 being considerably higher and narrower), indicating that something more than just water-water and attractive guest-host interactions are needed to explain the properties of methane hydrate. In contrast, the c.r.d.f.'s for *R*1 are indistinguishable from those for *M*1. This provides strong evidence that it is primarily the repulsive guest-host interactions that define the geometry of gas hydrate crystals.

The conclusions drawn above can be reinforced by looking at the m.s.d.'s for oxygen in the host lattice, which are shown in Figure 4. In this case the distinction between the *A*1 system and the other two is even clearer, with the limiting mean square displacement of water molecules (as characterised by the oxygen atoms) being about twice as large in *A*1 as it is in *M*1 and *R*1; this is indicative of a much more flexible crystal for the attractive hydrate. Again the curves for *M*1 and *R*1 are very similar, with the long time behaviour of both systems oscillating around a plateau value of 0.26 Å. Thus it appears that the hard core repulsive forces do restrict the motion of the water molecules, confining them to their lattice sites and hence stabilising the conformation of the host lattice.

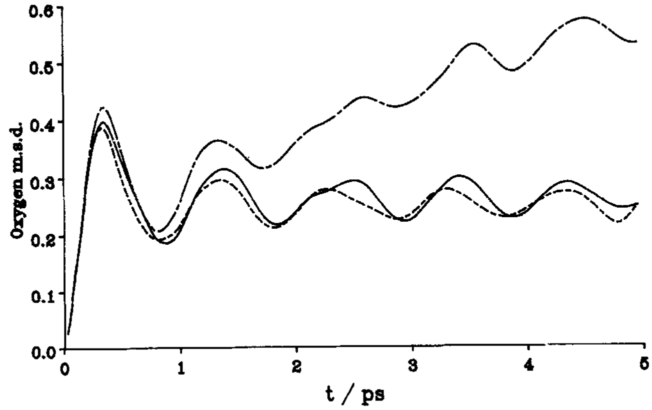

Figure 4 Mean square displacement (inÅ^2) of oxygen atoms in the host lattice: ——, *M*1; ----, *R*1; ——, *A*1.

These observations lend credance to the "excluded volume" mechanism proposed in section 2. While the attractive forces did stabilise the hydrate, the resulting crystal was quite flexible, suggesting that it would not be too difficult for it to rearrange in the bulk. On the other hand, the hard-core repulsive part of the guest-host interactions was sufficient to reproduce the host behaviour in methane hydrate almost exactly. The extent of this similarity is important, since it means that the unstable lattice modes observed in $M0$ are *completely* damped out by the presence of an excluded volume in just one of the cavities. This is consistent with the idea that any rearrangement of the bulk clathrate would involve substantial molecular overlap between guest and host molecules (*i.e.* water molecules would have to pass through a guest molecule), and as such would be very energetically unfavourable. Note that this is precisely the picture that is embodied in the "excluded volume" mechanism.

6. GUEST DYNAMICS

The third mechanism proposed in section 2 suggested that there was a mode coupling between the guest and host molecules. Strictly speaking, the lowering of the clathrate energy via this mechanism is a quantum mechanical effect, and so can't be reproduced in a classical technique like molecular dynamics; however, while classical mode coupling will not affect the system's energy, it will affect the dynamics, and should be manifest in properties such as the amplitude and lifetime of the various lattice modes. In this case, some idea of the importance of this mechanism can be obtained by varying the guest dynamics and looking for consequent changes in the motion of the host lattice.

In order to implement this procedure, one needs a means of varying the guest dynamics, and a probe of the lattice frequencies. Probably the best means of achieving the former is to vary the mass of the guest, and so we have performed three further sets of simulations that differ from the $M1$ system only in the mass of the guest; the masses used in these "heavy methane" simulations were ten times the methane mass

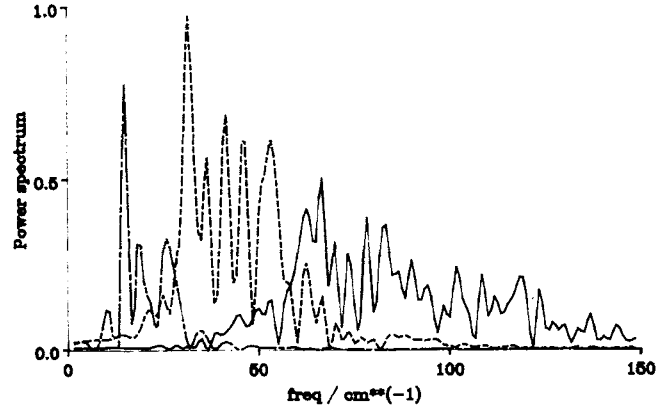

Figure 5 Power spectra calculated as the Fourier transform of the normalized velocity autocorrelation function of the guest molecules: ----, H^2; ——, $H^{1/2}$; — — —, H^{10}. The same (arbitrary) units have been used throughout (also in Figures 6 and 7) to facilitate comparison, but the guest spectra for H^{10} has been scaled down by a factor of 4.

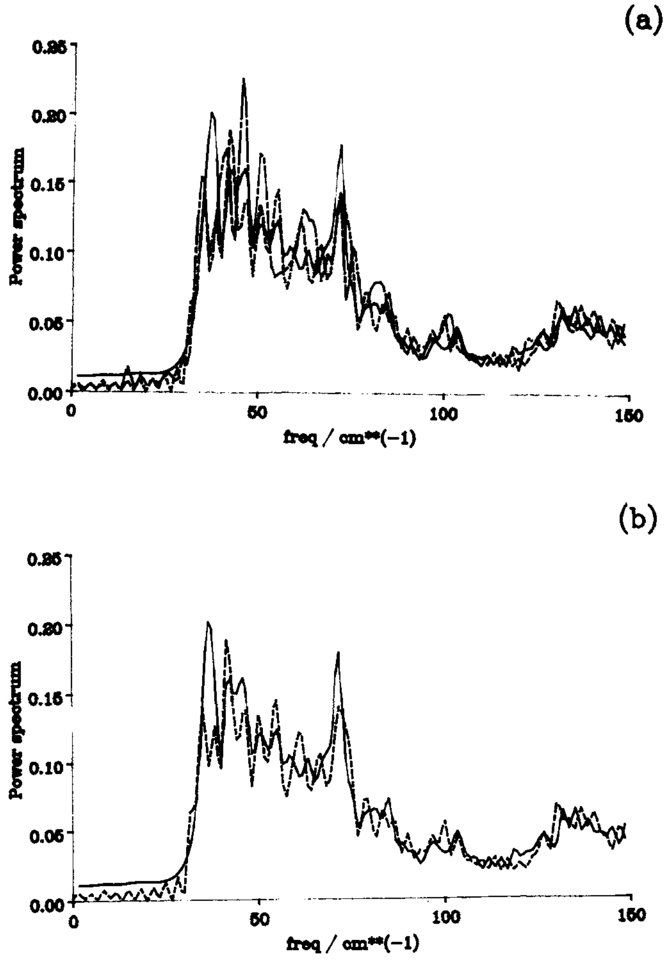

Figure 6 Power spectra (in arbitrary units) for the oxygen atoms in the host lattice: (a) ----, $H^{1/2}$; ——, H^2; ---, H^{10}, and (b) ——, H^2; ----, $M1$.

(H^{10}), twice the methane mass H^2), and half the methane mass ($H^{1/2}$). These masses should vary the characteristic guest frequencies by a factor of about 5. Note that, provided the equilibrium is properly sampled, the static equilibrium properties of a system are independent of mass, and so any energetic considerations in these systems will be the same as those in $M1$. For the probe of lattice dynamics we have adopted the vibrational spectrum arising from the motion of the oxygen atoms in the host lattice; this function is obtained from the Fourier transform of the relevant velocity autocorrelation function, and should be very similar to the density of states of the host lattice in the region of interest ($\leq 150\,\text{cm}^{-1}$).

The vibrational spectra for the guest molecules in these three systems are shown in Figure 5. It is apparent that the vibrations of the three guests occur in different parts of the spectrum, and so they should probe different regions of the host spectrum. The

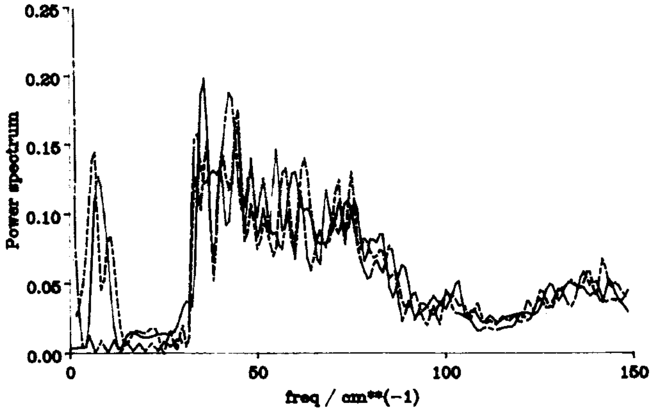

Figure 7 Power spectra (in arbitrary units) for the oxygen atoms in the host lattice: ——, *MS*; ----, *RS*; — — —, *AS*.

corresponding host spectra are shown in Figure 6 together with that for the *M*1 system, and in this case there does not appear to be much difference beyond statistical noise. In all systems the broad envelope of the spectrum is quite similar, exhibiting much the same band shape and intensity. Certainly there is no evidence of a correlation between variations in the host spectra and changes in the guest dynamics; indeed the dynamics of the host appear to be much the same whether the guest and host share common frequencies (H^2 and $H^{1/2}$) or not (H^{10}). In view of these results, we must conclude that dynamic coupling is not a significant factor in gas hydrates.

As a final test of guest dynamics, we have considered what happens when the guest is completely stationary, so that it always remains at the centre of the its cavity. Three systems were considered, involving a single stationary *M*,*R* or *A* molecule as the guest. Host vibrational spectra for these three systems (again calculated from the velocity autocorrelation function for the oxygen atoms) are depicted in Figure 7, and the m.s.d.'s of the oxygen atoms are shown in Figure 8. Once again there is a strong similarity between the *M* and *R* systems, but qualitatively different behaviour for the attractive hydrate. For the *M* and *R* systems, the behaviour of the host spectrum above about $20\,\mathrm{cm}^{-1}$ is quite similar to that of the mobile guest systems discussed above; however there is a dramatic change in their behaviour at very low frequencies, with the stationary guests inducing an intense peak at $\sim 7\,\mathrm{cm}^{-1}$. This low frequency peak is accompanied by large amplitude vibrations of the water molecules (root mean square displacements $> 1\,\text{Å}$). Thus the complete absence of the guest molecule's thermal motion causes a considerable change in the properties of the host lattice and results in a much more flexible clathrate. For a stationary attractive guest, the low frequency peak actually becomes a zero frequency peak, so that the absence of the guest's thermal motion has made the attractive hydrate completely unstable.

Clearly the dynamics of the guest do play an important role in stabilising the clathrate structure, but in view of the discussion at the beginning of this section, it is unlikely that this is through any sort of dynamic coupling. An alternative possibility is that the guest motion enters through a dynamic average. The rapidity of the guest motion with respect to the low frequency lattice modes means that these critical lattice vibrations will respond to the guest as though it were averaged over its motion within

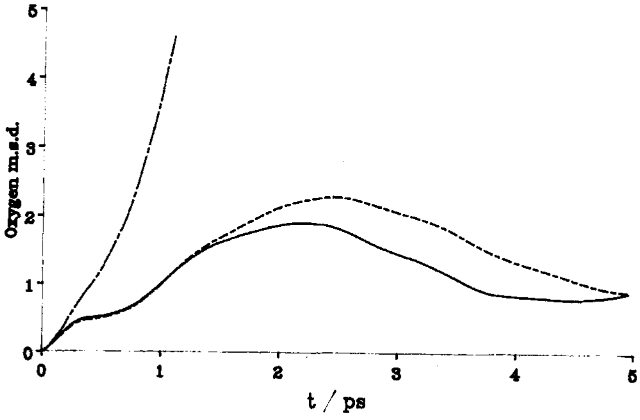

Figure 8 Mean square displacement (inÅ^2) of the oxygen atoms: ——, *MS*; ----, *RS*; – – –, *AS*.

the cavity. In other words the thermal motion of the guest molecule gives rise to an effective (or averaged) guest that is larger than the actual guest, and hence leads to a larger excluded volume. When the thermal motion of the guest is removed, the excluded volume inside the cavities is reduced, thus allowing the amplitude of the critical lattice vibrations to increase. More work is needed to confirm this interpretation, but if valid it implies that the dynamics of the guest will reinforce the excluded volume effects that underlie the second mechanism suggested in section 2.

7. CONCLUSION

In this article we have used molecular dynamics simulations to examine the source of stability in gas hydrates. Three possible mechanisms were suggested: one based primarily on the attractive guest-host interactions, one that also took account of the excluded volume provided by the guest molecules, and one based on mode coupling between the guest and host molecules. By varying the nature and number of guests in the clathrate it was shown that mode coupling is not significant, and that the attractive interactions are insufficient to describe the properties of a gas hydrate. On the other hand, the simulations were found to be quite consistent with the excluded volume mechanism.

In fact it appears that the structure and mechanical stability of gas hydrates is determined by the repulsive part of the guest-host interactions, and hence any theory must take account of the excluded volume provided by an encaged guest molecule. While these excluded volume effects will not determine the thermodynamic stability, they will make it impractical for certain reactions to take place (notably, the degredation of bulk hydrate directly to bulk water and bulk guest phases) and so will change the thermodynamic conditions required for hydrate stability. Ultimately, this mechanism suggests that the conditions for gas hydrate formation are not determined by the bulk properties of a gas hydrate, but rather by the properties of a thin hydrate film at a water/guest interface.

References

[1] Current estimates suggest that the amount of methane in naturally occurring methane hydrates may exceed that in other natural sources of methane by as much as a factor of ten-G. Gibson, British Gas plc, private communication.

[2] J.H. van der Waals and J.C. Platteeuw, "Clathrate solutions," *Adv. Phys. Chem.*, **2**,1 (1959).

[3] F.E. Anderson and J.M. Prausnitz, "Inhibition of gas hydrates by methanol," *AIChE J.*, **32**,1321 (1986).

[4] G.D. Holder, G. Corbin and K. Papadopoulos, "Thermodynamic and molecular properties of gas hydrates from mixtures containing methane argon and krypton," *Ind. Eng. Chem. Fund.*,**19**,282 (1980).

[5] G.H. Cady, "Composition of clathrate gas hydrates of chlorodifluoromethane, trichlorofluoromethane, chlorine, perchloryl fluoride, hydrogen sulfide, and sulfur hexafluoride," *J. Phys. Chem.*,**85**, 3225 (1981).

[6] H.J. Ng and D.B. Robinson, "The measurement and prediction of hydrate formation in liquid hydrocarbon-water systems," *Ind. Eng. Chem. Fund.*,**15**, 293 (1976).

[7] P.M. Rodger, "The stability of gas hydrates," *J. Chem. Phys.*, in press.

[8] P.K. Basu and R.D. Mountain, "Molecular dynamics evaluation of cell models for type I gas hydrate crystal dynamics," *J. Chem. Phys. Solids*,**49**, 587 (1988).

[9] P.M. Rodger, "The cavity potential in type I gas hydrates," *J. Phys. Chem.*,**93**, 6850 (1989).

[10] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, and J. Hermens, "Interaction models for water in relation to protein hydration," in *Intermolecular Forces;*Ed. Pullman, B., [Reidal] Dordrecht, Holland, (1981).

[11] J.D. Weekes, D. Chandler and H.C. Andersen, "The role of repulsive forces in determining the equilibrium structure of simple liquids," *J. Chem. Phys.*,**54**,5237 (1971).

[12] W.C. Swope, H.C. Andersen, P.H. Berens, and K.R. Wilson, "A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: application to small water clusters," *J. Chem. Phys.*, **76** ,637 (1982).

[13] H.C. Andersen, "Rattle: a 'velocity' version of the shake algorithm for molecular dynamics," *J. Comput. Phys.*,**52**,24 (1983).

[14] F. Hollander, and G.A. Jeffrey, "Neutron diffraction study of the crystal structure of ethylene oxide deuterohydrate at 80 K," *J. Chem. Phys.*,**66**,4699 (1977).

[15] D.W. Davidson, Y.P. Handa, and J.A. Ripmeester, "Xenon-129 NMR and the thermodynamic parameters of xenon hydrate," *J. Phys. Chem.*,**90**,6549 (1986).