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IN - 1141
May 1968

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SLOW NEUTRON SCATTERING FROM WATER

R. M. Brugger and J. P. Plummer

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IN-1141
Issued: May 1968
Physics
TID 4500

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by

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Issued Under Contract AT(10-1)-1230
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ACKNOWLEDGEMENTS

The authors wish to thank Drs. Randolph, McMurtry, Myers and Strong for many suggestions, encouragements, and help in this experiment. The contributions of Messrs. Beck, Miller and Jackson with the sample and electronics were of great help. The encouragement and supervision of Dr. Fluharty is gratefully acknowledged.

ABSTRACT

Neutrons of 0.05 eV energy were inelastically scattered from samples of water. The experiment was arranged so that a correction could be made for multiple scattering and so that the observed scattering law would be measured at momentum change $\hbar\kappa$ smaller than obtained in previous experiments. From the data it is concluded that

- a) at these low κ values the scattering law at fixed β is proportional to κ as predicted by the McMurry-Russell model but by no other models,
- b) that discrete transitions are no more distinct at these smaller κ 's than at larger κ 's contrary to the predictions of the McMurry-Russell model, and
- c) that multiple scattering is important but not as large as predicted and that accurate experimental corrections for it can be made.

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SLOW NEUTRON SCATTERING FROM WATER

I. INTRODUCTION

Parts of the scattering law for water have been measured^{1,2,3,4}, and McMurry and Russell² have developed a model to fit this scattering law. The model includes groups of water molecules of three sizes; the molecules in each group have a set of discrete vibrational states. The model does not specifically include diffusive motion in the liquid state. The model shows that at higher momentum change $\hbar\kappa$ the discrete vibrations are not observed as separated energy changes but are smeared beyond recognition by the recoil motion of the molecules. Here $\hbar$ is $1/2\pi$ times Planck's constant and κ is the magnitude of the change in wave vector. At lower κ , lower than has been measured in previous experiments, the model indicates that the recoil motion has less effect and the discrete transitions will be observed as separated peaks in the neutron scattering cross section. This effect has been demonstrated for scattering from ethane gas⁵. If the model is a good representation of H_2O , similar peaks will be more pronounced in the experimental neutron scattering as one measures at smaller and smaller κ . One purpose of the experiment reported here was to extend the measurements to lower values to see if a low enough range of κ could be reached where the peaks could be easily distinguished and their energies and intensities could be measured. Then having measured the energies of the vibrational states of the molecules, these could be inserted into the model to give a better kernel for water.

Experimentally, to get to regions of smaller κ at a particular energy change β , it is necessary to go to smaller scattering angles and

larger incident neutron energies. The region of β of interest in this particular experiment is from about 10 meV to 70 meV. Using the evacuated flight path⁵ with the MTR velocity selector⁶, the minimum scattering angle that can be reached at the present time is about 3° . To reach the minimum κ values with this scattering angle, incident energies of about 400 meV would be ideal. However, the intensities and resolution of the velocity selector at 400 meV are poor. As a compromise the velocity selector was set to deliver neutrons of incident energy of 50 meV which allowed measurements at κ values smaller than had been obtained previously.

Besides the limited κ range, another shortcoming of previous measurements is their lack of correction for multiple scattering which is relatively more important at smaller κ values. There is disagreement^{3,4} in the fitting of most models^{7,8,9} to the scattering data at small κ 's when $\beta \neq 0$. Usually this has been observed in data which are on the edge of the κ - β range covered by the experiment and where statistical accuracy is poorest. Because of the possible experimental causes for disagreement and the desire to accept the theory, the disagreement has been assumed to be experimental and multiple scattering has become the chief culprit. Slaggie¹⁰ has made calculations which show that multiple scattering can be quite important, but these calculations are very sensitive to the kernel used. A second purpose of this experiment was to correct the data for multiple scattering and see if the disagreement still exists. The correction was made experimentally⁵ because of the kernel sensitivity of Slaggie's correction calculation.

Data were obtained at scattering angles between 3° and 18° for incident energies of 50 meV. These data extend to smaller κ values

than previous data obtained for water. The data at fixed β as a function of κ^2 show that the scattering law is κ dependent and not κ^2 dependent as required by most models. The κ dependence is in agreement with the McMurry-Russell theory when the β is on resonance with a particular transition from a molecular vibration. Except for the 60 meV hindered rotational band which has been observed previously¹, and humps in the cross section at energy gains and losses of 6.9 meV¹, the data even at the lowest κ value obtained in this experiment did not show other discrete peaks corresponding to the discrete vibrational transitions. One thus concludes that either the McMurry-Russell theory which predicts discrete states is not a complete description for water or the states are spaced closely enough that even at the small κ values reached in this experiment the recoil effect was not sufficiently small to allow the discrete peaks to be seen.

II. THEORY

The McMurry-Russell scattering law² (hereafter called MR) can be represented approximately at small κ in the following way:

$$\frac{S_v}{\sigma_{bv} \frac{1}{4\pi} \frac{1}{K_B T}} = e^{-w} e^{-\frac{\alpha}{4}} \left\{ \frac{e^{-\frac{\beta^2}{4\alpha}}}{\sqrt{4\pi\alpha}} + I_1(g_{v\tau}) \frac{e^{-\frac{(\beta+\beta_\tau)^2}{4\alpha}} + e^{-\frac{(\beta-\beta_\tau)^2}{4\alpha}}}{\sqrt{4\pi\alpha}} + \sum_{\tau\tau'} \dots \right\} \quad (1)$$

where

$$\alpha = \frac{\hbar^2 \kappa^2}{2MK_B T}$$

and

$$g_{v\tau} = \frac{\hbar^2 \kappa^2}{2MK_B T} \frac{\bar{\delta}_{v\tau}(E_\tau)}{\beta_\tau \sinh(\frac{\beta_\tau}{2})} = \alpha M \frac{\bar{\delta}_{v\tau}(E_\tau)}{\beta_\tau \sinh(\frac{\beta_\tau}{2})}.$$

In these equations S_v is the scattering law for the v atom, σ_v is the total bound atom cross section for the v atom, K_B is Boltzmann's constant, T is the absolute temperature, e^{-W} is the Debye-Waller factor, τ represents a particular vibrational states, I_1 is a Bessel function of the second kind, M is the globule mass and m is the mass of the neutron and $\delta_{v\tau}$ is the amplitude factor for the v th vibration which has been orientation averaged.

From these equations one sees that when $\beta = \beta_\tau$, i.e. the energy change observed by the neutron is the same as the energy of excitation of a particular molecular state, the scattering law S_v is proportional to κ . One can also demonstrate that the energy width $\epsilon_{1/2}$ of the peaks in the scattering law is proportional to $\sqrt{\frac{\kappa^2 T}{M}}$. From this relation one realizes that to see the molecular vibrations as discrete energy changes in the scattering law with no overlap of peaks one must go to very small κ values.

In the MR model for water three different size groups of molecules are used to represent the globules that are expected to form in water. The molecules in each group or globule are assigned a different set of vibrational states. Because of the limited capacity of the computer, only six vibrational states plus the two well known intramolecular states at $\beta = 8$ and 17 can be inserted into each globule. While this limited number of states may be an oversimplification of the true nature of the globule it does allow computation to be made. Table I shows² the fraction of molecules in each of the three globules, the mass assigned to each globule and the vibrational states for the molecules in each globule. With these parameters and a temperature of 16°C, cross section curves were calculated for several conditions corresponding

Table I
McMurry-Russell Model Parameters*

A. Molecule 1; $f_1 = 0.1$; $M_{H1} = 1.89$; $M_{O1} = 17.0$

$E_{\tau 1}(\text{eV})$	0	0.2	0.46
$\delta_{H\tau 1}$	1.590	0.5	0.91
$\delta_{O\tau 1}$	0.1760	0.0045	0.0070

B. Molecule 2; $f_2 = 0.45$; $M_{H2} = 150$; $M_{O2} = 150$

$E_{\tau 2}(\text{eV})$	0	0.005	0.01	0.15	0.02	0.025	0.05	0.075	0.1	0.125	0.2	0.46
$\delta_{H\tau 2}$	0.02	0.013	0.018	0.020	0.018	0.047	0.35	0.45	0.3	0.354	0.5	0.91
$\delta_{O\tau 2}$	0.02	0.0005	0.005	0.01	0.01	0.015	0.02	0.025	0.03	0.0405	0.0045	0.007

C. Molecule 3; $f_3 = 0.45$; $M_{H3} = 75$; $M_{O3} = 75$

$E_{\tau 3}(\text{eV})$	0	0.0075	0.0125	0.0175	0.0225	0.0375	0.0625	0.0875	0.1125	0.2	0.46
$\delta_{H\tau 3}$	0.04	0.027	0.019	0.022	0.024	0.19	0.69	0.54	0.038	0.5	0.91
$\delta_{O\tau 3}$	0.04	0.0005	0.005	0.01	0.015	0.02	0.025	0.030	0.0305	0.0045	0.007

*All aggregates contain a vibrational mode of zero energy. The δ_{v0l} for this mode determines M_{vl} through the relation $M_{vl} = 3/\delta_{v0l}$.

to the experimental conditions, i.e. $E_0 = 50$ meV, $\theta = 3^\circ$ and 10° . These cross section curves are shown in Figures 1 and 2. The triangles on the baseline indicate the energy resolution of the velocity selector. Each curve shows that the inelastic scattering is small compared to the elastic peak, but that inelastic peaks are evident even at the 10° scattering angle. The small globule with no low lying vibrational states contributes most to the scattering at the lower κ 's and tends to hide the peaks produced by the two heavier globules. If the MR model is an accurate description, Figures 1 and 2 indicate that peaks should be observed in the scattering in spite of the limited resolution. However, it is possible that the MR model is not a perfect description; many more discrete transitions could be present and so close together that κ is not yet small enough for the peaks to be separated in the data. Another possibility is that intermolecular forces in the liquid perturb the discrete vibrational transitions into overlapping bands.

III. EXPERIMENT

The velocity selector was arranged to deliver bursts of mononenergetic neutrons of 50 meV energy with the choppers of the velocity selector rotating at 12,000 rpm. The counters were in the evacuated small angle flight path about 2.25 meters from the target. The smaller angles were each defined by two 6" long He^3 counters while the 11th and 12th angles each had two 4" long BF^3 counters. The counter angles were 3.078° , 4.446° , 5.814° , 7.182° , 8.550° , 9.918° , 11.286° , 12.654° , 14.022° , 15.390° , 16.758° , and 18.126° .

The sample was made of aluminum tube with 0.028° bore and 0.004° wall. The tubes were held horizontally in a frame which provided a sample area greater than $2\text{-}1/2''$ wide by $4\text{-}1/2''$ high. About $0.003''$ was

Figure 1 - MR calculation of the cross section for inelastic scattering of neutrons from water. The incident energy is 0.05 eV and the scattering angle is 3.087° . The triangles on the baseline indicate the energy resolution.

Figure 2 - MR calculation of the cross section for inelastic scattering of neutrons from water. The incident energy is 0.05 eV and the scattering angle is 10.0° . The triangles on the baseline indicate the energy resolution.

left between each tube so that 0.002" thick pieces of gadolinium foil could be inserted to suppress multiple scattering. The frame was cadmium covered. The sample was mounted at an angle of about 10° perpendicular to the beam facing the 10° detector. The sample temperature was 16°C . The measured transmission of this sample was about 0.87.

In this sample water flowed continuously during the sample part of each cycle, while air was forced through the tubes during the open part of each cycle. This arrangement prevented bubble formation in the water which was a problem with previous water samples². It also guaranteed that the sample and open data observed the same sample holder components.

The gadolinium foil prevented neutrons which were scattered up or down in the water of one tube from reaching another tube and being scattered out toward the counters. Data were obtained with the sample with gadolinium foil in every space between tubes and then with gadolinium in every third space. The every-third space arrangements allowed more multiple scattering.

Each set of data was processed by the standard velocity selector data processing programs. Then a linear extrapolation of each channel of data was made from the data for gadolinium every third space, to the data for gadolinium every space to a "zero" space cross section. From these extrapolations factors were obtained which, when the data for gadolinium in every space is multiplied by these factors, the data is corrected for multiple scattering. This type of multiple scattering correction has been demonstrated in neutron diffraction experiments¹¹ and has proven very successful for gas samples⁵. It

is felt that it is a more reliable correction than a calculation based on an uncertain kernel.

Figure 3 shows the multiple scattering correction factors obtained for the data. One notes that they have the same general shape as predicted by Slaggie's calculations but that the maximum correction is less than 15% which is less than his calculations predict.

IV. DATA

With the gadolinium between every tube, a total of 126 hours of sample data was obtained. Even with this long running time the statistical accuracy was not good. A set of partial differential cross section data $d^2\sigma/d\lambda d\Omega$ for the 3° angle is shown in Figure 4. The large quasi elastic peak is evident at channel 95 and the 60 meV hindered rotational band is seen as a peak centered at channel 47.

To gain statistical accuracy at the expense of low κ values, data from all the angles were summed. The resulting cross section curve is shown in Figure 5. The improved statistics still do not reveal any peaks other than that corresponding to the hindered rotations. The data were also averaged over 0.5 meV intervals to improve the statistical accuracy of the energy loss data. Figure 6 is an example of this presentation. In this presentation, humps at an average energy change of 6.9 meV in gain and loss were detected in almost all the cross sections. This energy ΔE was independent of κ as shown in Figure 7. No additional humps other than the 60 meV peak were observed.

Presenting the data as in Figures 4, 5, and 6 emphasizes the energy dependence of the data. The data were also converted to the scattering law $S(\kappa^2, \beta)$ presentation in which the κ dependence is emphasized; these are shown in Figure 8. The new points to the left

Figure 3 - The experimentally determined correction factor by which the data with gadolinium between every tube should be multiplied to correct it for multiple scattering.

Figure 4 - The measured cross section for scattering neutrons from water. The incident energy was 0.05 meV and the scattering angle was 3.078° . The triangles along the baseline represent the energy resolution. These data have not been corrected for multiple scattering.

Figure 5 - The measured cross section for scattering neutrons from water. The incident energy was 0.05 eV and the scattering angle was from 3 to 18° centered at 10°. The triangles along the baseline represent the energy resolution. These data have not been corrected for multiple scattering.

Figure 6 - An example of the cross section data when averaged over energy intervals of 0.5 meV. These data have not been corrected for multiple scattering.

Figure 7 - The energy of the hump as a function of momentum change. Closed points represent neutron energy gain and open points represent neutron energy loss. The average change is $\Delta E = 6.9$ meV or $\beta = 0.27$.

Figure 8 - The scattering law for neutrons scattered from water. These data have been corrected for multiple scattering.

are from the 3° detector while the new data on the right are from the 18° detector. In Figure 8 one notes that the new data agree with older data² and these data agree with data from other labs^{1,2,4} where they overlap. For $0.3 < \beta < 3.0$, S is seen to be proportional to κ as predicted by the MR model when $\beta = \beta_T$; S is not proportional to κ^2 or $\frac{1}{\kappa} e^{-\frac{\beta^2}{4\alpha}}$ as is predicted by the solid model¹² or the ideal gas model¹³. One also notes that as κ increases there is a slight increase of S over the κ dependence near the maximum of each S curve. This gives each curve a slight hump; the reason for this hump is not known at present.

V. DISCUSSION OF DATA

Peaks in the cross section data, other than the 60 meV hindered rotational band, were not observed in this experiment. Small humps were observed at $\Delta E = \pm 6.9$ meV. This lack of peaks could be attributed to inadequacies of the experiment which will be considered first. A compromise had to be struck between obtaining low κ , obtaining acceptable resolution and obtaining acceptable counting rates. The compromise was the experimental arrangement of $\theta > 3^\circ$ with $E_0 = 50$ meV. The energy resolution was not perfect and in Figures 1, 2, 4 and 5 the triangles on the baseline indicate the resolution. But if the peaks are as widely spaced as in the MR model this finite resolution should not completely mask them. The counting statistics for the $\theta = 3^\circ$ is not good as seen in Figure 4. If the peaks are present but as weak as in the cold neutron experiments, they would not be observed in the 3° data. The counting statistics are much improved in the summed data of Figure 5, and here even though the κ range is not as small as in the $\theta = 3^\circ$ data, the

peaks should be observed as they are observed with cold neutrons. The κ^2 values at which the $\theta = 90^\circ$ cold neutron data are obtained are shown in Figure 6 for comparison. The hump at about 6.9 meV has been observed previously^{1,3}. Rahman⁸ suggests that this hump might be due to a state of vibration of the entire molecule around its center of gravity. This hump does not become more pronounced at smaller κ values indicating that it is not an intramolecular vibration of a free molecule. The energy of this hump is constant independent of κ indicating that it is not a coherent effect as observed in liquid lead, but its constant energy indicates that it is an incoherent effect which might be interpreted as a discontinuity in the "frequency spectrum" for a liquid. Its behavior indicates that this hump will be no better defined at lower κ values.

Turn now to the κ dependence of the data. Other models do not predict this dependence; diffusion theories¹³ and theories of solids¹² predict a κ^2 dependence of S at small κ . The data definitely show the κ dependence over a large range of κ . Since the data is experimentally corrected for multiple scattering it is difficult to attribute the dependence to this experimental error. Theories that will adequately explain water must fit this κ dependence.

The MR model does predict a κ dependence when $\beta = \beta_T$ at small κ and this has been experimentally demonstrated for isolated molecules such as ethane⁵. If the MR model is modified to allow for a continuum of states instead of a discrete set, this κ dependence is lost, the κ dependence is a result of the discreteness of the vibration and only exactly holds when $\beta = \beta_T$ (see Appendix A).

The MR model does have several shortcomings. It does treat all vibrations as being discrete which is satisfactory for isolated molecules as in a gas. But in a liquid the translational motion must hinder the vibrations and rotations to some extent, and a model with a continuous frequency distribution, at least at small κ , seems to be desirable. The attempt presented in the Appendix to put a continuous frequency distribution into the MR model was made because a frequency spectrum is indicated by the data. The κ dependence of the 6.9 meV humps indicates that the "frequency spectrum" must extend from 0 to at least an energy of 6.9 meV. The range of κ covered at the 60 meV peak $\beta = 2.4$ is too narrow to show whether this peak has a width that is dependent on κ .

Even though an exact model is not available, a model that gives the best fit to water is important for use in kernel calculations. The MR model is the best at this time and satisfactorily fits the data to as low a κ value as has been measured¹⁴. All other models do not fit the data at these low κ 's and are thus insufficient.

A limiting condition on any model to describe a liquid is that $S_{\kappa \rightarrow 0} \propto \kappa^2$ to satisfactorily describe diffusion on a long time basis. The present data indicate that the lowest κ 's reached experimentally have not approached this limit of small κ and that between the S at high κ where $S_{\kappa \text{ large}} \propto \kappa^2$ and $S_{\kappa \text{ small}} \propto \kappa^2$ there is a region where $S_{\kappa \text{ intermediate}} \neq \kappa^2$. Since this $S_{\kappa \text{ intermediate}}$ is at the lowest κ reached in this experiment, the question of what is "small κ " where only long term diffusion is observed in neutron scattering measurements is in question. The meaning of diffusion constants determined from the width of the quasi elastic peak¹⁵ obtained in neutron experiments in this range of κ so far observed is questionable.

The present experiment has extended to smaller κ 's than have previously been reached. However, these κ 's are still not small enough to assure the observation in liquids of intramolecular vibrations unhindered by intermolecular interactions. Data extending to even lower κ 's by at least a decade are needed so that these vibrations can be observed. Data over a wide range of κ are needed to determine the κ dependence of such vibration transitions and "frequency spectrum" humps. The data should be extended to low enough κ , so that the diffusive limit of S where S is proportional to κ^2 is reached. Once S has been shown to be proportional to κ^2 , accurate diffusion constants can then be measured.

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APPENDIX A

A Continuous MR Model

The present data suggest that a continuous instead of a discrete set of vibrational states should be inserted into the MR model. The following is a derivation of such a model for the limit of small κ . Starting with Eq. 1 we want to modify it to have a form similar to the LEAP and ADDELT formulas. LEAP and ADDELT (abbreviated LA hereafter) is a computational procedure developed to define neutron scattering from a monoatomic crystalline incoherent scattering solid with a continuous frequency distribution. LA gives a method of handling multiphonon scattering, the $\sum_{\tau\tau'}$ of Eq. 1, which is a convenience and LA has been applied to water with reasonable success except in the small κ range. MR defines

$$w = \frac{\kappa^2 \hbar^2}{2mK_B T} \sum_{\tau} \frac{m \bar{\delta}_{v\tau} \cosh\left(\frac{\beta_{\tau}}{2}\right)}{\beta_{\tau} \sinh\left(\frac{\beta_{\tau}}{2}\right)} \quad (A-1)$$

$$= \alpha M \sum_{\tau} \frac{\bar{\delta}_{v\tau} \cosh\left(\frac{\beta_{\tau}}{2}\right)}{\beta_{\tau} \sinh\left(\frac{\beta_{\tau}}{2}\right)} = \frac{\lambda}{\alpha} \quad (A-2)$$

where $e^{-\alpha\lambda}$ is in the Debye Waller factor of LA.

The scattering law from LA can be written as

$$\frac{S_{\cdot LA}}{\sigma_{bv} \frac{1}{4\pi} \frac{1}{K_B T}} = e^{-w} \left\{ \delta(\beta) + \alpha \frac{\rho(\beta)}{2\beta \sinh \beta/2} + \text{multiphonon terms} \right\}$$

LA defines

$$\lambda = 2 \int_0^{\infty} \frac{\rho(\beta)}{\beta^2} \cosh\left(\frac{\beta}{2}\right) d\beta \quad (\text{A-3})$$

and

$$\frac{2\rho(\beta)}{\beta^2} = \frac{\rho(\beta)}{\beta \sinh\left(\frac{\beta}{2}\right)} \quad (\text{A-4})$$

where $\rho(\beta)$ is the frequency distribution for the ideal solid (monoatomic, incoherent, crystalline, cubic) and $\rho(\beta)$ is called the frequency spectrum.

From (A-3) and (A-4)

$$\lambda = \int_0^{\infty} \frac{\rho(\beta)}{\beta \sinh\left(\frac{\beta}{2}\right)} \cosh\left(\frac{\beta}{2}\right) d\beta. \quad (\text{A-5})$$

To compare (A-2) with (A-5), let us take the sum in (A-2) from discrete space to the continuum, defining in the process a density-of-states function for the MR model $\rho_{\text{MR}}(\beta)$. Then

$$M \sum_{\tau} \frac{\cosh\left(\frac{\beta_{\tau}}{2}\right)}{\beta_{\tau} \sinh\left(\frac{\beta_{\tau}}{2}\right)} = M \int_0^{\infty} \frac{\cosh\left(\frac{\beta}{2}\right)}{\beta \sinh\left(\frac{\beta}{2}\right)} \rho_{\text{MR}}(\beta) d\beta \quad (\text{A-6})$$

where

$$\int_0^{\infty} \rho_{\text{MR}}(\beta) d\beta = \text{total number of states.}$$

Comparing (A-6) with (A-5), one concludes that

$$\rho(\beta) = M \bar{\delta}_{\nu} \rho_{\text{MR}}(\beta) \quad (\text{A-7})$$

where $\overline{\delta}_v$ is the weighted frequency distribution for a more complicated material like H_2O . It is weighted for the directional average amplitude of motion of each atom of each kind.

Returning to Eq. 1 for the small κ range of interest, approximate

$$I_0(g_{v_\tau}) \approx 1 \quad (A-8)$$

and

$$I_1(g_{v_\tau}) \approx g_{v_\tau} / 2. \quad (A-9)$$

Also, let the sum over τ be extended to an integral over β' exactly as was done in (A-6), and then make the replacement indicated in (A-7).

The result is that Eq. 1 becomes

$$\begin{aligned} \frac{S_v}{\frac{\sigma_{bv}}{4\pi} \frac{1}{K_B T}} \approx e^{-w} e^{-\frac{\alpha}{4}} & \left\{ \frac{e^{-\frac{\beta^2}{4\alpha}}}{\sqrt{4\pi\alpha}} + \frac{\rho(\beta')}{2\sqrt{4\pi\alpha}} \int_0^\infty \frac{\rho(\beta')}{\beta' \sinh(\frac{\beta'}{2})} \right. \\ & \times \left. \left[e^{-\frac{(\beta-\beta')^2}{4\alpha}} + e^{-\frac{(\beta+\beta')^2}{4\alpha}} \right] d\beta' + \sum_{\tau, \tau'} \right\} \quad (A-10) \end{aligned}$$

In order to simplify this expression, let

$$g(\beta') = \frac{\rho(\beta')}{\beta' \sinh(\frac{\beta'}{2})}$$

and

$$f(\beta \pm \beta') = e^{-\frac{(\beta \pm \beta')^2}{4\alpha}}$$

Then the integral in (A-10) becomes

$$\int_0^\infty g(\beta') F(\beta + \beta') d\beta' + \int_0^\infty g(\beta') f(\beta - \beta') d\beta'. \quad (A-11)$$

Although $\rho(\beta')$ is not defined for negative β' , let us define it such that $\rho(\beta')$ is an even function, i.e. $\rho(\beta') = \rho(-\beta')$. Then $g(\beta')$ is an even function of β' . This makes it possible to make the substitution $\beta'' = -\beta'$ in the second integral in (A-11), and if one then switches the order of the limits together with changing the sign in front of the integral, (A-11) becomes

$$\begin{aligned} & \int_0^\infty g(\beta') f(\beta+\beta') d\beta' + \int_{-\infty}^0 g(\beta'') f(\beta+\beta'') d\beta'' \\ &= \int_{-\infty}^\infty g(\beta') f(\beta+\beta') d\beta'. \end{aligned} \quad (\text{A-12})$$

Using this result, and the fact that the scattering law for an ideal gas can be represented as

$$\tilde{\Phi} = \frac{1}{\sqrt{4\pi\alpha}} e^{-\frac{(\alpha^2+\beta^2)}{4\alpha}}, \quad (\text{A-13})$$

(A-10) becomes

$$\frac{S_v}{\frac{\sigma_{bv}}{4\pi} \frac{1}{K_B T}} \approx e^{-W} \left\{ \tilde{\Phi} + \frac{\alpha}{2} \int_{-\infty}^\infty \frac{\rho(\beta')}{\beta' \sinh(\frac{\beta'}{2})} \frac{e^{-\frac{[\alpha^2+(\beta+\beta')^2]}{4\alpha}}}{\sqrt{4\pi\alpha}} d\beta' + \sum_{\tau, \tau'} \right\} \quad (\text{A-14})$$

Here, one notes that the first two terms on the right hand of (A-14) are simply the Fourier transform convolution of LA with $\tilde{\Phi}$. Assuming this convolution holds for multiphonon terms as well, one can write

$$\begin{aligned} \frac{S_v}{\frac{\sigma_{bv}}{4\pi} \frac{1}{K_B T}} &\approx e^{-W} \int_{-\infty}^\infty \text{LA}(\beta') \tilde{\Phi}(\beta+\beta') d\beta' \\ &\approx e^{-W} \{\tilde{\Phi} * \text{LA}\}. \end{aligned} \quad (\text{A-15})$$

That a molecular liquid can be described by the convolution of a solid-like description and a gas-like description is an intriguing result. Unfortunately, $S_v(\beta \neq 0)$ of (A-15) is proportional to κ^2 , not κ , at small κ . The κ dependence of the original MR model depends in a fundamental way on the spectrum of states being discrete, and then holds only when $\beta \approx \beta_T$ at small κ . Diffusive motion still needs to be correctly inserted into the model.