Lattice of Partly Permanent Dipoles

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The electric susceptibility of a lattice of partly permanent dipoles is determined as a function of the temperature and molecular parameters. The calculation is based on the spherical model approximation. The susceptibility has a discontinuous slope at a critical temperature T_c. Numerical techniques are developed for the evaluation of T_c which may have application elsewhere in the statistical theory of lattices. The theory predicts a critical temperature of 98°K for solid hydrogen bromide which corresponds to a measured value of 89°K.

1. INTRODUCTION

IN a previous paper[1] the statistical behavior of a lattice of permanent dipoles was determined to within the spherical model approximation. It was shown that such a model exhibits cooperative behavior and possesses a critical temperature at which the slope of the susceptibility as a function of the temperature suffers a discontinuity. Recent measurements on the susceptibility of solid hydrogen bromide[2] indicate that this material might serve as an appropriate application of the theory; however, most real materials of interest in this respect, possessing a permanent electric dipole moment in crystalline form, in addition have appreciable molecular polarizability. As the calculations on the spherical model presented here bear out, this induced component of the total dipole moment at each lattice site can be expected to modify the cooperative behavior due to the permanent component. We have found that the susceptibility of a lattice of dipoles possessing both an induced and permanent component of electric dipole moment is determined parametrically through the relations,

$$\chi=(t-4\pi L')^{-1} \tag{1.1}$$

$$n\mu^2/3kT=n\alpha(1-n\alpha t)+(1-n\alpha t)^2F(t), \tag{1.2}$$

where n is the volume density of lattice sites, μ the magnitude of the permanent moment, α the polarizability, and L' is a constant whose value depends on the lattice structure. The critical temperature T_c is determined by

$$n\mu^2/3kT_c=n\alpha(1-n\alpha\lambda_M)+(1-n\alpha\lambda_M)^2F(\lambda_M), \tag{1.3}$$

where λ_M is another parameter whose value is fixed by the lattice structure. In Appendix B we have made an estimate of the molecular parameters n, α, and μ which substituted in (1.3) yields a critical temperature $T_c=98$°K. This calculated value compares favorably with the measured value of 89°K given by Brown and Cole.[2] Quantitative predictions of the spherical model require the evaluation of the function $F(t)$ which is defined by an integral of the form

$$F(t)=(1/3)\int\sum_{\alpha=1}^{3}[t-\lambda_\alpha(\mathbf{p})]^{-1}d\mathbf{p}\Big/\int d\mathbf{p}, \tag{1.4}$$

where the region of integration is the unit cell of the reciprocal lattice and the functions $\lambda_\alpha(\mathbf{p})$ are the eigenvalues of a matrix defined by a poorly convergent sum. Since similar integrals seem to arise in other lattice problems, we have described in some detail in an appendix a practical method for the evaluation of this and similar functions. A more detailed discussion of the spherical model theory than is contained here can be found in the references.[1,3]

2. PARTITION FUNCTION

Let $\mathbf{m}_i$ denote the total dipole moment of the ith lattice site,

$$\mathbf{m}_i=\mu\boldsymbol{\varepsilon}_i+\boldsymbol{\eta}_i, \tag{2.1}$$

where $\boldsymbol{\varepsilon}_i$ is a unit vector of arbitrary orientation, μ the magnitude of the permanent moment, and $\boldsymbol{\eta}_i$ the induced component of the total dipole moment. The potential energy of the lattice when interacting with an externally applied electric field E_0 can be put in the form,

$$-U=\tfrac{1}{2}n\sum_{i,j}\mathbf{m}_i\cdot\mathbf{G}_{ij}\cdot\mathbf{m}_j+\sum_i\mathbf{m}_i\cdot\mathbf{E}_0-(2\alpha)^{-1}\sum_i\boldsymbol{\eta}_i\cdot\boldsymbol{\eta}_i, \tag{2.2}$$

where α is the polarizability and n the number of lattice sites per unit volume. The dyadic $\mathbf{G}_{ij}$ is the dipole-dipole interaction matrix given by

$$\mathbf{G}_{ij}=r_{ij}^{-5}[3\mathbf{r}_{ij}\mathbf{r}_{ij}-r_{ij}^2\mathbf{1}], \tag{2.3}$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $r_{ij}=|\mathbf{r}_{ij}|$ and $\mathbf{r}_i$ is the position vector of the ith lattice site measured in units of n.

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[1] M. Lax, J. Chem. Phys. **20**, 1351 (1952).

[2] N. L. Brown and R. H. Cole, J. Chem. Phys. **20**, 1961 (1952); **21**, 1920 (1953).

[3] T. H. Berlin and J. L. Thomsen, J. Chem. Phys. **20**, 1368 (1952).

The partition function for the lattice can be written in the form

$$Q=\int_{\eta_i=-\infty}^{\infty}\cdots 2N\cdots\int_{\epsilon_N=-\infty}^{\infty}e^{-U/kT}\times\prod_{i=1}^{N}\delta(1-\boldsymbol{\varepsilon}_i\cdot\boldsymbol{\varepsilon}_i)d\boldsymbol{\varepsilon}_i d\boldsymbol{\eta}_i. \quad (2.4)$$

Now we have the general result,

$$\int_{-\infty}^{\infty}\cdots N\cdots\int_{-\infty}^{\infty}\exp(\mathbf{x}'\mathbf{A}\mathbf{x}+\mathbf{b}'\mathbf{x})d\mathbf{x}=\pi^{\frac{1}{2}N}[\det A]^{-\frac{1}{2}}\exp(-\tfrac{1}{4}\mathbf{b}'\mathbf{A}^{-1}\mathbf{b}), \quad (2.5)$$

where $\mathbf{x}'\mathbf{A}\mathbf{x}$ is a negative definite quadratic form in N variables $\mathbf{x}$. The integrations over the induced dipole degrees of freedom in (2.4) are of the general form (2.5). The quadratic terms in the $\boldsymbol{\eta}_i$ will be negative definite provided $w=1/n\alpha>\lambda_M$, where λ_M is the maximum eigenvalue of $\mathbf{G}_{ij}$. This maximum value depends on the lattice structure. Assuming this condition to hold on the magnitude of the polarizability and the density of lattice sites, we obtain using (2.5), the following intermediate result for Q.

$$Q=\pi^{\frac{1}{2}N}[\det KG(w)]^{-\frac{1}{2}}\times\exp(-(K/n^2\mu^2))\mathbf{E}_0\cdot\sum_{ij}(\mathbf{G}(w))_{ij}^{-1}\cdot\mathbf{E}_0 \quad (2.6)$$
$$e^{-U'/kT}\prod_i\delta(1-\boldsymbol{\varepsilon}_i\cdot\boldsymbol{\varepsilon}_i)d\boldsymbol{\varepsilon}_i$$

where $K=n\mu^2/2kT$ and we have introduced the notation

$$\mathbf{G}_{ij}(x)\equiv\mathbf{G}_{ij}-x\mathbf{1}\delta_{ij}, \quad (2.7)$$

and set

$$-U'/kT=\exp[K\sum_{ij}\boldsymbol{\varepsilon}_i\cdot(\mathbf{G}_{ij}-\sum_{kl}\mathbf{G}_{ik}\cdot\mathbf{G}_{kl}^{-1}(w)\cdot\mathbf{G}_{ij})\cdot\boldsymbol{\varepsilon}_j+(2/n\mu)\sum_i\boldsymbol{\varepsilon}_i\cdot(\mathbf{1}-\sum_{kl}\mathbf{G}_{ik}\mathbf{G}_{kl}^{-1}(w)\cdot\mathbf{E}_0]. \quad (2.8)$$

Owing to the cyclic character of the dyadic $\mathbf{G}_{ij}=G_{ij}{}^{\mu\nu}$ in its dependence on the particle indices i and j, we may readily reduce $\mathbf{G}_{ij}$ to block form with diagonal elements whose dimension is $D=3m$, where m is the number of particles per unit cell. This partial diagonalization yields the eigenvectors $\mathbf{y}$ and "eigenmatrices" $\boldsymbol{\lambda}$,

$$\mathbf{y}(\mathbf{p})=N^{-\frac{1}{2}}\sum_i e^{-i\mathbf{p}\cdot\mathbf{r}_{ij}}\boldsymbol{\varepsilon}_i \quad (2.9)$$

$$\boldsymbol{\lambda}(\mathbf{p})=\sum_i\mathbf{G}_{ij}e^{i\mathbf{p}\cdot\mathbf{r}_{ji}} \quad (2.10)$$

$$\boldsymbol{\lambda}(\mathbf{p},x)=\boldsymbol{\lambda}(\mathbf{p})-x\mathbf{1}. \quad (2.11)$$

For monatomic lattices, $\boldsymbol{\lambda}(\mathbf{p})$ is a 3×3 matrix and the vector $\mathbf{p}$ ranges over the unit cell of the reciprocal lattice. With the help of these expressions, we may rewrite (2.6) in the alternative form,

$$Q=\pi^{\frac{1}{2}N}\prod_p\prod_a[w-\lambda_a(\mathbf{p})]^{-\frac{1}{2}}\times\exp KN/(n^2\mu^2)\mathbf{E}_0\cdot[w-\boldsymbol{\lambda}(0)^{-1}]\cdot\mathbf{E}_0\times\int e^{-U'/kT}\prod_i\delta(1-\boldsymbol{\varepsilon}_i\cdot\boldsymbol{\varepsilon}_i)\prod_p d\mathbf{y}(\mathbf{p}), \quad (2.12)$$

where U'/kT as a function of $\mathbf{y}(\mathbf{p})$ takes the form

$$-U'/kT=\exp[K\{\sum_p\mathbf{y}(\mathbf{p})\cdot[1-n\alpha\boldsymbol{\lambda}(\mathbf{p})]^{-1}\cdot\boldsymbol{\lambda}(\mathbf{p})\cdot\mathbf{y}^*(\mathbf{p})+2N^{-\frac{1}{2}}/(n\mu)\mathbf{E}_0\cdot[1-n\alpha\boldsymbol{\lambda}(0)]^{-1}\cdot\mathbf{y}^*(0)\}]. \quad (2.13)$$

In the foregoing expressions $\lambda_a(\mathbf{p})$, $a=1, 2, 3$, denotes the three eigenvalues of $\mathbf{y}(\mathbf{p})$. Comparing the expression (2.13) for the case $\alpha\neq0$ with the corresponding expression with α set equal to zero shows that the existence of a finite polarizability results in a modified energy contribution of the pth mode and an effective field

$$\mathbf{E}_0'=\mathbf{E}_0\cdot[1-n\alpha\boldsymbol{\lambda}(0)]^{-1}.$$

The analysis to this point has been without approximation. As is well known, the purely induced dipole lattice problem can be treated in exact fashion employing the methods just outlined in reducing the mixed problem to a modified permanent dipole lattice problem. The difficulties arise in the evaluation of an integral of the type occurring in (2.6). Since the purely induced lattice problem exhibits no transition phenomenon, such cooperative behavior must be attributed to the permanent part of the dipole moment at each lattice site. The spherical model consists of a retreat from the problem just posed to a consideration of an approximating model which is mathematically tractable and which retains at least one essential feature of interest; it displays a predictable transition temperature in the susceptibility.

3. SPHERICAL MODEL

We may regard the original problem of evaluating the integral expressing in (2.6) as the problem of averaging a function of the $3N$ coordinates $\boldsymbol{\varepsilon}_i$ over a $2N$-dimensional subspace of those variables. All of the points of the subspace lie on a sphere of radius $N^{\frac{1}{2}}$, but do not cover it. Formally, the spherical model consists of replacing the average over the $2N$-dimensional subspace by the average over the entire sphere of radius $N^{\frac{1}{2}}$ in the $3N$-dimensional space of the $\boldsymbol{\varepsilon}_i$, whence the name spherical model. We can determine the spherical average by replacing the N constraints represented by the product of delta functions in (2.6) by the single constraint $\delta(N-\sum_i\epsilon_i^2)$. Then, introducing the integral

representation of this delta function,

$$\delta(N-\sum_i \epsilon_i^2)=(K/2\pi i)\times\int_{c-i\infty}^{c+i\infty}\exp[K(N-\sum_i \epsilon_i^2)t]dt, \quad (3.1)$$

we can write the partition function for the spherical model as follows:

$$Q=(K/2\pi i)\int_{c-i\infty}^{c+i\infty} e^{NKt}Q(t)dt \quad (3.2)$$

$$Q(t)=\pi^{\frac{1}{2}N}|K\mathbf{G}(w)|^{-\frac{1}{2}}\exp(-(K/n^2\mu^2)\mathbf{E}_0)\cdot\sum_{kl}\mathbf{G}_{kl}^{-1}(w)\cdot\mathbf{E}_0\int e^{-U''/kT}\prod_l d\boldsymbol{\varepsilon}_i \quad (3.3)$$

$$-U''/kT=K\{\sum_{ij}\boldsymbol{\varepsilon}_i\cdot[\mathbf{G}_{ij}(t)-\sum_{kl}\mathbf{G}_{ik}\mathbf{G}_{kl}^{-1}(w)\mathbf{G}_{lj}]\cdot\boldsymbol{\varepsilon}_j+(2/n\mu)\sum_i\boldsymbol{\varepsilon}_i\cdot[\mathbf{1}-\sum_{kl}\mathbf{G}_{ik}\mathbf{G}_{kl}^{-1}(w)]\cdot\mathbf{G}_0\}. \quad (3.4)$$

The integral (3.4) is now of the standard form (2.5), and after some algebraic manipulation the result of the integration may be stated as follows:

$$Q(t)=K^{-\frac{3}{2}N}\prod^N(1+n\alpha t)/(n\alpha)\prod_p\prod_a[t'-\lambda_a(\mathbf{p})]^{-\frac{1}{2}}\times\exp(KN/n^2\mu^2)E_0\cdot[\mathbf{1}t'-\boldsymbol{\lambda}(0)]^{-1}\mathbf{E}_0, \quad (3.5)$$

where we have put $t'=t/(1+n\alpha t)$. A necessary condition for the convergence of the integral (3.3) is that $t'>\lambda_M$ or equivalently, $t>\lambda_M/(1-n\alpha\lambda_M)$.

We are left with the integration (3.2) over the parameter t, which, owing to the large value of N, can be effected by the method of steepest descent. A transition phenomenon in this formalism is exhibited by the disappearance of a true saddle point in the allowed region of t for which the previous integrals exist.

Putting $Z(t)=\lim_{N\to\infty}Q(t)^{1/N}$, the equation determining the saddle point is

$$d/dt[\ln Z(t)+Kt]=0 \quad (3.6)$$

which can be put in the form

$$(n\mu^2/3kT)[1-\{\mathbf{E}_0\cdot[\mathbf{1}t'-\boldsymbol{\lambda}(0)]^{-1}(1-n\alpha t')/(n\mu)\}^2]=n\alpha(1-n\alpha t')+(1-n\alpha t')^2\langle(\mathbf{1}t'-\boldsymbol{\lambda})^{-1}\rangle. \quad (3.7)$$

The bracket symbol appearing in the above expression is defined as follows:

$$\langle(\mathbf{1}t'-\boldsymbol{\lambda})^{-1}\rangle\equiv(1/3)\sum_a\int[t'-\lambda_a(\mathbf{p})]^{-1}d\mathbf{p}\Big/\int d\mathbf{p}. \quad (3.8)$$

Now, the root t_s' of the saddle point equation is a function of the parameters T, $\mathbf{E}_0$, α, etc. If t_s' $(T, \mathbf{E}_0, \cdots)$ $>\lambda_M$, a true saddle point exists in the allowed region of the t plane. It was shown in *I* that, for such values of the parameters, then in the $\lim_{N\to\infty}$, the partition function is given by $Z=Z(t_s')$, $t_s'>\lambda_M$, whereas, for all values of the parameters leading to a root $t_s'<\lambda_M$, $Z=Z(\lambda_M)$. Having thus determined Z, the polarization $\mathbf{P}$ is given in the usual way

$$\begin{aligned}\mathbf{P}&=nkT\partial\ln Z/\partial\mathbf{E}_0\\&=[\mathbf{1}t_s'-\boldsymbol{\lambda}(0)]^{-1}\cdot\mathbf{E}_0 \quad t_s'>\lambda_M\\&=[\mathbf{1}\lambda_M-\boldsymbol{\lambda}(0)]^{-1}\cdot\mathbf{E}_0 \quad t_s'<\lambda_M.\end{aligned} \quad (3.9)$$

The susceptibility tensor, $\boldsymbol{\chi}$, defined by $\mathbf{P}=\boldsymbol{\chi}\cdot\mathbf{E}$, where $\mathbf{E}$ is the field at an interior point of the specimen, $\mathbf{E}=\mathbf{E}_0-4\pi\mathbf{L}$, and $\mathbf{L}$ is the depolarization tensor which depends on the shape of the specimen, by comparison with (3.9), is given by

$$\begin{aligned}\boldsymbol{\chi}&=[\mathbf{1}t_s'-\boldsymbol{\lambda}(0)-4\pi\mathbf{L}]^{-1} \quad t_s'>\lambda_M\\\boldsymbol{\chi}&=[\mathbf{1}\lambda_M-\boldsymbol{\lambda}(0)-4\pi\mathbf{L}]^{-1} \quad t_s'<\lambda_M.\end{aligned} \quad (3.10)$$

But $\boldsymbol{\lambda}(0)$ is a lattice sum whose distant terms contribute a shape dependent tensor $-4\pi\mathbf{L}$; hence, $\boldsymbol{\lambda}(0)+4\pi\mathbf{L}=4\pi\mathbf{L}'$, is a shape independent tensor depending only on the lattice structure. As required then,

$$\boldsymbol{\chi}=[\mathbf{1}t_s'-4\pi\mathbf{L}']^{-1} \quad (3.11)$$

is a tensor independent of the shape of the specimen.

It is evident that for fixed values of all parameters except the temperature, the function $\boldsymbol{\chi}=\boldsymbol{\chi}(T)$ suffers a discontinuity in slope at a critical temperature determined by $t_s'=t_s'(T_c)=\lambda_M$, where T_c depends on the values assigned the remaining parameters.

4. COMPARISON WITH THE ONSAGER THEORY

The spherical model bears an interesting but seemingly accidental relationship to the theory developed by L. Onsager for polar liquids.[4] We have made the comparison in a way that we now describe.

If one retains only the zero-order terms in the electric field $\mathbf{E}_0$, the saddle points equation (3.7) reduces to the following

$$(n\mu^2/3kT)=n\alpha(1-n\alpha t')+(1-n\alpha t')^2F(t'), \quad (4.1)$$

where we have further shortened the notation by setting

$$F(t')=(1/3)\sum_a\int[t'-\lambda_a(\mathbf{p})]^{-1}d\mathbf{p}\Big/\int d\mathbf{p}. \quad (4.2)$$

A final determination of the susceptibility of the spherical model as a function of the temperature requires a numerical evaluation of the function $F(t)$ which is a three-dimensional integral over the unit cell of the reciprocal lattice whose integrand must be obtained from a poorly convergent lattice sum. This involves considerable labor, as will be apparent on examination of the appendices where we have outlined

[4] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

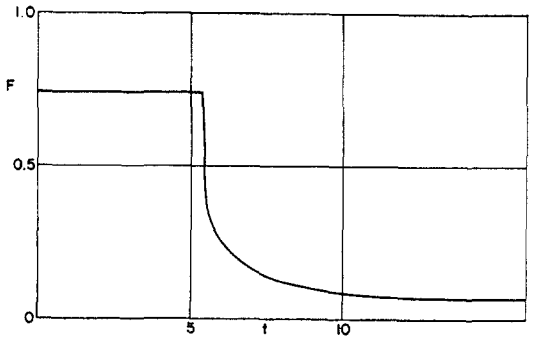

FIG. 1. The function $F(t)=\langle(t-\lambda_\alpha(p))^{-1}\rangle$ that appears in the spherical model saddle point equation (3.7).

the numerical techniques developed for this purpose. However, if we make the crude approximation that the three eigenvalue branches $\lambda_\alpha(\mathbf{p})$ are constants as $\mathbf{p}$ ranges over the unit cell, the averages are obtained trivially. Let us choose the constant values

$$\lambda_1(\mathbf{p})=4\pi/3, \quad \lambda_2(\mathbf{p})=4\pi/3, \quad \lambda_3(\mathbf{p})=-8\pi/3, \quad (4.3)$$

where the constants are such that the eigenvalues agree with the simple cubic values if $|\mathbf{p}|\ll 1$. The spectrum (4.3) implies that

$$F(t')=(2/3)(t'-4\pi/3)^{-1}+(1/3)(t'+8\pi/3)^{-1}. \quad (4.4)$$

Rewriting (3.11) in terms of the dielectric constant, $\epsilon=4\pi\chi+1$, (3.11) takes the form

$$(4\pi/3)(\epsilon+2)/(\epsilon-1)=t'. \quad (4.5)$$

Setting $\mu=0$ in the saddle point Eq. (4.1) requires, for this case, that $1-n\alpha t'=0$, and this in turn by (4.5) implies that the dielectric constant of the purely induced lattice has a value ϵ_∞ given by

$$(\epsilon_\infty-1)/(\epsilon_\infty+2)=4\pi n\alpha/3. \quad (4.6)$$

This is the well-known Clausius-Mosotti law. It should be noted that (4.6) follows independently of the form of $F(t)$. Combining (4.5) and (4.6) with the saddle point condition (4.1), and using (4.6) to eliminate $n\alpha$, we find

$$4\pi n\mu^2/9kT=(\epsilon-\epsilon_\infty)(2\epsilon+\epsilon_\infty)/\epsilon(\epsilon_\infty+2)^2. \quad (4.7)$$

This result is identical to that of Onsager's for the polar liquid.

5. COMPARISON WITH EXPERIMENT

Employing the numerical techniques outlined in appendices A and B, we have carried out the numerical work on the simple cubic lattice. Figure 1 is a graph of the function $F(t)$, where the function

$$F(t)=0.73-0.53((t-5.35))^{\frac{1}{2}}, \quad t\sim 5.35$$

was fitted smoothly onto the asymptotic form of F,

$$F(t)=(t+9.68)^{-1}[1+(t+9.68)^{-1}+110.58(t+9.68)^{-2}+1356(t+9.68)^{-3}], \quad t\gg 5.35.$$

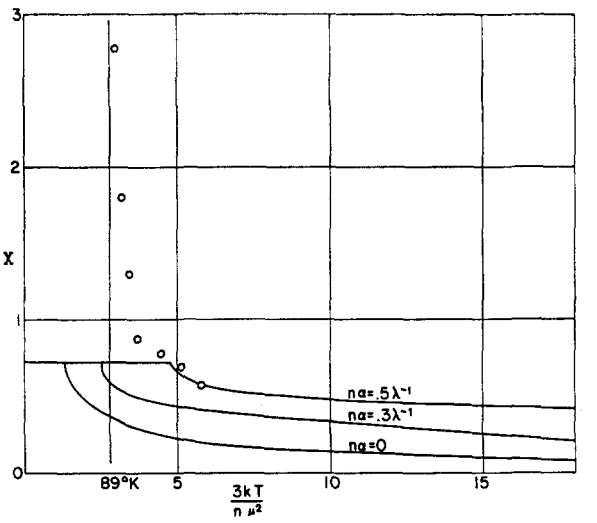

FIG. 2. The susceptibility χ of the simple cubic spherical model as a function of temperature for various values of the ratio $(n\alpha/\lambda_\mu)$. The circles are according to the experimental data of Brown and Cole on solid hydrogen bromide.

Unfortunately, there does not seem to be any experimental data available for a simple cubic dipolar crystal. Extensive measurements have been made by Brown and Cole[2] on HBr, an orthorhombic structure with three axes 5.555, 5.64, and 6.063 that belongs to the space group V_h^{23}. In order to get a qualitative comparison between experiment and theory we whall calculate the dielectric constant *versus* temperature for a simple cubic lattice which has the same value of $n\alpha$ and the same permanent moment μ as HBr.

We estimated the material parameters $n\alpha$ from the data of Brown and Cole,[2] where the extrapolated dielectric constant at infinite frequency, ϵ_∞, fixes the value of $n\alpha$ through the relation

$$n\alpha=3(\epsilon_\infty-1)/4\pi(\epsilon_\infty+2).$$

Setting $\epsilon_\infty=2.35$, we get $n\alpha=0.074$. Then, taking the value $\mu=0.85$ debye units for the permanent moment as deduced from the gaseous dielectric constant of HBr, we are able to calculate a value of the critical temperature from (1.3). We find this calculated value to be $T_c=98.3K$. This is to be compared with the experimental value for the dielectric transition temperature of solid HBr found by Brown and Cole, $(T_c)_{\text{exp}}=89K$. Figure 2 is a graph of the susceptibility as a function of the dimensionless parameter $3kT/n\mu^2$ for various values of $n\alpha$. The experimental data of Brown and Cole are also plotted in these units for comparison.

We see that the theory does not predict as sharp a rise in the susceptibility as $T\to T_c$ from above as was observed experimentally. Below the critical temperature, the experimental susceptibility shows an equally rapid drop. The present theory shows a constant susceptibility below the Curie temperature. The latter result is an error in the spherical model that can be

corrected by calculating the molecular field in the spherical model and treating the dipole on which it acts correctly.[5] The resulting susceptibility, in accordance with section 6 of reference 5, would show a lambda-type behavior near the critical point.[6] The general conclusion will remain valid, however, that the experimental susceptibility exhibits a sharper peak than can be obtained from spherical model theory, even with the molecular field modification.

APPENDIX A

We describe in this Appendix the techniques we have used to determine the function $F(t)$ defined by

$$F(t)=(1/3)\sum_{a=1}^{3}\int[t-\lambda_a(\mathbf{p})]^{-1}d\mathbf{p}\Big/\int d\mathbf{p}. \quad \text{(A1)}$$

The region of integration is the unit cell of the reciprocal lattice and the functions $\lambda_a(\mathbf{p})$ are the three eigenvalues of the matrix defined by

$$\mathfrak{\lambda}(\mathbf{p})=\sum_i \mathbf{G}_{ij}\exp[i\mathbf{p}\cdot\mathbf{r}_{ji}]. \quad \text{(A2)}$$

A brief discussion of Ewald's method of summing this poorly convergent sum is given in Appendix B. Let $I(\mathbf{p},t)$ denote the integrand in (A1),

$$I(\mathbf{p},t)=\sum_a[t-\lambda_a(\mathbf{p})]^{-1}. \quad \text{(A3)}$$

Let λ_m denote the minimum eigenvalue so that $\lambda_a(\mathbf{p})\geqslant\lambda_m$ for all $\mathbf{p}$, and as before let $\lambda_a(\mathbf{p})$ be everywhere less than or equal to λ_M. For all $t>\lambda_M$ we have a convergent power series for $I(p,t)$ given by

$$I(\mathbf{p},t)=[t-\lambda_m]^{-1}\sum_{a=1}^{3}\sum_{n=0}^{\infty}\left[\frac{\lambda_a(\mathbf{p})-\lambda_m}{\lambda_M-\lambda_m}\right]^n\left[\frac{\lambda_M-\lambda_m}{t-\lambda_m}\right]^n. \quad \text{(A4)}$$

The asymptotic behavior of $F(t)$ for $t\gg\lambda_M$ is determined by the integrals of the leading terms in (A4). We have then

$$F(t)=[t-\lambda_m]^{-1}\sum_{0}^{\infty}A_n[t-\lambda_m]^{-n}, \quad \text{(A5)}$$

where

$$A_n=1/3\int\sum_a[\lambda_a-\lambda_m]^n d\mathbf{p}\Big/\int d\mathbf{p}. \quad \text{(A6)}$$

The coefficients A_n can be reduced to the form

$$A_n=\sum_{j=0}^{n}[n!][(n-j)!j!]^{-1}(-\lambda_m)^j a_{n-j}, \quad \text{(A7)}$$

where the a_n's are given by

$$a_k=(1/3)\int tr\mathfrak{\lambda}^k(\mathbf{p})d\mathbf{p}\Big/\int d\mathbf{p}. \quad \text{(A8)}$$

Inserting the definition of $\mathfrak{\lambda}(\mathbf{p})$ from (A2), we verify that the a_k's are equivalent to cluster sums having the form

$$a_k=(1/3)\sum_{ij\cdots ml}\mathbf{G}_{ij}\cdots\mathbf{G}_{ml}\cdot\mathbf{G}_{li}. \quad (k \text{ factors}) \quad \text{(A9)}$$

Sums of this type occur in the high temperature approximation to the dipole lattice partition function. Values of the first three a_k's for a simple cubic lattice are given by R. Rosenberg and M. Lax.[7] They find that for this case, $a_0=1$, $a_1=0$, $a_2=16.8$, $a_3=38.7$. Also, for the simple cubic lattice $\lambda_m=-9.68$. Using this data, and (A5)–(A7), we obtain an asymptotic formula for $F(t)$ consisting of the first four terms in the series (A5) which yields accurate values of F for sufficiently large t.

In order to determine $F(\lambda_M)$ and the behavior of $F(t)$ for $t\sim\lambda_M$, we have integrated (A1) numerically. Since the integrand $I(\mathbf{p},\lambda_M)$ is singular at all points $\mathbf{p}$ where $\lambda_a(\mathbf{p})$ takes on its maximum value, we have used the following device to facilitate the numerical integration. We have expressed F in the form

$$F(t)=1/3\int(I-I_A)d\mathbf{p}\Big/\int d\mathbf{p}+1/3\int I_A d\mathbf{p}\Big/\int d\mathbf{p}, \quad \text{(A10)}$$

where the function $I_A(\mathbf{p},t)$ is chosen so that the difference $(I-I_A)$ remains finite at all points $\mathbf{p}$ as $t\to\lambda_M$. The first integral in (A10) was evaluated using a three-dimensional analog of Simpson's rule. The function I_A was chosen so that the second integral in (A10) could be evaluated by a special technique which we shall describe later. For the simple cubic lattice, the region of integration is the cube bounded by the planes $p_1=\pm\pi$, $p_2=\pm\pi$, $p_3=\pm\pi$; however, owing to the cubic symmetry, it is sufficient to average over the first octant of this cube. For the purpose of the numerical integration, the integrand $(I-I_A)$ was evaluated at each of the points $(R_1\pi/4, R_2\pi/4, R_3\pi/4)R_i=0,1,2,3,4$. The function $I_A(\mathbf{p},t)$ was constructed as follows: At each of the points $\mathbf{p}_x$, $\mathbf{p}_1=(\pi,\pi,0)$, $\mathbf{p}_2=(\pi,0,\pi)$, $\mathbf{p}_3=(0,\pi,\pi)$, there is one branch $\lambda_a(p)$, $a=3,2,1$, of the eigenvalue spectrum which attains the maximum simple cubic value of $\lambda_M=5.35$. It is for these values of $\mathbf{p}$ and the corresponding values of a, that taking the limit $t\to\lambda_M$ leads to a divergent series (A4). The coefficients $[(\lambda_a(p)-\lambda_m)/(\lambda_M-\lambda_m)]^n$ of the terms in this series for these values of $\mathbf{p}$ and a and for $n>3$ were proximated by a three-dimensional Gaussian functions whose matrices of second-order partial derivatives were made to coincide with the second-order derivatives of the actual coefficients in the series. Let $\lambda_{x,\mu\nu}$ denote the second-order partial derivatives $\partial^2\lambda_x/\partial p^\mu\partial p^\nu\,|_{\mathbf{p}=\mathbf{p}_x}$ where $\lambda_x(\mathbf{p})$ is that branch of the eigenvalue spectrum which

[5] M. Lax, Phys. Rev. **97**, 629 (1955).

[6] Such a λ-type behavior was first obtained by J. H. van Vleck, J. Chem. Phys. **9**, 85 (1941) using a molecular field approach.

[7] R. Rosenberg and M. Lax, J. Chem. Phys. **21**, 424 (1953).

attains the maximum value λ_M at the point $\mathbf{p}_x$. Let us further condense the notation by setting

$$S_a(\mathbf{p},t)=(\lambda_a(\mathbf{p})-\lambda_m)/(t-\lambda_m) \quad \text{(A11)}$$

$$\sigma_x(\mathbf{p},t)=[(\lambda_M-\lambda_m)/(t-\lambda_m)]\exp W_x(\mathbf{p},t), \quad \text{(A12)}$$

where

$$W_x(\mathbf{p},t)\equiv\lambda_{x,\mu\nu}(p^\mu-p_x{}^\mu)(p^\nu-p_x{}^\nu)/2(t-\lambda_m). \quad \text{(A13)}$$

We then have

$$I_A=(t-\lambda_m)^{-1}[\sum_a\sum_{n=0}^{3}S_a{}^n+\sum_x\sum_{n=4}^{\infty}\sigma_x{}^n] \quad \text{(A14)}$$

and

$$I-I_A=(t-\lambda_m)^{-1}\times[\sum_a S_a{}^4/(1-S_a)-\sum_x\sigma_x{}^4/(1-\sigma_x)]. \quad \text{(A15)}$$

Now put

$$F(t)=L(t)+M(t)+N(t), \quad \text{(A16)}$$

where $L(t)$ is the contribution to F from the finite sum in (A14), $M(t)$ is the contribution to F from the infinite sum in (A14) and $N(t)$ is the contribution to F obtained by numerical integration of $I-I_A$. We have already indicated how the function $L(t)$ which determines the asymptotic behavior of F can be determined in terms of the first few moments (A8) and (A9) of the eigenvalue spectrum of the dipole interaction tensor $\mathbf{G}$. We now describe how the function $M(t)$ can be determined. $M(t)$ can be written in the form

$$M(t)=(t-\lambda_m)^{-1}\sum_{n=4}^{\infty}B_n[(\lambda_M-\lambda_m)/(t-\lambda_m)]^n \quad \text{(A17)}$$

where the B_n are given by

$$B_n=(1/3)\pi^{-3}\sum_x\int_0^\pi\int_0^\pi\int_0^\pi\exp[nW_x(\mathbf{p},t)]\times dp^1dp^2dp^3. \quad \text{(A18)}$$

For the simple cubic lattice the matrix $\lambda_{x,\mu\nu}$ of second-order partial derivatives which occurs in the expression (A13) for $W_x(\mathbf{p},t)$ is diagonal with two equal elements. The contribution to B_n is the same for each of the points $\mathbf{p}_x=(\pi,\pi,0)$, $(\pi,0,\pi)$, and $(0,\pi,\pi)$; hence, the sum over x in (A18) is simply three times the result of any one term, say that which corresponds to $\mathbf{p}_x=(\pi,\pi,0)$. This integral factors and we obtain the following expression for B_n:

$$B_n=(t-\lambda_m)^{\frac{1}{2}}[\det\lambda_{x,\mu\nu}]^{-\frac{1}{2}}(2\pi)^{-\frac{1}{2}}E_n{}^1E_n{}^2E_n{}^3n^{-\frac{1}{2}}, \quad \text{(A19)}$$

where the E_n are given by

$$E_n{}^\mu=\operatorname{erf}[\pi\{n\lambda_{x,\mu\mu}/2(t-\lambda_m)\}^{\frac{1}{2}}] \quad \text{(A20)}$$

$$\operatorname{erf}x\equiv(2/\sqrt{\pi})\int_0^x\exp(-u^2)du.$$

As $n\to\infty$, $E_n{}^\mu\to 1$ so that the B_n tend rapidly to their asymptotic value given by (A19) with the $E_n{}^\mu$'s replaced by 1. Now, the dominant *variation* in $F(t)$ as $t\to\lambda_M$ is determined by the series $M(t)$ whose distant terms are a constant multiple of $n^{-\frac{1}{2}}$. Hence, for t in the neighborhood of λ_M, we have made the following approximation to F:

$$\begin{aligned}F(t)&\simeq F(\lambda_M)-C[(t-\lambda_m)-(\lambda_M-\lambda_m)]^{\frac{1}{2}}\\&=F(\lambda_M)-C(t-\lambda_m)^{\frac{1}{2}}\times\sum_{n=0}^{\infty}g_n[(\lambda_M-\lambda_m)/(t-\lambda_m)]^n \quad \text{(A21)}\\&\equiv R(t),\end{aligned}$$

where $g_n\equiv(\frac{1}{2}!)(-1)^n/(\frac{1}{2}-n)!n!$ tends asymptotically to the value $1/(2\pi^{\frac{1}{2}})n^{-\frac{3}{2}}$. The constant C in (A21) was fixed by requiring that the series (A17) and (A21) have the same asymptotic form. This demands that we set $C=(\det\lambda_{x,\mu\nu})/(\sqrt{2}\pi)$.

Finally, the contribution $N(t)$ to $F(t)$ was determined by numerical integration of $I(\mathbf{p},t)-I_A(\mathbf{p},t)$ for the single value $t=\lambda_M$ of the parameter t. This is the most important value of the parameter t since $F(\lambda_M)$ determines the critical temperature. Also, when $F(\lambda_M)$ is substituted in (A21), we obtain good values of F for t sufficiently near λ_M. The two curves $F(t)\simeq R(t)$, $t\sim\lambda_M$ and $F(t)\simeq L(t)$, $t\gg\lambda_M$ can be joined reasonably smoothly to obtain values of F for intermediate values of t. See Fig. 1.

APPENDIX B

Required in the course of the analysis of Appendix A were the values of the dipole matrix elements $\lambda(\mathbf{p})$ and the second derivatives of the branch of the eigenvalue spectrum of this tensor field which attains the maximum value $\lambda_M=5.35$ at the point $(0,\pi,\pi)$ and the eleven other points related by symmetry. The dipole matrix elements were computed by first transforming the poorly convergent sum (2.10) by Ewald's method into the sum of two rapidly convergent sums, one sum over the space lattice and the other sum over the reciprocal lattice. These dipole sums have been calculated for the three cubic structures by M. H. Cohen and F. Keffer. A good survey of the values of $\lambda(\mathbf{p})$ is given in their report.[8] The Ewald form of the dipolar sum is

$$\lambda^{\mu\nu}(\mathbf{p})=S^{\mu\nu}(\mathbf{p})+R^{\mu\nu}(\mathbf{p}), \quad \text{(B1)}$$

where

$$S^{\mu\nu}(\mathbf{p})=4\pi^2\tau^{\frac{3}{2}}{\sum_l}'r_l{}^\mu r_l{}^\nu\varphi_{\frac{3}{2}}(\tau\pi r_l{}^2)\exp[i\mathbf{p}\cdot\mathbf{r}]-2\pi\tau^{\frac{1}{2}}\delta^{\mu\nu}{\sum_l}'\varphi_{\frac{1}{2}}(\tau\pi r^2)\exp[i\mathbf{p}\cdot\mathbf{r}], \quad \text{(B2)}$$

[8] M. H. Cohen and F. Keffer, Sci. Paper 60-94469-2P2, Westinghouse Research Laboratories (1954).

where the r_l^μ are the position vectors to the space lattice sites, the primed sum denoting omission of the term $\mathbf{r}=0$. The $R^{\mu\nu}(\mathbf{p})$ are defined by the following sum over the points b_l^μ of the reciprocal lattice,

$$R^{\mu\nu}(\mathbf{p})=-(V/\tau)\sum_l \varphi_0(R_l^2/4\pi\tau)R_l^\mu R_l^\nu \qquad \text{(B3)}$$

with V equal to the volume of the unit cell, and the vector R_l^μ is defined by $R_l^\mu=(p^\mu-2\pi b_l^\mu)$. The functions φ_m are defined by

$$\varphi_m(x)=\int_1^\infty u^m e^{-ux}du. \qquad \text{(B4)}$$

They satisfy the recurrence relations

$$\varphi_m(x)=\varphi_0(x)+(m/x)\varphi_{m-1}(x) \qquad \text{(B5)}$$

$$d\varphi_m/dx=-\varphi_{m-1}. \qquad \text{(B6)}$$

The value of any φ_m may, by use of the above recurrence relations, be deduced from tabulated functions and

$$\varphi_0(x)=e^x/x \qquad \text{(B7)}$$

$$\varphi_{-1}(x)=-Ei(-x) \qquad \text{(B8)}$$

$$\varphi_{-\frac{1}{2}}(x)=(\pi/x)^{\frac{1}{2}}[1-\operatorname{erf}(x^{\frac{1}{2}})]. \qquad \text{(B9)}$$

The sum, $R^{\mu\nu}+S^{\mu\nu}$, is independent of the value of the parameter τ which is chosen so as to make the two sums converge equally rapidly. The proper choice of τ for the three cubic lattices is listed in a table given in reference 8. For the simple cubic lattice, one may take $\tau=\frac{1}{2}$. The derivatives of an eigenvalue branch were determined as follows: Consider for the moment the general case of a symmetric tensor field $A_{\mu\nu}(\mathbf{p})$ whose rectangular cartesian components in some region R of $\mathbf{p}$ space are assumed to be continuously differentiable functions of the coordinates p_μ. Let λ^a denote the eigenvalues and $y_\mu{}^a$ the corresponding eigenvectors of $A_{\mu\nu}$,

$$A_{\mu\nu}y_\nu{}^a=\lambda^a y_\mu{}^a;\quad y_\mu{}^a y_\mu{}^b=\delta^{ab}. \qquad \text{(B10)}$$

In R let at least one of the eigenvalues, say λ^1, be everywhere distinct (nondegenerate); then it is easily shown that $\lambda_{,\mu}{}^1\equiv\partial\lambda^1/\partial p_\mu$ and $y_{\mu,\nu}{}^1\equiv\partial y_\mu{}^1/\partial p_\nu$ exist. That is, in a region where the elements of the tensor are differentiable functions, a distinct eigenvalue and the components of the corresponding eigenvector of the tensor are differentiable functions. Then differentiating the eigenvalue equation for the distinct eigenvalue λ^1, we get,

$$A_{\mu\nu,\sigma}y_\nu{}^1+A_{\mu\nu}y_{\nu,\sigma}{}^1=\lambda_{,\sigma}{}^1 y_\mu{}^1+\lambda^1 y_{\mu,\sigma}{}^1. \qquad \text{(B11)}$$

From the orthonormality conditions on the eigenvectors, it follows that

$$y_{\mu,\nu}{}^1 y_\mu{}^1=0;\quad \sum_a y_\mu{}^a y_\nu{}^a=\delta_{\mu\nu}. \qquad \text{(B12)}$$

In particular, we use the result $(\text{B12})_2$ in the form

$$\sum_{a\neq 1} y_\mu{}^a y_\nu{}^a=\delta_{\mu\nu}-y_\mu{}^1 y_\nu{}^1. \qquad \text{(B13)}$$

Multiplying (B11) by $y_\mu{}^1$ and summing as indicated, we get, using $(\text{B12})_1$ and (B10),[9]

$$\lambda_{,\sigma}{}^1=A_{\mu\nu,\sigma}y_\mu{}^1 y_\nu{}^1. \qquad \text{(B14)}$$

Let us denote the quantities $A_{\mu\nu,\sigma}y_\mu{}^a y_\nu{}^b$ by the symbols $\Delta_\sigma{}^{ab}$, so that (B14) reads $\lambda_{,\sigma}{}^1=\Delta_\sigma{}^{11}$. Now, multiply (B11) by $y_\mu{}^a$, $a\neq 1$, and sum on a. Then, using (B13), we obtain,

$$y_{\mu,\sigma}{}^1=\sum_{a\neq 1}\Delta_\sigma{}^{1a}y_\mu{}^a/(\lambda^1-\lambda^a). \qquad \text{(B15)}$$

Now, differentiate (B14) and obtain,

$$\lambda_{,\sigma\tau}{}^1=A_{\mu\nu,\sigma\tau}y_\mu{}^1 y_\nu{}^1+2A_{\mu\nu,\sigma}y_\mu{}^1 y_{\nu,\tau}{}^1. \qquad \text{(B16)}$$

Substituting from (B15), this becomes

$$\lambda_{,\sigma\tau}{}^1=\Delta_{\sigma\tau}{}^{11}+2\sum_{a\neq 1}\Delta_\sigma{}^{1a}\Delta_\sigma{}^{1a}/(\lambda^1-\lambda^a) \qquad \text{(B17)}$$

where we have set $\Delta_{\sigma\tau}{}^{ab}=A_{\mu\nu,\sigma\tau}y_\mu{}^a y_\nu{}^b$.

The conditions under which we have derived the above result hold for the dipole tensor field $\mathfrak{A}(\mathbf{p})$ in a region containing the point $(0,\pi,\pi)$. At this point λ^1 is distinct and we have the further simplifying features: (1) $\mathfrak{A}(\mathbf{p})$ is diagonal, hence each $\mathbf{y}^a$ has but a single nonvanishing component; (2) each of the $\Delta_\mu{}^{ab}$ vanishes; (3) $\Delta_{\mu\nu}{}^{11}$ is zero unless $\mu=\nu$. For the case at hand, we then have the simple result,

$$\begin{aligned}&\lambda_{,\mu\nu}{}^1=0\quad \mu\neq\nu\\ &\lambda_{,\mu\mu}{}^1=\lambda_{11,\mu\mu}\quad (\mu=1,\ 2,\text{ and }3).\end{aligned} \qquad \text{(B18)}$$

Furthermore, the second derivatives $\mu=2,\ 3$ are equal.

The derivatives $\lambda_{\mu\nu,\sigma\tau}$ of the components $\lambda_{\mu\nu}$ of $\mathfrak{A}$ can be obtained in rapidly convergent form by differentiating the Ewald formulas (B1)–(B3). This process yields the formulas,

$$\begin{aligned}\lambda_{\mu\nu,\sigma\tau}&=S_{\mu\nu,\sigma\tau}+R_{\mu\nu,\sigma\tau}\\ S_{\mu\nu,\sigma\tau}&=-4\pi^2\tau^{\frac{5}{2}}\textstyle\sum'r_\mu r_\nu r_\sigma r_\tau\varphi_{\frac{5}{2}}(\pi\tau r^2)\exp(i\mathbf{p}\cdot\mathbf{r})\\ &\quad+2\pi\tau^{\frac{3}{2}}\textstyle\sum' r_\sigma r_\tau\delta_{\mu\nu}\varphi_{\frac{3}{2}}(\pi\tau r^2)\exp(i\mathbf{p}\cdot\mathbf{r}),\\ R_{\mu\nu,\sigma\tau}&=-V/(\tau)\textstyle\sum\varphi_0(R^2/4\pi\tau)[\delta_{\mu\sigma}\delta_{\nu\tau}+\delta_{\nu 0}\delta_{\mu\tau}]\\ &\quad+V/(2\pi\tau^2)\textstyle\sum\varphi_1(R^2/4\pi\tau)[\delta_{\sigma\tau}R_\mu R_\nu+\delta_{\mu\tau}R_\nu R_\sigma\\ &\quad+\delta_{\nu\tau}R_\mu R_\sigma+\delta_{\nu\sigma}R_\mu R_\tau+\delta_{\mu\sigma}R_\nu R_\tau]\\ &\quad-V/(4\pi^2\tau^3)\textstyle\sum\varphi_2(R^2/4\pi\tau)R_\mu R_\nu R_\sigma R_\tau.\end{aligned} \qquad \text{(B19)}$$

This general result was then used to obtain the two distinct numbers $\lambda_{11,11}=-2.8$ and $\lambda_{11,33}=0.25$ at the point $(0,\pi,\pi)$. The derivatives of the eigenvalue branch $\lambda_1(\mathbf{p})$ at that point were then known with the aid of the result (B18).

[9] T. Y. Thomas, J. Math. and Phys. **23**, 167 (1944).