The Thermodynamics of the Glassy State. I. The Heat Capacity of One-Dimensional Disordered Harmonic Systems from Moments

F. I. Mopsik and C. M. Guttman

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

September 26, 1976

Upper and lower bounds on the thermodynamic quantities of disordered one-dimensional systems are computed using the spectral moments of Domb et al. [1][1] and a modification of a computational technique of Wheeler and Gordon [2]. The heat capacity so produced is defined to better than 0.01 percent for all temperatures. Models for glasses in one dimension are presented. The difference in the heat capacity between a disordered state and a comparable ordered one is examined. Normal low temperature behavior of heat capacity differences between glasses and crystals is seen. From models for glasses in one dimension it is argued that when the measured heat capacity of a glass exceeds that of its crystal, the glass must have regimes of higher density than that of the crystal. Various approximation schemes and bounds for the heat capacity of glasses in one and higher dimensions are also proposed.

Key words: Disordered chain; glass; heat capacity; one-dimension; thermodynamic bounds; thermodynamics; thermodynamics of disordered systems.

1. Introduction

Differences in the heat capacity between glasses and crystals of the same material have been extensively studied experimentally (see ref. [3] for literature references and compilation of data). The general feature of the difference curve shows that the glasses have an excessive heat capacity displaying a peak around 50 K followed by a monotonic increase to higher temperatures. In reference [3], one of us suggested that the volume difference between the glass and related crystals caused most of the excess heat capacity including the low temperature peak. In that paper we estimated the contribution to the low temperature peak due to disorder and concluded it was small compared to the contribution due to volume.

As a result of that study, we have begun a program to determine more precisely the effect of disorder on the vibrational thermodynamic properties of glassy systems in as systematic a manner as possible. Others have introduced soft modes or modified Debye or Einstein functions to estimate the thermal properties of glasses [4]. We shall avoid the introduction of such ad hoc models for the frequency spectra of the glass. Rather starting from a general picture of disordering in the solid, we shall try to determine the thermodynamic functions of the disordered material in order to determine what specific model assumptions are necessary to mimic the properties of a glass. To eliminate material dependent properties in the spirit of reference 3, we shall study the difference in the properties between the glass or disordered state and the crystalline state of the same material.

A variety of models are available for the structure of the glass. From our point of view they generally divide themselves into two classes (1) homogeneous glasses where one assumes a glass is a disordered material with each "bond" or interaction less strong than that of the crystal; (2) a Bernal-type glass where one assumes, as Bernal did for a liquid [5], that the glass has structures in it of higher density (and thus higher energy) than its crystal. These structures are connected to each other by low energy regions. The high energy structures do not result in the stable crystal since these structures are non-propagating.

We shall model both such classes of glasses; we shall show that some Bernal-like glasses have heat capacities less than that of their crystals for a range of temperatures.

In order to keep the answers quantitative we shall restrict ourselves, in this paper, to models of glasses which are representable by one-dimensional chains of uniform masses with a distribution of force constants. Here the calculation of the thermodynamic functions may be made. We hope the results will indicate what would be significant in a more realistic three-dimensional treatment and lead to further work on three-dimensional systems.

There have been many studies to date of the frequency spectra of the one-dimensional disordered solid, with most of the emphasis on the case where atoms of two different masses are randomly distributed along the chain [6–14]. This work involves analytic studies as well as computer calculations by root sampling techniques. Further, Dean [9] has studied more general distributions of force constants, by means of computer calculations of the frequency spectra. Studies of the heat capacity or thermodynamic functions are much rarer. Maradudin et al. [16] have obtained the differences in the thermodynamic functions for the two-mass case using an expansion in the disordering parameter. We shall show later on in the paper that this technique predicts too small an effect of disordering. A difference curve for the heat capacity of a randomly distributed two mass chain with equal numbers of masses m and 2m was determined by Domb and Isenberg [8]. This calculation used Padé approximates and was of uncertain accuracy.

---

[1] Figures in brackets indicate literature references at the end of this paper.

Since the thermodynamic quantities involve averages over the frequency spectrum, it is possible to compute them directly to good accuracy without knowledge of the entire frequency distribution itself. Wheeler and Gordon [2] have shown that it is possible to derive rigorous bounds on thermodynamic quantities from the moments of the frequency distribution and, furthermore, that these bounds are capable of defining the thermodynamic quantities quite accurately even if there are not enough moments to define the spectrum itself very well. Since Domb, Maradudin, Montroll and Weiss [1] have given explicit expressions for the first eleven even moments for the random one-dimensional chain, and since Domb [6] has given completely the first two terms in the low frequency expansion of the spectrum of the same chain, we felt that we should be able to answer the question as to the contribution of disorder to thermodynamic quantities in a one-dimensional system to a high degree of accuracy.

In the next section we discuss the computational method we use; following that, in section 3, we propose some models for a glass system and compute their thermodynamic properties with high precision. In section 4, we discuss various approximation procedures to obtain the same thermodynamic quantities and compare them to the exact calculations. In section 5 we discuss our results and how they relate to real glasses.

In all of this paper our main emphasis shall be on computing the heat capacity. This is because most experimental data available at low temperatures are on heat capacities; furthermore heat capacity data are the only experimental data we know where the properties of both glasses and their crystals have been measured at such low temperatures.

For this paper we shall restrict our comparison with experiment to the range below 140 K as we did in reference [3]. This will allow us to consider only heat capacity at constant volume differences. In a future paper we shall look into modeling and computations where we allow the system to expand.

A final note should be made. Nothing in this paper is directed at the problem of explaining the heat capacity of glasses below 1 K [16]. Nothing in these models would explain the experimentally observed results; furthermore our computational procedures are not particularly good in this temperature range.

2. Computational Methods

2.1 Method of Moments

All the computations reported in this paper use the even moments of the frequency spectrum, μ_n defined as

$$\mu_n = \int_0^1 w^{2n} g(w) dw, \tag{1}$$

$n = 0, 1, 2, \cdots,$

$$w = \omega/\omega_M,$$
$$0 < \omega < \omega_M, \tag{2}$$

$g(\omega)$ is the density of states at the frequency ω and ω_M is the maximum frequency for the spectra. For a one-dimensional

chain with uniform masses m and random force constants with a maximum force constant k_M, by Rayleigh's theorem

$$g(\omega) = 0, \ \omega > 2\sqrt{k_M}/m, \tag{3a}$$

so that in all that follows ω_M will be defined as

$$\omega_M = 2\sqrt{k_M}/m. \tag{3b}$$

Domb, Maradudin, Montroll and Weiss [1], have shown that for a one-dimensional system mass disordering and force constant disordering are equivalent, a distribution of force constants being equivalent to a distribution of reciprocal masses. We will, therefore, speak of mass or force constant distributions when one or the other is convenient for comparison with other results even though we are interested here in force constant disorder.

We are interested in computing the thermodynamic properties of a harmonic or quasi-harmonic system which can be written as

$$H(\tau) = \int_0^1 H_E(w/\tau) g(w) dw, \tag{4}$$

where H is the thermodynamic property of interest, H_E is the appropriate Einstein function and τ is the normalized temperature defined as

$$\tau = kT/\hbar\omega_M.$$

Wheeler and Gordon [18] have shown how it is possible to derive Gaussian integrators of the form

$$H(\tau) = \sum_i \rho_i H_E(x_i/\tau) + R, \tag{5}$$

with weights ρ_i, points x_i and remainder R such that the weights and points are determined from the moments so that the integrators give the first n moments correctly and rigorously bound all possible values for $H(\tau)$ for any distribution $g(w)$ having the same n moments. Furthermore, these bounds are sharp enough so that they define $H(\tau)$ quite accurately even with a limited number of moments.

For the actual computations we used the recursive methods developed in Wheeler and Blumstein [17]. We did not make use of the modified moments defined by them to compute the integrators as we had only eleven moments and the double precision arithmetic (18 significant figures) on the computer used for the calculations was adequate to avoid numerical problems caused by the use of the moments directly. Since we did not desire answers to an accuracy of more than six significant figures, the calculations leading to the integrators were essentially exact.

For the moments of the frequency distribution, we used the results of Domb, Maradudin, Montroll and Weiss [1]. They give the first eleven even moments for the randomly disordered linear chain exactly in terms of the moments of the mass distribution with a fixed force constant. However, they also show that this is the same answer as for the fixed mass, randomly disordered force constant problem with distribution of force constants expressed as reciprocals. Thus mass disorder and force constant disorder are equivalent in one-dimension.

In the above paper by Domb, et al., the moments of the high frequency series are derived for only the two mass distribution. Their results are, in fact, applicable to a more generalized mass distribution. To correct a typographic error in the coefficient of $\nu_3\nu_2^2\nu_1$ of μ_8, we redid their work up to μ_8 and found that the coefficients for a generalized mass distribution were the same as their coefficients if we define

$$\nu_e = \frac{1}{N}\sum_{i=1}^{N} m_i^{-e} \qquad (6)$$

using their notation.

2.2 Low Frequency Series

We are interested in the thermodynamic functions at low temperatures. In order to have meaningful results to five or six significant figures, we had to supplement the moments of the distribution $g(w)$ with a low frequency expansion for the frequency distribution. As discussed in Wheeler and Gordon [2], we then can use the moments to describe a new frequency distribution

$$g'(w) = g(w) - g_L(w), \ w < w_C$$
$$g'(w) = g(w), \ w > w_C \qquad (7)$$

where $g_L(w)$ is a polynomial in w valid for $w < w_C$ such that it bounds $g(w)$ from below so that $g'(w)$ is always positive and as close to zero as possible below w_C. For $g_L(w)$, we used the first two exact terms in the series expansion for $g(w)$ as given in Domb [6]. This is given as

$$g_L(\omega) = (1/\pi\omega_H)[2 + (1 - K_3 \qquad\qquad (8)$$
$$+ (15/16)K_2^2)(\omega/\omega_H)^2]$$

where ω_H is the maximum frequency for a uniform chain with a mass equal to the mean mass of the chain. The K_j are defined as

$$K_j = \sum_{i=1}^{N} (\epsilon_i)^j/N \qquad (9)$$

where ϵ is given by the expression

$$m_i = <m>(1 + \epsilon_i). \qquad (10)$$

Equation (8) represents the first two terms of a series with an unknown radius of convergence and with possible negative terms. Therefore, it is possible for a given w that $g'(w)$ could be negative. Since the theory associated with the method of moments assumes a positive distribution, if the integrators can be formed, the integrators will be for only those distributions which are always positive and, therefore, the bounds obtained will not include the desired distribution. It should be noted that if there is no positive distribution possible, then an integrator cannot be formed at all [18].

In practice the use of eq (8) has not been too much of a problem. If the K_i rapidly go to zero for increasing i, then from a relatively rough knowledge of the spectrum which can be obtained from the moments themselves, w_c can be chosen such that $g_L(w)$ is less than $g(w)$ for all $w < w_c$ so that good accuracy is obtained. The only case where this was not true

was for the case of two masses randomly distributed with a mass ratio of 6 to 1 with 0.9 of the masses being light (this model will be discussed later in more detail). For this case the K_i grow with increasing i and it was not possible to form integrators if $w_C/w_H > \omega/\omega_H = 0.4$ even though, for the uniform chain the series is convergent for $\omega/\omega_H = 1$. The errors resulting from this problem appear mainly at low temperatures, do not effect our results and are discussed in appendix A.

2.3. Thermodynamic Functions

The functions that were evaluated were the total energy, free energy and heat capacity. This involved evaluating the integrals

$$U/N\hbar\omega_M = \tau \int_0^1 [(w/2\tau)\coth(w/2\tau)]g(w)dw, \quad (11)$$

$$F/N\hbar\omega_M = \tau \int_0^1 \{ln[2\sinh(w/2\tau)]\}g(w)dw, \qquad (12)$$

$$C/Nk = \int_0^1 \left[\frac{(w/2\tau)}{\sinh(w/2\tau)}\right]^2 g(w)dw. \qquad (13)$$

The total energy, free energy and heat capacity are all expressible in terms of appropriate Debye functions, Einstein functions and a few elementary forms. Although we had F and U available, only C is reported in this paper. We have computed F and U for use in another paper where the systems are allowed to expand.

3. Models and Results

Since we are in one dimension and are only dealing with the thermal (vibration) properties of the glasses and their crystals, we do not propose here to present a detailed model of a glass. Rather we shall consider models which display the force constant differences one might expect to see between glasses and their crystals.

The view that a glass arises from the appearance of a multiple minimum of an averaged molecular potential energy function seen by a molecule has been discussed in some detail by DiMarzio and Stillinger [19] and Goldstein [20]. Besides the effects on heat capacity which we shall study here, we note that the multiple minima model for a glass leads to an entropy per atom (or segment) of the glass at $T = 0\ K$ different from that of a crystal at $T = 0\ K$. This is in disagreement with some thermodynamic theories of glasses [21a]. These theories are for idealized glasses and are in disagreement with experiment on just this point. That is, these theories predict a zero residual entropy per atom for the glass at $T = 0\ K$ while all experiments we are aware of where the entropy of the glass and crystal have been measured yield finite entropy differences at absolute zero. Chang and Bestul [21b] compiled much of the extant data and showed that the residual entropy is in the range 0.6 to 6.0 joules per degree per moveable segment unit. For models used in this paper, the residual entropies are between 0.8 to 8.0 joules per degree per unit. Thus, the multiple minima model does not seem to be in disagreement with experimental residual entropies.

In light of the above arguments and for convenience of modeling we shall use a multiple minima model of glasses. Thus the average potential energy function we consider here has a multiplicity of minima, generally the deepest relating to the crystal. Since most molecules which form a glass are either polar or chained or three-dimensional bonded structures, a many minima energy surface describing the mean interaction of a molecule with its neighbors as a function of separation seems very reasonable.

In figure 1a we display the simplest example of a potential energy function which allows for glassy configurations; a double minima or two-well model. Figure 1b shows the other extreme, the case of a many minima potential energy or multiple-well model. Any vibrational model which hopes to approximate the properties of real glasses needs not only the form of the potential energy function but also the distribution of molecules which reside in each of the minima. Thus we need minimally to obtain the distribution of force constants. (In other theories of glasses this would be connected to the distribution of free volume.) This we do not have for a glass. However, a measure of this in one dimension is given by the compressibility. Compressibility differences between the glass and its crystal have been measured or approximated; these range from about 125 to 400 percent.[2] All our models fall within this range. The models we have studied are listed in Table I.
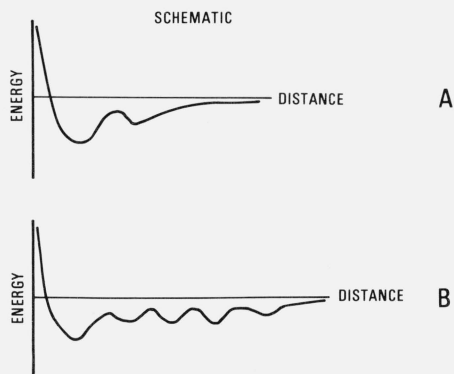

FIGURE 1. *Two possible averaged potential energy functions for well models of a glass.*
(A) shows a simple two-well model. (B) shows a multiple-well model.

Figure 2 shows the effect of a choice of force constant distribution in a ΔC_v plot where ΔC_v is defined as the difference between the glass and crystal heat capacity at constant volume. In this figure and all subsequent figures reporting heat capacity in this paper, the heat capacity difference plots are given since that is the quantity in which we are interested for comparison with experiment. In this figure and the heat capacity figures, a portion of the low temperature part of the curves will appear doubled. These lines represent the correctly taken upper and lower bounds for the difference. Where the curve is not doubled, both bounds are closer than can be represented. The force
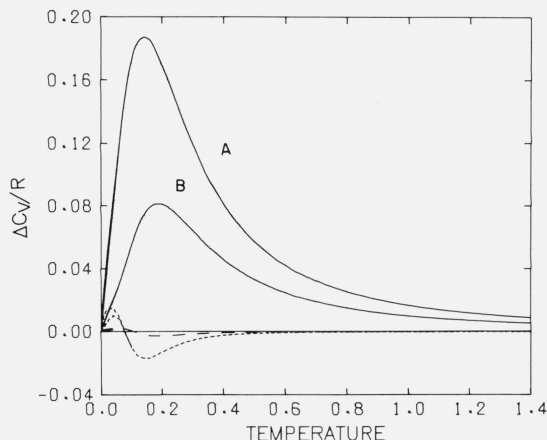
² Little data exist where moduli have been measured on glasses and crystals of the same material. For SiO₂ the ratio of the moduli between the glass (fused silica) and quartz may be estimated from Bridgeman's data as 1.4 to 1.5 (P. W. Bridgeman, Proc. Am. Acad. Arts and Sci. **76**, pg. 68, 1948). For semicrystalline polymers an estimate of the ratio of the moduli of the glass to that of the crystal may be made by using the data of Broadhurst and Mopsik (M. G. Broadhurst and F. I. Mopsik, J. Chem. Phys., **54**, 4239, 1971), on polyethylene. Assuming the density of 100 percent crystalline polyethylene is 1.0 g/cm³ and 100 percent amorphous is 0.85 g/cm³ then data yield a moduli ratio of 3.5 to 4.

FIGURE 2. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A and B are for glasses defined in table I. The dotted line is eq (16) minus C_v for glass 2A. The dashed line is eq. (16) minus C_v for glass 2B. In this figure and all those following, doubled lines indicate upper and lower bounds.

constant of the crystal is assigned a value of 1; all other force constants are then relative to the crystal force constant.

The heat capacity displayed in these figures is normalized so it is in units of R, the gas constant; the maximum heat capacity possible for our data is by definition one. The temperature in the figures is scaled in units of T/Θ_M where

$$\begin{aligned}\Theta_M &= h\omega_M/k \\ \omega_M &= \text{is the maximum frequency of the crystal.}\end{aligned} \quad (14)$$

In order to compare these calculations with the experimental data such as given in figure 1 and 2 of reference [3] the heat capacity needs to be multiplied by 3R, the assumed total maximum contribution to the lattice modes. To compare the temperature one needs an estimate of the Debye theta of the crystal of the material. Then our T/Θ_M can be scaled relative to this Debye theta for a comparable three dimensional structure. A variety of arbitrary scaling factors may be chosen. In reference [3], figure 3 Θ_M is defined so that the normalized heat capacity of the one dimensional crystal (the ordered state) at $T = \Theta_M$ equals the heat capacity of the three dimensional Debye solid at $T = \Theta$, the Debye theta. From these assumptions one then obtains the true temperature by multiplying T/Θ_M by 1.09 times the Debye theta of the crystal.

For the case of the double minima in the potential we assume, as is normal, that the deepest minimum, which is also the minimum closest to the origin, is the most stable state crystal; by the same reasoning the crystal for this case has the highest force constant. We look first at 50:50 random distribution of force constants, 1 and 0.5, and 1 and 1/6. For these two models we do not expect long runs of either of the force constants. In two state models in one dimension one expects that there is a approximate one to one correspondence between volume and force constant. Thus, one would expect the average density over the space of a few masses for such models. Figure 2 shows the effect of this volume distribution for the two choices of force constants in a plot of ΔC_v. Notice as one weakens the non-crystalline force constant the heat capacity differences for fixed force constant distribution increases.

286

TABLE I.

Curve	Force Constant Ratio	Force Constant Distribution	Mean Force	Harmonic Mean Force Constant
2 A	1:1/6	0.5:.5	0.583	0.286
2 B	1:.5	.5:.5	.75	.667
3 A	1:1/6	.9:.1	.9167	.667
3 B	1:.5	.9:.1	.95	.909
4 A	2:1:1/12	1/3:1/3:1/3	1.02777	.222
4 B	2:1:1/6	1/3:1/3:1/3	1.05555	.4
4 C	2:1:.5	1/3:1/3:1/3	1.16666	.857
5 A	2:1/6	.5:.5	1.083333	.307
5 B	2:.5	.5:.5	1.25	.800
6 A	2:1/6	.25:.75	0.625	.216
6 B	2:.5	.25:.75	.875	.615
7 A	1 to 1/3	Dean (1/2-3/2)	.6666	.607
7 B	1 to .6	Dean (3/4-5/4)	.8	.783
8 A	1.5 to .5	Dean (1/2-3/2)	1	.910
8 B	1.25 to .75	Dean (3/4-5/4)	1	.979
8 C	1.60 to .5333	Dean (1/2-3/2)	1.06666	.970

We also choose a two state model with 90:10 distribution of the 1 and 0.5 force constant glass and of the 1 and 1/6 force constant glass. These are models of chains with relatively long runs of the higher force constant; this gives one a view onto a mixed amorphous and crystalline system or, from another point of view, a microcrystalline view of the glassy state. Figure 3 displays the results of the heat capacity difference between this glass and the crystal. The effect of changing the weak force constant here is the same as in figure 2, while the effect of decreasing the fraction of molecules having the weak force constant will decrease the total heat capacity difference as one would expect.
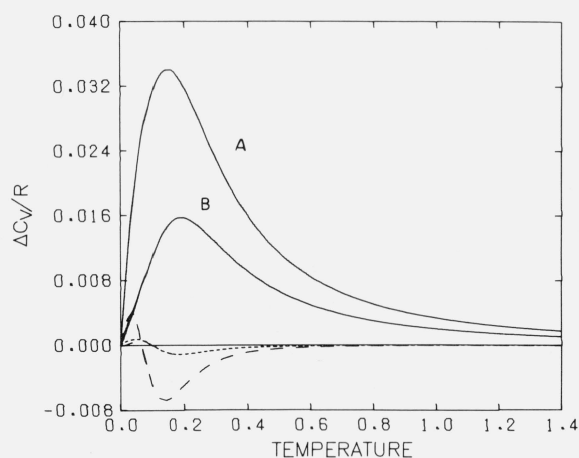

FIGURE 3. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A and B are for glasses defined in table I. The dashed line is eq (16) minus C_v for glass 3A. The dotted line is eq (16) minus C_v for glass 3B.

Another view of glasses comes from the Bernal's considerations on the liquid or amorphous state [5]. In Bernal's models of the liquid state small groups of molecules are bound in a deep energy minimum but geometric considerations leading to this structure do not allow for the structure to propagate. In this view the energy minimum related to the crystal is not the most attractive potential energy minimum; rather it is the most attractive minimum which allows for a propagating structure. In simplest terms applicable to one dimension this would cause a glass to have three available force constants, k_1 the force constant for the stable but nonpropagating structure, k_2 the force constant for the crystal, chosen here as 1, and k_3 the force constant for the region between the two structured regimes. By the view that the most stable potential energy state also yields the highest force constant we have $k_1 > k_2 > k_3$. In figures 4 to 6 we display some results of the ΔC_v calculation for this model. The reader should note that some of the Bernal model glasses in figure 4–6 display negative heat capacity differences between glasses and their crystals; that is, the glass has a lower heat capacity at constant volume than the crystal for some temperature range. This unusual phenomenon is experimentally observed for some measured differences of heat capacity at constant pressure [22]. We shall discuss the meaning of this result later on in this section and in section 5.

Here we only discuss the effects of the changing of the force constants on the ΔC_v. If we compare figure 2 curve B with figure 4 curve C we see the effect of adding a force constant greater than that of the crystal to the glass. Figure 2 curve B shows ΔC_v for a 50:50 distribution of 1. and 0.5 force constants while figure 4 curve C shows the ΔC_v of a 0.33:0.33:0.33 distribution of force constants 2, 1, and 0.5. The effect of adding the stronger force constant is to lower the magnitude of the low temperature peak as well as to introduce a negative ΔC_v regime.

In figure 4 we see the effect of changing the weak force constant as we hold the other two force constants fixed and keep the distribution of force constants the same. As the weak force constant drops from 0.5 to 1/12 the size of the first peak increases while the size of the negative region decreases. In figure 5 we leave out the crystal-like force constant of relative magnitude 1 showing that this trend is not changed by the loss of such a force constant. In both figures 4 and 5 we see negative heat capacity difference
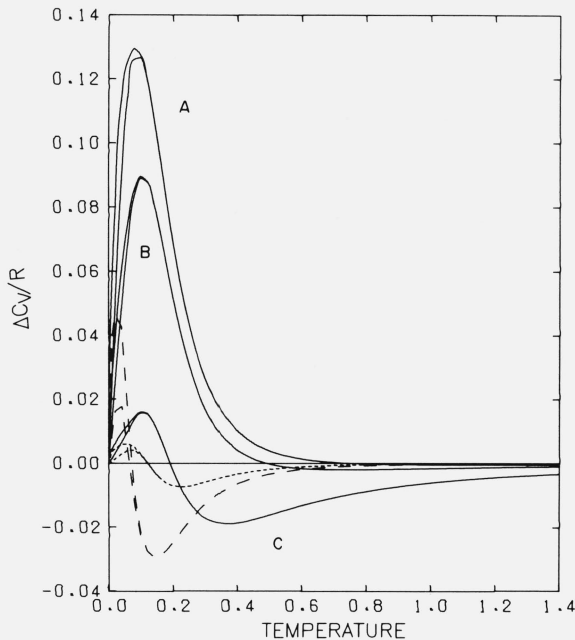
287

FIGURE 4. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A, B and C are for glasses defined in table I. The dashed curve is eq (16) minus C_v for glass 4A. The dotted line is eq (16) minus C_v for glass 4C.
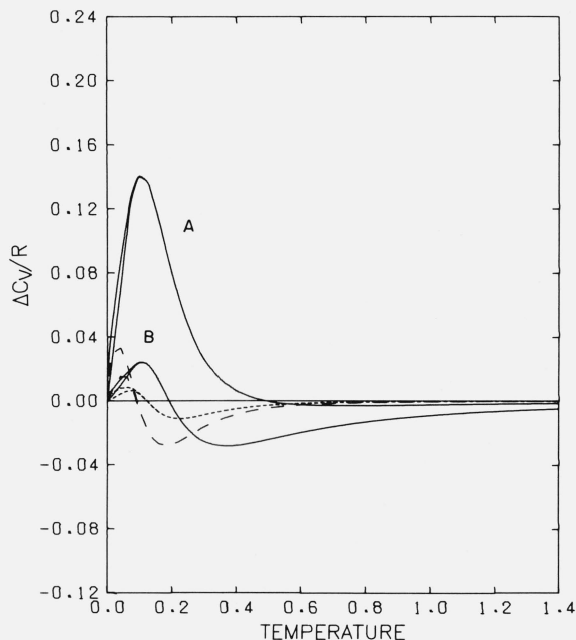

FIGURE 5. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A and B are for glasses defined in table I. The dashed line is eq (16) minus C_v for glass 5A. The dotted line is eq (16) minus C_v for glass 5D.

regimes and peaks at low temperatures. Inspection of Table I shows that all those curves with negative heat capacity difference regimes have mean force constants greater than that of the crystal (that is, greater than 1).

In figure 6 we show the effect of decreasing the fraction of the strong force constant in a Bernal-like model so as to get no negative heat capacity regime. This is seen in curves A and B. Inspection of Table I shows for these cases the mean force constant is less than 1. In fact, in all those cases where the harmonic mean force constant is less than 1 and the mean force constant is greater than 1 the ΔC_v curve shows both a positive and negative regime. When the harmonic mean force constant is less than 1 and the mean force constant is less than 1 we only have the normal low temperature peak.
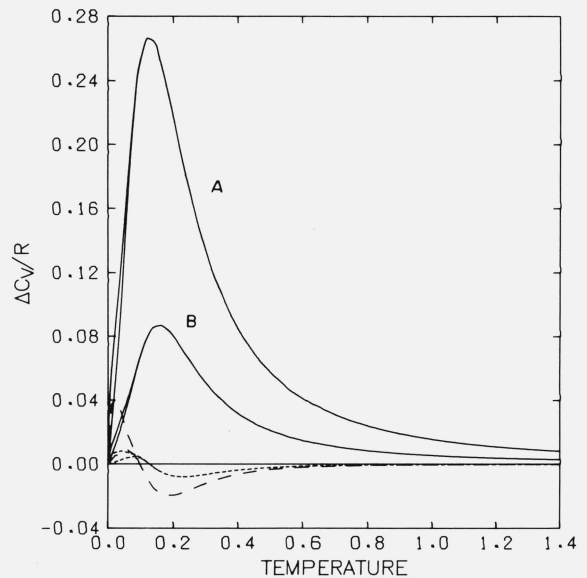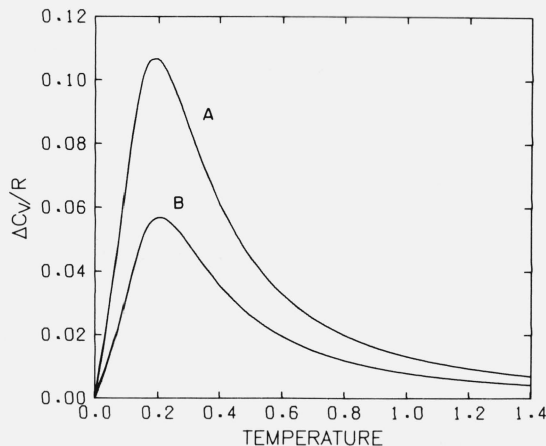

FIGURE 6. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A and B are for glasses defined in table I. The dashed line is eq (16) minus C_v for glass 6A. The dottedline is for eq (16) minus C_v for glass 6B.

The potential energy function leading to a multiple state model of a glass is shown in figure 1b. Here many equivalent minima are seen with one minimum, that relating to the crystal, being somewhat deeper. Here also we have allowed for a minimum closer into the origin than the crystal. In the extreme, the many-minima model leads to a continuous distribution of force constants; such a model is like the model Dean [9] used in his computation of the frequency distribution of a glass-like structure. We have calculated ΔC_v for two of the Dean distributions of force constants. In figure 7 we display the heat capacity difference for a uniform distribution of force constants between the force constant limits of 1 to 3/5 and 1 to 1/3 to be compared with Dean's distributions designated as 3/4–5/4 and 1/2–3/2 but with the strongest force constant of the distribution chosen to be that of the crystal. In this case we see only a normal low temperature peak in ΔC_v. In figure 8 curves A and B we display heat capacity differences for Dean's distribution 1/2–3/2 and 3/4–5/4. Here we still allowed the force constant of the crystal to be 1, i.e., have a value in the center of the force constant distribution of the glass. Notice we still have only the low temperature peak even though the mean force constant of these cases are identical to that of the crystal. In figure 8, curve C we have allowed the 1/2–3/2 Dean distribution to be

288

FIGURE 7. *Heat capacity at constant volume of a glass minus that of a crystal.*
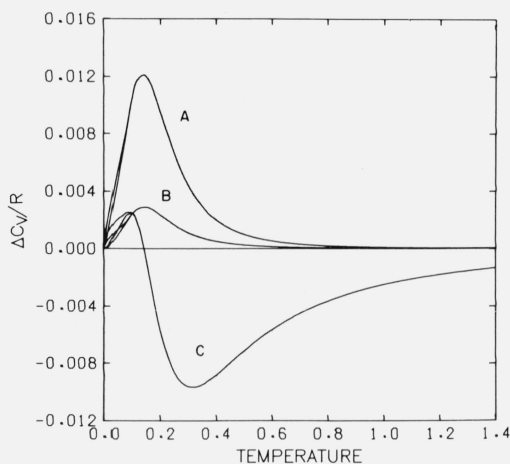Curves A and B are for glasses defined in table I.

FIGURE 8. *Heat capacity at constant volume of a glass minus that of a crystal.*
Curves A, B and C are for glasses defined in table I.

shifted to pick up a stronger force constant and we immediately pick up a pronounced negative regime at higher temperatures.
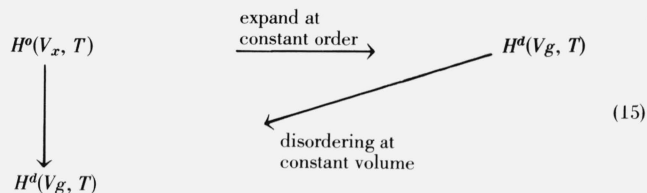
The ΔC_v peaks displayed in all the curves in figures 2–8 show low temperature curves similar to those obtained from experiment. By using the scaling constants discussed earlier in the section the order of magnitude of the heat capacity difference displayed in figure 3 is smaller than one sees experimentally, while those in figures 2 and 4 are about the right order of magnitude. In general we see by a proper choice of either distribution or force constants we may pick up the generally observed heat capacity differences.

However, as was discussed in reference [3] the upswing seen in most measured heat capacity difference curves is not seen here. This is due to the fact that we are computing the heat capacity at constant volume and not allowing the system to expand. In a later paper we shall compute the heat capacity at constant pressure; for such models we will in fact see such an upsweep.

4. Approximations to the Heat Capacity of the Disordered State

In this section we shall look at various schemes to approximate the heat capacity of the disordered state. We do this with the view that approximations which work well in one dimension should be extendable with some validity into higher dimensions where it is not possible to compute rigorously the heat capacity of the disordered state.

The difference in a thermodynamic function between a glass and its crystal may be computed by the following cycle:

$$H^o(V_x, T) \xrightarrow{\text{expand at constant order}} H^d(Vg, T)$$

(15)

$$H^o(V_x, T) \downarrow \qquad H^d(Vg, T) \qquad \text{disordering at constant volume}$$

$$H^d(Vg, T)$$

$H^0(V, T)$ is any thermodynamic property of the material which is in the ordered state at volume, V, and temperature T; $H^d(V, T)$ is the thermodynamic quantity of a disordered material at volume V and temperature T. V_x is the volume of the crystal, Vg is the volume of the glass.

Thus to compute the difference in thermodynamic functions between a glass and its crystal we compute the difference in thermodynamic functions between the crystal and an "expanded" crystal which has a force constant which is the same as the mean force constant of the glass; then we compute difference in thermodynamic functions at fixed mean force constants between the glass and the "expanded" crystal.

Guttman [3] proposed that the first step was easy to compute using a Grueneisen type theory; the second term he found difficult to compute. However, using estimates from some calculations of Dean [9] Guttman argued that the contribution of the second step was small compared to the first. We are able to test that assumption here.

Before we test his assumptions a few words are necessary concerning the cycle itself. The cycle is not unique, as one would expect. In fact the "expanded" crystal could have had, just as sensibly, a force constant whose value was the harmonic mean of the force constants of the glass. This leads to a "expanded" crystal with the same bulk modulus as the glass. Either choice of models is suitable for describing the heat capacity of the glass. Therefore, we performed calculations for both models. In fact each model has a temperature regime where its heat capacity is identical to that of the glass. The mean force constant model has the same heat capacity as the glass at high temperatures; the harmonic mean force constant yields low temperature heat capacities identical to that of the glass. This is discussed further in appendix C.

In figures 9 to 11 we display heat capacity differences between the glass and the "expanded crystal" approximation to the glass. The curves show the effect of the second step of the process discussed previously; the change in heat capacity at constant volume due to a change in order. The negative heat capacity difference curve is always the difference in the heat capacity between the "expanded" crystal with the same
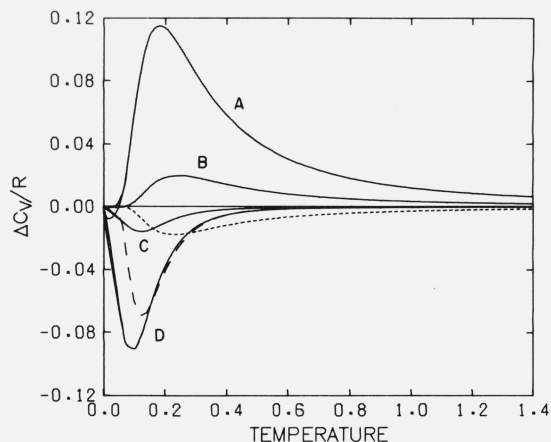
FIGURE 9. *Curve A is the heat capacity of an "expanded" crystal with a harmonic mean force constant of glass 2A minus that of glass 2A.*
Curve D is the heat capacity of an arithmetic mean force constant crystal minus that of glass 2A. Curves B and C are the same as curves A and D but referred to glass 2B. The dashed curve is the Maradudin et al. [15] approximation heat capacity for glass 2A minus that of glass 2A. The dotted line is the same for blass 2B.
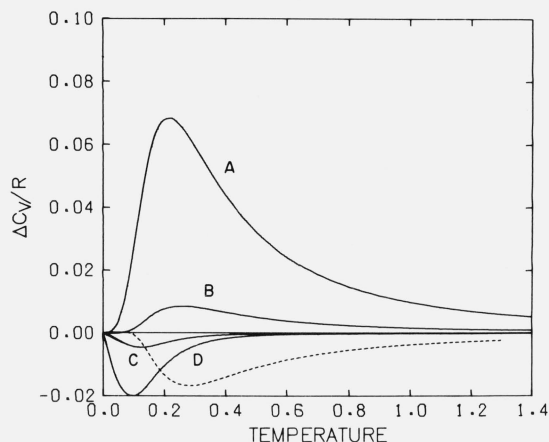

FIGURE 11. *Curve A is the heat capacity for a crystal with a harmonic mean force constant of glass 4A minus that of glass 4A.*
Curve F is the heat capacity for an arithmetic mean force constant crystal minus that of glass 4A. Curves B and E are the same as curves A and F but referred to glass 4B. Curves C and D are the same as curves A and F but referred to glass 4C.

FIGURE 10. *Curve A is the heat capacity of an "expanded" crystal with a harmonic mean force constant of glass 3A minus that of glass 3A.*
Curve D is the heat capacity of an arithmetic mean force constant crystal minus that of glass 3A. Curves B and C are the same as curves A and D but referred to glass 3B. The dotted curve is the Maradudin et al. [15] approximation heat capacity for glass 3B minus that of glass 3B.

main, true. However, significant and measurable effects due to disordering at constant volume seem to be apparent from the above data. This is especially true when one compares figure 2 curve A with figure 9 curve A for the 50:50 ratio of force constants 1 and $1/6$. Here the heat capacity due to disordering is about 30 percent of the total heat capacity difference between the glass and the crystal.

For three force constants, shown in figure 11, the heat capacity difference between the "expanded crystal" and the glass is much larger then observed in figures 9 and 10 for two force constants. In the case of 2:1:1/12 glasses, the approximation to the heat capacity by using its "expanded" crystal gives no better an estimate than the crystal heat capacity to the heat capacity of the glass.

Inspection of figures 9 to 11 shows immediately another significant fact. As long as one goes to temperatures where our bounds are good, the mean force constant "expanded" crystal has a heat capacity which is always less than that of the glass, and the "expanded" crystal with the same mean modulus as the glass always has a heat capacity greater than that of the glass. One is an upper bound to the heat capacity of the glass and the other a lower bound for all cases we have looked at. We have not as yet been able to prove the above fact rigorously but this data leads one to believe the hypothesis. Certainly in any extension or in any description of glassy properties in three dimensions this hypothesis should be considered. In fact, one might consider that a good approximation to the heat capacity of the disordered state is the average of the two above approximations. We shall present a different and considerably better approximation later on in this section.

Before we consider this approximation we should point out, for historical purposes, that Maradudin et al [15] have computed the heat capacity of a two-well glass using an expansion technique for the thermodynamic functions. Their results are shown by the dashed and dotted curves in figures 9 and 10. These curves display the difference between their approximate C_v and our computed C_v. It is seen that although their scheme yields results better than the mean force

mean force constant as the glass and the glass; the positive heat capacity difference is always the difference between the "expanded" crystal with the same harmonic mean force constant as the glass and the glass.

We first note that when there are two force constants, no matter which of the two choices we make for the "expanded" crystal, the magnitude of the heat capacity difference displayed for the force constant case in figures 9 and 10 for step 2 of the cycle is always much less than the heat capacity difference between the glasses and their crystals displayed in figures 2 and 3. (The reader should note the scale changes on the graphs). In fact this disordering heat capacity is less than the total heat capacity difference often by a factor of 3 or 4. Thus for these glasses Guttman's assertion that volume changes dominated the heat capacity differences is, in the
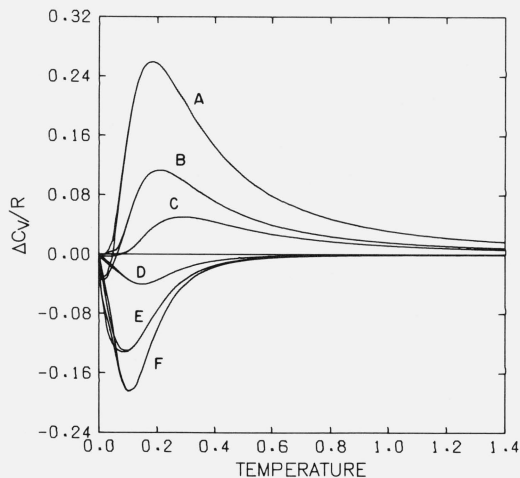
constant or harmonic mean force constant approximation to the glass, their scheme still shows significant deviations from the true curve. Furthermore, for the 1 and $1/6$ force constant with a force constant distribution of 0.9:0.1 their expansion procedure fails: thus their formulae in that case give very large errors. That case is not displayed here.

Finally we propose a new approximation scheme to compute the heat capacity of the disordered state. For this purpose let us define the heat capacity for an ordered (crystalline) system with force constant k as $C_v(k, T)$, where we have explicitly displayed the force constant k for this monatomic system. Then for a disordered system with two force constants k_1 and k_2 in the system in fractions x and $1-x$, respectively, we define an approximate heat capacity of the glass, $C_v^a(T)m$ as

$$C_v^a(T) = xC_v(k_1, T) + (1 - x)C_v(k_2, T). \qquad (16)$$

The extension of this formula to more force constants is obvious. In figures 2–6 the difference between the glass heat capacity and the approximate heat capacity is shown by a dotted line or dashed curves for the various models we have discussed earlier. The reader immediately sees by inspection of figures 2–6 that this approximation is amazingly good.

Why such a "mean field" approximation scheme works to give such precise values of the heat capacity is itself not clear. One should, however, note that the approximation scheme yields the same high temperature limiting behavior as the exact heat capacity. This is shown in appendix C.

5. Discussions and Conclusions

The models and approximation schemes presented here for the heat capacity of the disordered state lead to some interesting and simple conclusions about the heat capacity differences between glasses and their crystals.

First, the low temperature peak around $T/\theta_M = 0.2$ is characteristic of the glass-crystal differences. Much of the peak can be attributed to the fact that glasses have larger volumes than their crystals and thus larger bulk moduli as Guttman proposed; however, the fact that there are significant differences between the heat capacity of the glasses and the so-called expanded crystals with the same mean or harmonic mean force constants as discussed in section 3 suggests that a significant portion of the difference curves arises from disordering alone.

Second, the approximation to the glass of an "expanded" crystal with the same mean force constant as the glass seems to be a lower bound to the heat capacity of the glass; the "expanded" crystal with a force constant which is the harmonic mean of the force constants of the glass seems to be an upper bound to the heat capacity of the glass. This idea is born out by all the runs we have made. Furthermore, these results are indicated by the methods used in this paper. For any distribution of force constants, the harmonic mean must be less than the arithmetic mean. The low temperature heat capacity is linearly related to the harmonic mean force constant from Domb's expansion and the high temperature heat capacity is linearly related to the arithmetic mean force constant by use of moment expansion. Thus while we cannot predict what happens in the middle, the limits are consistent with these bounds. While the lack of a low frequency

expansion in three dimenions leaves part of the argument open, these bounds probably still will apply.

Third, the approximation scheme presented in eq (16) is available for even three dimensions. As we mentioned before, the choice of lattice structures for the crystal structures which make up the approximation to the glass is open to question. Since there is no series expansion presently available, either for high or low temperatures for a three dimensional glass, we have no way presently to check such a scheme in three dimensions. Even with all these drawbacks it would seem like it is a sensible scheme to try for three dimensional models of glasses.

Fourth, we propose that the negative heat capacity differences between glasses and other crystals as displayed at higher temperatures in figures 4 and 5 and about 50 K beyond the low temperature peak in experimental data lead one to some hypothesis on the structure of the glass. Specifically we suggest that systems which show regimes of negative heat capacity differences between the glass and the crystal following the low temperature peak must have regions in the glass itself which have higher force constants than the crystal. This furthermore suggests that these glasses are Bernal-like glasses—that is, glasses that have non-propagating structures in the glass which are of higher density and stronger force constants than the crystal. If this proposal is true we are led to the surprising conclusion that thermal measurements can tell us something about the detailed structure of the glass. This hypothesis follows straightforwardly from the data presented in this paper. We shall develop the argument in the following paragraphs.

It is seen from figures 2 to 8 that not all the systems which have force constants greater than that of the crystal have negative heat capacity difference regimes. In fact we pointed out before that the negative heat capacity regime at higher temperatures will occur only if the mean force constant of the glass is greater than that of the crystal; the low temperature peak will occur if the harmonic mean force constant of the glass is greater than that of the crystal. The second condition is obeyed by all our models. This is true, since in one dimension the harmonic mean force constant is the bulk modulus of the material. Since we assume that all glasses are softer than their crystals, we always assume the second condition. The first condition doesn't necessarily hold if the second holds since the mean force constant must be greater than the harmonic mean force constant. In fact a simple inspection of the harmonic mean and the mean force constant for the models we have used will convince the reader that the mean force constant may be either above or below that of the crystal. We are thus led to the idea that when there is no negative regime in heat capacity differences between glasses and their crystals we know little about the structure of the glass. However, when there is a temperature regime where the glass has a lower heat capacity than the crystal we may say that the glass has some force constants which are stronger than the crystal.

Three caveats need be made about the above arguments. First, the argument is only for one dimensional systems and might not necessarily hold for three dimensional systems. In a future paper we shall show that an almost equivalent statement may be made for three dimensional glasses. Second, we have not included the effect of thermal expansion in the argument. As we noted previously a subsequent paper will discuss thermal expansion effects in one dimensional disordered systems to get an accurate idea of these effects.

Suffice it to say here that in general thermal expansion effects on the heat capacity (either C_p or C_v) should not affect the general nature of the above arguments. Finally, the above arguments hold only if taking the difference between the glass and the crystal truly subtracts out the effects of molecular force constants on heat capacity. Clearly these effects should be small at these temperatures. However, for the above arguments to hold, any effects from these must be small or in a sense similar to the effects we have computed.

Appendix A: Computational Problems

As in Wheeler and Gordon [2], we find an extra difficulty involved in evaluating the free energy. The free energy F can be rewritten as [2]

$$F/n\hbar\omega_M = -\tau ln\,\tau + \tau \int_0^1 ln(w)g(w)dw \\ + \tau \int_0^1 [ln\,\frac{sinh\,(w/2\tau)}{(w/2\tau)}\,g(w)dw]. \qquad (A1)$$

In this expression, only the second term causes any difficulty, although it has to be evaluated only once. The presence of the logarithm causes any integrator with weight at $x = 0$ to diverge, thus only an upper bound can be calculated. Wheeler and Gordon's scheme of estimating this term from the other two does not work too well in one dimension since $F = U_o + 0\,(\tau^2)$ as $\tau \to 0$ rather than $0\,(\tau^4)$ as in three dimensions, so that the slope of the sum of the other two does not give much help except as a check. Therefore, the upper bound was studied for different distributions of two force constants of the form of eq (7) as w_C was varied. Also the results for the monotonic chain were compared to the exact answer ln 0.5. For all cases but one the integral showed an uncertainty in the sixth significant figure. Thus, the free energies for these cases are uncertain to a term proportional to τ of magnitude $10^{-6}\,\tau$. The only exception was the two mass case, mass ratio 6 to 1, with 0.9 of the masses the light ones. Here, because the series could not be carried for large w_C, the uncertainty may be as large as $10^{-4}\,\tau$. Also, for the reasons indicated below, the logarithmic intergral may not be a rigorous upper bound.

The 6 to 1 mass case with 0.9 light masses has been used as an example of a difficult case. Unlike the other cases studied, the K_i as defined in eq (9) do not for this case decrease as a function of i but rather increase. In fact, the K_i become large enough so that the second term of eq (8) becomes negative. This raises serious questions as to the convergence of the series; one cannot now guarantee that $g'(w)$ as defined in eq (7) is always positive. However, our method is such as to generate only positive g'.

The difficulty was demonstrated when we tried to generate integrators for eq (7) for increasing values of w_C. We could not form an integrator for $w_C > 0.4$ and for $w_C = 0.4$, the weight at $w = 0$ was very small. When the polynomial expansions for $g(w)$ were examined, $g_L(w)$ seemed to be greater than $g(w)$ for w near 0.3 but the ripple in the calculation made determination of the difference uncertain.

To study a precise case with a known error, we considered the $g_L(w)$ for the monatomic chain with

$$g_L(w) = 1/\pi(2 + w^2 + 3.5w^4). \qquad (A2)$$

We have purposefully increased the term in w^4 as it is the next unknown term in $g(w)$ for the 6 to 1 case and such a choice makes $g'(w)$ negative in a known manner. The integrators behaved for this case in a manner similar to the integrator for the 6 to 1 case and the g' had a negative region that was similar in magnitude to the ripple displayed in the polynomial expansion for the 6 to 1 case. The errors in the thermodynamic functions from the erroneous monoatomic chain distribution were used to gauge the errors we were making for the 6 to 1 case.

For example, we computed the heat capacity for a monatomic chain using eq (A2) and $w_C = 0.4$. This value of w_C is close to the maximum value for which we could form an integrator. In terms of the six significant figures we computed, the lower bound was higher than the correct value of the heat capacity in the least significant figures by 21, 279, 25, 6, 2 for $\tau = .02, .04, .08, .1$ respectively. Above $\tau = 0.1$, the bounds converged to six significant figures in the correct answer. Both the free energy and total energy were well behaved. If we went to $w_C = .3$ then the heat capacity lower bound was high only at $\tau = .04$ by 16. Therefore, we restructed w_C to 0.3 for the 6 to 1 case and expect to commit errors of the same magnitude which are insignificant for our purposes.

We will not display any of the results for the free energy or energy functions since they are very smooth functions that monotonically decrease and increase respectively. They will be displayed and used in a later paper.

Appendix B: The Frequency Spectra

The purpose of the present work was to compute the thermodynamic functions of disordered systems, not the frequency spectra. However, since so much work has been done on frequency spectra of one dimensional disordered systems it is of some interest to see if these techniques compute the spectra properly.

The only spectra that the moments define are delta function spectra corresponding the Gaussian integrators that are derived from them [18]. Since the delta function spectra are not too useful for giving an idea of the spectrum, we have used orthogonal polynomial expansions to derive representations of the spectra. These expansions will be the most rapidly convergent sequences possible having the proper first n moments.

We used two different expansions. For the first, we used an expression in terms of Chebyshev polynomials of the first kind, following Wheeler [23]. For a monatomic chain this gives the exact answer in one term since the expansion is

$$g(w) = \frac{1}{\pi\sqrt{1 - w^2}} \sum_{n=1} a_n T^*_n\,(w^2) \qquad (B1)$$

where T^*_n is the shifted Chebyshev polynomial. No use of the low frequency expansion was necessary or used since the use of Chebychev polynomials assumes the proper leading term. The other method used was an expansion in Legendre polynomials, P^*_n, similar in manner to Lax and Lebowitz [24]. Since only the even moments of the spectrum are

known, one actually determines $G(w^2)$ where $G(w^2)\,dw^2 = 2wg(w)dw$. In one dimension there is the known singularity of $G(w^2)$ at the origin. This was subtracted out by the use of eq (8) as

$$G^+(w^2) = G(w^2) - \frac{1}{2w}g_L(w) + \frac{2w_M}{w_H}g_L(.25\,w_H/w_M), \quad \text{(B2)}$$

$$w < .25\,w_H/w_M$$

$$G^+(w^2) = G(w^2), \; w > .25\,w_H/w_M.$$

This definition of $G^+(w^2)$ was used to avoid any sharp breaks in G^+ and minimize oscillations in the fit. For all spectra the subsidiary conditions $G^+(w^2) = 0$ for $w = 1$ and $G^+(w^2) = 2\,\dfrac{w_M}{w_H}\,g_L\left(.25\,\dfrac{w_H}{w_M}\right)$ for $w = 0$ were employed as in Lax and Lebowitz. Only in the two mass case with a mass ratio of 6 to 1 was this not possible due to a singularity at $w = 1$, as evidenced by strong oscillations in the fitted spectrum. For this case, the subsidiary conditions were not employed at $w = 1$.

The results of some spectra fits are shown in figures 12 to 14. Both the Chebyshev and Legendre fits were similar with the Legendre fits being a little smoother and having a little less ripple. Thus we show three examples of the Legendre polynomial fits in figures 12 to 14.

In figure 12, for the case of a uniform distribution of force constants between the relative limits of 5/3 to 1, we have superimposed the results of Dean [6] which were presented as a histogram. It can be seen that the Legendre polynomial expansion is as good as the histogram, which was based on an 8000 unit chain for most of the spectrum. Only for large w where the spectrum falls rapidly does the Legendre expansion have any difficulty. Since the final 11 moments and two subsidiary conditions use polynomials up to degree 12, there is a limit as to the maximum decay rate of the spectrum. The compensation for this is shown in the small negative region of the expansion for $w > 0.9$. As in all the spectra displayed and computed, the expansions always have
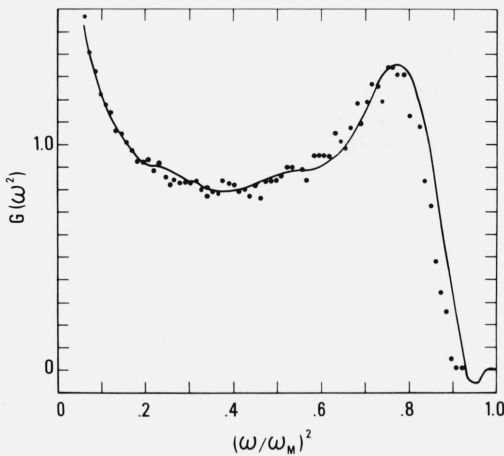
the proper first 11 moments. The spectrum in figure 13 for the uniform distribution of force constants with a 3 to 1 limit ratio has a smoother fall off at high frequencies and, while we do not superimpose Dean's results, the fit is now uniformly better. That is, the spectrum has a much smaller negative region at high frequencies.

The limits to spectral knowledge can be seen in figure 14 for the two mass chain with mass ratio 2 to 1. If this spectrum was plotted as g(w) then it would strongly resemble the smoothed spectrum of Domb, Maradudin, Montroll and Weiss [15]. As shown by Payton and Visscher [10], this spectrum should go to zero very steeply at $w = 0.5$ and thereafter there are many spikes and zeros in the spectrum. The results using Legendre polynomials cannot change so rapidly and hence only dips at $w = 0.5$ and gives a smoothed average thereafter. We did try to force a zero at $w = 0.5$ by a subsidiary condition and the use of polynomials up to 14th degree, but strong oscillations resulted so no meaningful
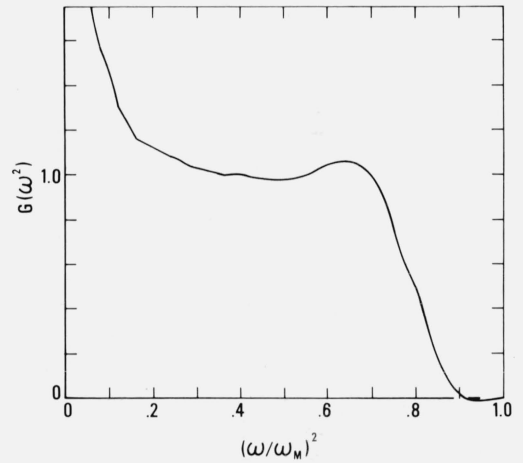
FIGURE 13. *The spectrum for a chain with a uniform distribution of force constants between the limits of 1 and 3 computed from Legendre polynomials.*
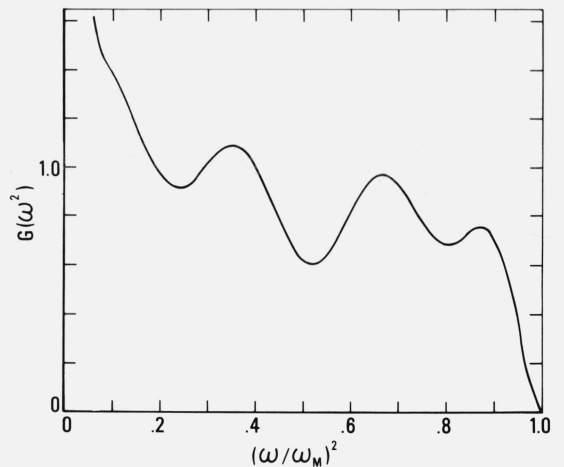
FIGURE 12. *The spectrum for a chain with a uniform distribution of force constant (Dean glass) between the limits of 1 and 5/3 computed from Legendre polynomials.*
The points are for a chain of 8000 units obtained by Dean [9].

FIGURE 14. *The spectrum for a chain having equal fractions of two randomly distributed masses with mass ratio 2 to 1.*

result was obtained. This was also evidenced by the large coefficient for P_{14}^*. Due to the rapidly changing magnitude of the spectrum it would take many higher moments to even begin to characterize the spectrum. Fortunately, it is seen that this is not true for the thermodynamic quantities.

Appendix C: Low and High Temperature Behavior for Heat Capacity Difference Curves

I. Low Temperature Expansions

Domb [6] has shown that for a one dimensional disordered chain the expansion in terms of frequency ω of the frequency spectra $g(\omega)$ is to zeroth order in ω.

$$g(\omega) = \frac{2}{\pi}\left(\frac{m}{N}\sum_{i=1}^{N}\frac{1}{k_i}\right)^{\frac{1}{2}} \tag{C1}$$

where m is the mass of the atom and k_i is the force constant of the ith atom. Domb's equation is in fact for a mass disordered chain. He gives

$$g(\omega) = \frac{2}{\pi}\left(\frac{1}{\gamma N}\sum_{i=1}^{N}m_i\right)^{\frac{1}{2}} \tag{C2}$$

where m_i is the mass of the ith atom and γ is the force constant between species. As we have discussed before, Domb's arguments in ref. [1] show that we may interchange inverse mass and force constants in such one dimensional models. Then to lowest order in temperature the heat capacity of the system becomes

$$C_v = \frac{4NTm^{\frac{1}{2}}}{\pi}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{k_i}\right)^{\frac{1}{2}} \tag{C3}$$

For a crystal like system the lowest order term in temperature then is

$$C_v = \frac{4NTm^{\frac{1}{2}}}{\pi}\left(\frac{1}{k_c}\right)^{\frac{1}{2}} \tag{C4}$$

where k_c is the crystalline force constant.

A. Low Temperature Differences in C_v Between Glasses and Crystals

Now from the above equations the difference between glass and crystal heat capacity at low temperatures, ΔC_v, is

$$\Delta C_v = \frac{4NTm^{\frac{1}{2}}}{\pi}\left[\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{k_i}\right)^{\frac{1}{2}} - \left(\frac{1}{k_c}\right)^{\frac{1}{2}}\right] \tag{C5}$$

Thus at low temperatures the slope of the ΔC_v versus T curve initially depends on the difference between the square root of the harmonic mean force constant of the glass and the square root of the force constant of the crystal. In one dimension the modulus β of the glass at $T = 0$ is given by

$$\beta = \left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{k_i}\right)^{-1} \tag{C6}$$

As long as the glass is viewed as being softer than the crystal — by softer we tend to mean that the modulus of the crystal is less than that of the glass—then at low temperatures ΔC_v will be positive.

B. Approximation Scheme at Low Temperatures

We shall now show that the approximation scheme proposed in equation 16 is a lower bound at low temperatures to the exact heat capacity of the disordered system. The extension of eq (16) to many force constants can be written as

$$C_v^a = \sum_{i=1}^{N} C_v(k_i, T)/N \tag{C7}$$

For low temperature each $C_v(k_c, T)$ may be written from eq (C4)

$$C_v(k_i, T) = \frac{4T}{\pi}\left(\frac{m}{k_i}\right)^{\frac{1}{2}}. \tag{C8}$$

Then the approximate heat capacity is

$$C_v^a = \frac{4T}{\pi}\frac{m^{\frac{1}{2}}}{N}\sum_{i=1}^{N}\left(\frac{1}{k_i}\right)^{\frac{1}{2}}. \tag{C9}$$

By Schwartz's inequality [25]

$$\sum_{i=1}^{N}\left(\frac{1}{k_i}\right)^{\frac{1}{2}} \le N^{\frac{1}{2}}\left(\sum_{i=1}^{N}\frac{1}{k_i}\right)^{\frac{1}{2}} \tag{C10}$$

then

$$C_v^a < C_v \tag{C11}$$

Thus for low temperatures the approximation to heat capacity given by eq (16) is a lower bound to the exact heat capacity of the disordered system.

It is obvious from the discussion in section I-A of this appendix that a crystal with a force constant which has the harmonic mean of the force constant of the glass yields the same low temperature heat capacity as the glass.

II. High Temperature Behavior

By Maradudin et al [15] the high temperature behavior series for C_v is given by

$$C_v = N - \frac{1}{12T^2}\sum_{i=1}^{N}\omega_j^2 \tag{C12}$$

where ω_j are the frequencies for the harmonic system. But it is easy to show for our one dimensional model with mass m and force constants k_j that

$$\sum_{j=1}^{N}\omega_j^2 = \frac{1}{2m}\sum_{j=1}^{N}k_j \tag{C13}$$

Thus

$$C_v = N - \frac{1}{24\,mT^2}\left(\sum_{i=1}^{N} k_i\right) \qquad (C14)$$

In a similar manner the high temperature behavior for a crystalline chain is

$$C_v = N - \frac{N}{24\,T^2 m}\,k_c \qquad (C15)$$

where k_c is again the force constant of the crystal.

A. High Temperature Differences in C_v from Glasses to Their Crystal

Now by eqs C14 and C15 the difference between the heat capacity of a glass and its crystal at high temperatures is given by

$$\Delta C_v = \frac{N}{24\,T^2 m}\left(k_c - \sum_{i=1}^{N} k_i/N\right) \qquad (C16)$$

When the mean force constant of the glass is less than that of the crystal, ΔC_v at high temperatures is positive; when the mean force constant of the glass is greater than that of the crystal ΔC_v at high temperatures is negative. Comparison of values of the mean force constant from table I with figures 4–6 bear out this statement. In fact it would seem from an inspection of these examples and from all others we have run that the high and low temperature series differences discussed in this appendix completely control the appearance of peaks and of positive and negative regions in the ΔC_v curve.

B. Approximation Scheme at High Temperatures

As in eq (C7) the approximation to the heat capacity from section 4 is given by

$$C_v^a = \sum_{i=1}^{N} C_v(k_i,\,T)/N \qquad (C17)$$

Now for high temperature we have then by eq (C13) and the above

$$C_v^a = N - \frac{1}{24\,T^2 m}\sum_{i=1}^{N} k_i \qquad (C18)$$

which is again the exact result for the glass at high temperatures. Thus the approximation scheme yields the correct high temperature heat capacities for the disordered system.

It is obvious from the discussion in IIB of this appendix that a crystal with the same mean force constant as the glass will have the same leading term in temperature as the glass and will thus show the same high temperature behavior as the glass.

6. References

[1] Domb, C. Maradudin, A. A., Montroll, E. W., Weiss, G. H., Phys. Rev. 115, 18 (1959); 115, 24 (1959). We take the opportunity here with the agreement of Professor Domb to note an error in μ_{16} in the notation of the original paper. There is a term that should read 336 ν_3 $\nu_2^2 \nu_1$.
[2] Wheeler, J. C. and Gordon, R. G., J. Chem. Phys. 51, 5566 (1969).
[3] Guttman, C. M., J. Chem. Phys., 56, 627 (1972).
[4] Antoniov, A. A. and Morrison, J. A., J. Appl. Phys. 36, 1873 (1965) and Tucker, J. E. and Reese, W., J. Chem. Phys. 46, 1388 (1967).
[5] Temperley, H. N. V., Rowlinson, J. S., Rushbrooke, G. S., Physics of Simple Liquids, Wiley Interscience Div. New York (1968) see Chapter 6.
[6] Domb, C., Proc. Royal Soc. (London) 276A, 418 (1963).
[7] Weiss, G., Maradudin, A. A., J. Phys. Chem. Solids 7, 327 (1958).
[8] Domb, C., Isenberg, C., Proc. Phys. Soc. (London) 79, 659 (1962).
[9] Dean, P., Proc. Phys. Soc. (London) 84, 727 (1964).
[10] Payton, D. N., Visscher, W. M., Phys. Rev. 154, 802 (1967).
[11] Hindley, N. K., Phys. Rev. 153, 952 (1967).
[12] Leath, P. L., Goodman, B., Phys. Rev. 181, 1062 (1969).
[13] Wu, S., Taylor, P. L., Phys. Rev. 181, 1136 (1969).
[14] Taylor, D. W., Phys. Rev. 156, 1017 (1967).
[15] Maradudin, A. A., Montroll, E. W., Weiss, G. H., Ipatova, I. P., The Theory of Lattice Dynamics in the Harmonic Approximation, 2nd ed. (Academic Press, New York, 1971).
[16] Stevens, R. B., Phys. Rev., 8B, 2896 (1973).
[17] Wheeler, J. C., Blumstein, C., Phys. Rev. 6B, 4380 (1972).
[18] Shohat, J. A., Tamarkin, J. D., The Problem of Moments (American Mathematical Society, Providence, R.I., 1950), American Mathematical Surveys, Vol. 1, 2nd Ed.
[19] Stillinger, E. H., Jr., DiMarzio, E. A., Kornegay, R. L., J. Chem. Phys., 40, 1564 (1964).
[20] Goldstein, M., J. Chem. Phys, 51, 3728 (1969).
[21a] Gibbs, J. H. and DiMarzio, E. A., J. Chem. Phys., 28, 373 (1958).
[21b] Chang, S. S., Bestul, A. B. and Horman, J. A., Proc. Intern. Cong. Glass 7th Brussels, 1965, 26-1.3.1 (1966).
[22] See S. S. Chang, J. A. Horman and A,. B. Bestul, J. Res. Nat. Bur. Stand. (U.S.), Vol. A71, No. 4, 293, (July–Aug. 1967) for an example and references to other work.
[23] Wheeler, J. C., Phys. Rev. A9, 825 (1974).
[24] Lax, M., Lebowitz, J. L., Phys. Rev. 96, 594 (1954).
[25] Abramowitz, M., Stegun, I. A., Handbook of Mathematical Functions, Nat. Bur. Stand. (U.S.), Appl. Math. Series 55, 9th Ed. (1970).