Localized Oscillators and Heat Conduction in Clathrate Hydrates *

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Abstract. The glassy behaviour of the thermal conductivities of structure I xenon and structure II hydrate at high temperature are found to be described surprisingly well by a localized oscillator model. This observation leads to the suggestion of strong coupling between the localized vibrations of the guest with the lattice acoustic phonons. This conjecture is confirmed by a phenomenological calculation using the Anderson–Fano resonant scattering model.

Key words: Clathrate, hydrate, thermal, conductivity, theoretical, model.

Introduction

Clathrate hydrates are nonstoichiometric crystalline inclusion compounds composed of a water lattice with cavities in which guest atoms or molecules can be encaged [1]. Since water is the dominant component of the structure, it is not too surprising that many of the properties are similar to that in ice. There are two noticeable exceptions. The thermal expansitivity of hydrates [2–4] is often larger than ice but their thermal conductivities are smaller [5–11]. More importantly, the temperature profile of the thermal conductivity is anomalous as it closely resembles a glassy (amorphous) material in spite of its well defined crystalline structures [12]. Another remarkable feature of the hydrate thermal conductivities is the weak dependence on the nature of the guests and details of the crystal structures. Obviously, the lower thermal conductivities in the hydrates are the consequence of larger anharmonicities in the intermolecular interactions as compared to ice [13]. Molecular dynamics calculations have shed some light on the understanding of some of these unusual properties [3, 14–17]. It was shown that the guest vibrations are localized and their presence responsible for the large thermal expansion in the hydrates. Recently the temperature dependence of the thermal conductivity of a clathrate hydrate of tetrahydrofuran (THF) has been analysed using a resonant scattering model [12]. The major conclusion derived from the analysis is that the coupling between the low frequency localized vibrations of the guest with the lattice phonons is the major dominant phonon-scattering process although details of the mechanism are still unknown. A similar anomaly in the thermal conductivity

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has been observed in other crystalline systems such as doped alkali halides [18–20] and crystalline polymers with bulky side groups [21]. Apparently, low energy localized vibrations are good scatterers of heat-carrying phonons [24].

It has been recognized that the behaviour of the thermal conductivity of glassy materials at high temperature can be described very well by a localized oscillator model first proposed by Einstein [22] and extended by Slack [23] and Pohl [24, 25]. This model has been used to calculate the high temperature thermal conductivity of a variety of amorphous solids and the results are generally in semiquantitative agreement with experiments. In this investigation, the localized oscillator model is also found to reproduce the thermal conductivity in clathrate hydrates at high temperature. The success of this model indicates that the lattice vibrations in clathrate hydrates are heavily damped as in the case for amorphous materials. A phenomenological model based on resonant scattering of lattice phonons *via* the interactions with the localized guest vibrations is proposed to explain this observation.

Localized Oscillator Model for Thermal Conduction

In this model, the localized vibrations are assumed to be heavily damped with lifetimes of half a period of the oscillation and that the distribution of the localized modes in a solid can be approximated by the Debye model. Using the equivalent of the gas kinetic equation an expression for the *minimum* thermal conductivity, Λ_{min}, can be derived [23, 24]

$$\frac{\Lambda_{min}}{\Lambda_\infty} = 2 \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} \, dx \, . \tag{1}$$

At high temperature when $T \gg \Theta_D$, the transport integral in Equation (1) approaches unity. The limiting thermal conductivity, Λ_∞, is given by

$$\Lambda_\infty = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} k_B n^{2/3} (2v_t + v_l) \, . \tag{2}$$

In Equation (2), k_B is the Boltzman constant, n is the atomic number density and v_t and v_l are the transverse and longitudinal sound velocities, respectively. The limiting thermal conductivity, Λ_∞ may be determined from experimental density and acoustic velocities. Then the thermal conductivity at any temperature can be computed from Equation (1).

Equation (1) has been demonstrated to give a semiquantitative prediction of the thermal conductivity for most glassy materials [23]. More significantly, it is relevant to the present study that the glassy behaviour of cyanide-doped crystalline potassium bromide is correctly predicted. The thermal conductivity was shown to fall within the range of the minimum thermal conductivity of the crystalline solid, indicating the existence of localized excitations, presumably due to the librational

modes of the cyanide ions. Encouraged by these results, the modified Einstein oscillator model is applied in this article to the study of the thermal conductivity of clathrate hydrates.

Results and Discussion

The thermal conductivity of THF hydrate has been determined independently by several groups [5, 9, 10] over a wide temperature range. The experimental values obtained are fairly scattered, reflecting the inherent technical difficulties involved in the determination of the absolute thermal conductivity of poorly conducting materials. Nevertheless, the qualitative features of the thermal conductivity profile are similar. At high temperature, the thermal conductivity decreases slowly until 80 K, where it starts to drop more rapidly [9, 10]. The thermal conductivity of clathrate hydrates is known to be largely independent of the crystal structure and the nature of the guests. For xenon hydrate, the thermal conductivity has been measured at 235, 245 and 255 K. There is no noticeable temperature dependence within this range and the average thermal conductivity is 0.36 $Wm^{-1} K^{-1}$.

The localized oscillator model has been used to calculate the thermal conductivity of structure I xenon hydrate and structure II THF hydrate. The experimental densities and sound velocities [22, 23] were used in the calculations. In view of the high frequency intramolecular O–H vibrations, the water molecule was treated as a rigid atomic group [20]. The minimum thermal conductivities from 30 to 260 K calculated from the model are compared with the experimental results in Figure 1. The calculated temperature profiles as well as the absolute magnitude of the thermal conductivities are in substantial agreement with experiments. The predicted thermal conductivity for type II THF hydrate falls within the range of the experimental measurements. There is also good agreement between the calculated and measured thermal conductivity of type I xenon hydrate [11]. It is a pleasant surprise that the small difference in the minimum thermal conductivity between type I and II hydrate is reproduced by this simple model. This difference is due to a slightly smaller atomic number density for xenon hydrates. There is limited experimental evidence suggesting that the thermal conductivity of hydrates is slightly dependent on the size of the guest [8]. The thermal conductivity of hydrates was found to decrease as the size of the guest molecule increases. This observation has led to a conjecture that the (hindered) librational modes of the guest are the most efficient phonon scatterers. The modified Einstein localized harmonic oscillator model offers an alternative rationalization of the experimental observations. Equation (2) shows that the limiting thermal conductivity is proportional to both the number density and the sound velocities [32]. The number density is expected to increase with the size of the guest. The increase in number density, however, is weighed down by a concomitant decrease in the sound velocities for hydrates with large guests [32]. Consequently, the thermal conductivity of the hydrates remains fairly constant and exhibits only a weak dependence on the size of the guest molecule [8].
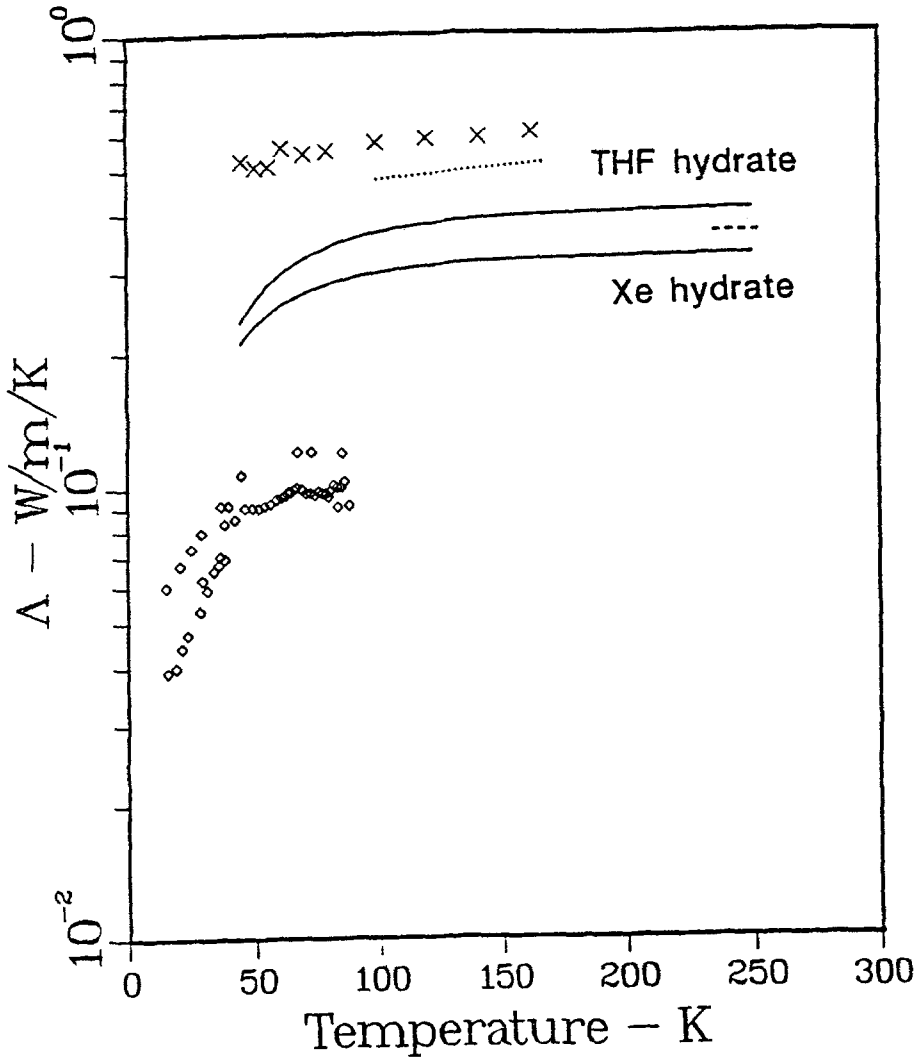
Fig. 1.   Experimental thermal conductivity for THF hydrate $-\cdots$ [5]; X [9] and $\Diamond$ [10]. Experimental thermal conductivity for Xe hydrate $---$ [11]. Theoretical minimum thermal conductivity Λ_{min} (solid) for structure I xenon hydrate (6 Xe·46 H_2O, $n = 0.030 \times 10^{30}$ m^{-3}, $v_t = 1535$ m sec^{-1} and $v_l = 2910$ m sec^{-1} [32, 33]); structure II THF hydrate (8 THF·136 H_2O and treating CH_2 as an atomic group, $n = 0.0358 \times 10^{30}$ m^{-3}, $v_t = 1663$ m sec^{-1} and $v_l = 3515$ m sec^{-1} [33]).

The observation made here raises a very important question. *Why do the vibrations in crystalline clathrate hydrates behave as amorphous materials?* Rephrasing the question: how do the lattice modes become localized oscillators when interacting with the guest vibrations.

A conceptual model for the phonon interactions in the clathrate hydrate can be thought of as the localized guest vibrations become embedded in a continuum of elastic lattice (acoustic) waves which are responsible for the transportation of the thermal energy. This description shares some similarity to problems associated with impurity states in the conduction band of solids or discrete electronic states embedded in the ionization continuum [26]. The interactions between a localized state with continuum can be described by the perturbation theory of Fano [27], or in an equivalent way, with the second quantization field theoretical method of Anderson [28]. The Anderson-Fano Hamiltonian appropriate for the present situation is given by [26],

$$H = \omega_g(a_g^+ a_g + \frac{1}{2}) + \sum_{\mathbf{k}} (\omega_l b_{l,\mathbf{k}}^+ b_{l,\mathbf{k}} + \frac{1}{2}) + \sum_{\mathbf{k}} M_{\mathbf{k},g}(b_{l,\mathbf{k}}^+ a_g + a_g^+ b_{l,\mathbf{k}}) \quad (3)$$

where a_g^+, $b_{l,\mathbf{k}}^+$ are the creation and a_g, $b_{l,\mathbf{k}}$ are the annihilation operators for the guest (g) and the lattice (l) phonons. The first two terms are just the Hamiltonians for the zeroth order (isolated) state of the localized oscillator and lattice vibrations. The last term in Equation (3) allows the mixing of the lattice modes with the guest vibrations. The strength of the interaction is governed by the matrix element $M_{\mathbf{k},g}$. If $M_{\mathbf{k},g}$ is nonzero, there will be exchange of energy between the lattice and the guest vibrational modes. In the following, the coupling term will be solved for a one-dimensional model system for the interaction of a localized state of energy ω_g with a single elastic (acoustic) lattice wave of energy ω_l.

Representing the localized state by a harmonic Einstein oscillator $u_n(x)$ and the lattice wave as a plane wave with wave vector $\mathbf{k}$, the matrix element according to first-order perturbation theory [27] is simply,

$$M_{\mathbf{k},g} \approx \langle u_n(x) | V(x) | e^{ikx} \rangle \quad (4)$$

Considering only the lowest quadratic term [29] in the polynomial expansion of the interaction potential $V(x)$ between the guest and the water lattice in the hydrate and that the harmonic oscillator is in the ground state $(n = 0)$, Equation (4) reduces to the following integral,

$$|M_{\mathbf{k},a}| \approx \left| \frac{\sqrt{\pi}}{2} \int_{-\infty}^{\infty} e^{ikx} x^2 e^{-\alpha^2 x^2} \, dx \right|$$
$$= \left| \frac{\sqrt{\pi}}{2} \frac{e^{-k^2/4\alpha^2}}{\alpha^3} \left(\frac{1}{2} - \frac{k^2}{4\alpha^2} \right) \right| \quad (5)$$

with α defined as,

$$\alpha = \sqrt{\frac{m_g \omega_g}{2\hbar}} \quad (6)$$

and the energy of the plane wave,

$$\hbar\omega_l = \frac{\hbar^2 k^2}{2m_l} \tag{7}$$

where m_g is the mass of the guest and m_l is the mass of the lattice wave, which can be approximated as the mass of a water molecule.

Equation (5) has several interesting analytical properties. When $k^2 = 2\alpha^2$ the coupling matrix element vanishes. That is, the lattice plane wave and the harmonic oscillator are out-of-phase. Equating the first derivative of Equation (5) with respect to the lattice wave vector k to zero, a maximum value of matrix element $|M_{\mathbf{k},\alpha}|$ can be found when,

$$k^2 = 6\alpha^2 . \tag{8}$$

An expression relating the lattice and guest vibrational frequencies at maximum $|M_{\mathbf{k},\alpha}|$ can be derived by combining Equations (6), (7) and (8),

$$\left(\frac{m_l \omega_l}{m_g \omega_g}\right) = \frac{3}{2} . \tag{9}$$

This relationship can be used to estimate the optimal lattice frequency which couples with a given guest vibration. For instance, the rattling motions of methane in the small and the large cages [14, 16, 30] have frequencies of 75 cm^{-1} and 42 cm^{-1}, respectively. Equation (9) predicts that the coupling matrix element will maximize at lattice modes of 100 cm^{-1} and 63 cm^{-1}. These predicted vibrational frequencies are remarkably close to the maxima of the transverse acoustic and transverse optic phonon branches of ice which are about 70 and 110 cm^{-1}, respectively [31]. The magnitude of the coupling matrix element $|M_{\mathbf{k},\alpha}|$ at the resonant frequency is about four times higher than at $k = 0$. For heavier guests where the translational vibrations are at lower frequencies, the coupling becomes more efficient with the lower energy translation and librational modes of the lattice. Molecular dynamics calculations have already shown that the energies of translational vibrations often decrease with increasing mass of the guest [16, 17]. It should be cautioned that Equation (9) is an oversimplified solution to a very complicated process. In actual calculation, the interaction term must be summed over all the vibrational states of the localized and lattice vibrations [26] and the higher terms in the potential expansion have to be included.

The physical picture emerging from the study of the Anderson-Fano model of interactions can be summarized as follows. Mediated by the interaction potential, phonons may hop back and forth between the lattice and the localized guest sites and exchange energies. The localized state has became a resonance scatterer. The mixing of the guest and lattice vibrational eigenfunctions may be important in reducing the conductivity of the heat carrying lattice phonons. This simple model is also intuitively appealing. The most efficient exchange of energy between the lattice and the guest is expected to occur when the localized vibrations of the guest matches that of the acoustic phonons near the zone boundary when the density

of states is the highest. Furthermore, scattering of longitudinal zone boundary phonons is the dominant contribution to the Umklapp processes which lowers the thermal conductivity of a solid [13, 24]. However, it should be noted that even though the present phenomenological calculation has demonstrated the existence of 'resonance' modes, further work is required to show that this kind of coupling is strong enough in substantially reducing the thermal conductivity. At present, first principles calculation of thermal conductivity of molecular solids remains a formidable problem [13].

An alternative theory for heat conduction in clathrate hydrates has been proposed earlier [34]. The essential feature of the earlier model [34] shares the similar spirit as the localized model discussed here although the details are quite different. It was argued that due to the large number densities of the hydrates, the phonon mean free path is quenched to a characteristic limiting value which is about the unit cell size of the type II structure (17 Å [36]). Implicit in this theory is that the guest molecule has no decisive effect on the thermal conductivity. The mechanism of thermal conduction in clathrates is basically the same as in crystalline solids and the role of glass-like localized excitations was not discussed. In contrast, according to the model described above, the small thermal conductivity of the hydrates is attributed to resonant scattering of the lattice modes by the localized guest vibrations thus quenching the normal modes of the host lattice. The minimum mean free path for the hydrate can be estimated from the atomic number density [24], $l = n^{-1/3}$, which is 3.2 Å for type I Xe hydrate and 3.0 Å for type II THF hydrate. The calculated lengths of the mean free path are consistent with the interatomic O–O distances in the hydrates (2.6–2.8 Å) and substantially smaller than that of the size of the unit cell [35, 36].

The most important assumption made in the present thermal conductivity model is the proposal of a strong coupling between the localized guest modes with that of the lattice phonons of similar energies. This conjecture may be examined experimentally if model clathrate compounds can be synthesized such that the energy of the zone boundary phonon branches of the host lattice differs significantly from that of the vibrational energies of the guest or, alternatively, from a comparison of the thermal conductivity of a clathrate compound in the presence and in the absence of the guest. The clathrasils, which are analogues of clathrate hydrates with lattice frameworks formed by SiO_2 units [37] may be the most promising candidates for the latter purpose. Clathrasil compounds of the same structure can be prepared with and without the presence of the guest [38, 39]. Work in this area is in progress. In passing, it is noteworthy that the coupling of an harmonic oscillator with a phonon bath had been studied using statistical mechanical methods [40]. Since only harmonic interactions were assumed in the previous investigations, no information on thermal resistivity was obtained [41].

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