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Phase transition in a class of Hamiltonians*

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Abstract. We consider a class of Hamiltonians for a system of one localized spin-$\frac{1}{2}$ particle per lattice site with the total spin as a good quantum number. We introduce a set of conditions in the form of a hypothesis relating the subpartition function, which is the partition function defined by the subset of energies with a specific value of spin. If the equality in the hypothesis is satisfied, then the system undergoes a phase transition as a consequence of Yang-Lee theorem. As an application, we estimate the bounds on the spectrum of the Heisenberg Hamiltonian.

Keywords. Phase transition; Yang-Lee theorem; partition function; Heisenberg Hamiltonian; critical temperature.

1. Introduction

It is well known that only few model Hamiltonians which undergo a phase transition can be solved exactly. Many attempts have been made to construct approximation procedures which provide at least a qualitative understanding concerning the critical region. In either case most of the insight obtained about the mechanism leading to a phase transition is obtained from model oriented analysis, with a notable exception, namely, the analysis of Yang and Lee (1952) (although, the analysis refers to the liquid-gas system). Their analysis tells us the " mathematical mechanism " leading to a phase transition. Briefly, the singularities that appear in the thermodynamic quantities are attributed as arising due to the existence of a finite density of zeros of grand partition function in an arbitrarily small neighbourhood of the positive real fugacity axis. If a line of roots cuts the positive real fugacity axis, then the limiting function $\bar{X} = \lim (1/V) \log \Xi$ has two distinct analytic pieces and $\bar{X}$ is continuous at the point, but the derivative in general has a discontinuity. The corresponding results also hold in the case of canonical partition function (*see* for example Fisher 1965 and Jones 1966). As we will see later, the hypothesis that we use in this paper is motivated from these considerations. We will restrict our considerations to ferromagnetic phase transitions.

The main purpose of the paper is to be able to use the Yang–Lee theorem in some way. This is achieved by introducing a hypothesis which is again motivated

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by the Yang–Lee analysis. Assuming that the hypothesis (for $T = T_c$) holds and by going over to the complex magnetic field plane, we show that there is a line of zeros of partition function closing on to the positive real activity axis in the thermodynamic limit. The form of the Hamiltonian is quite general (except that it represents a ferromagnetic system) and is so chosen that the partition function can be written as a symmetric function in the activity variable with coefficients which depend exclusively on the spectrum at zero magnetic field. The hypothesis relates these coefficients among themselves. The entire analysis is done in section 2. As an application, we estimate bounds on the spectrum assuming that the three-dimensional Heisenberg Hamiltonian undergoes a phase transition. Finally, section 4 contains concluding remarks.

2. Conditions for critical behaviour

Consider a lattice system with one spin–1/2 particle localized on each site. We wish to consider a general Hamiltonian which has a symmetry that enables us to express the partition function as a symmetric function in the activity variable. The Hamiltonian characterizing the interaction may be spin or spin-free (Matsen *et al* 1971) or both. The symmetry property that we require for the Hamiltonian is that it commutes with the total spin of the system, *i.e.*,

$$[H_0, S^2_{\text{tot}}] = 0 \tag{2.1}$$

where

$$S^2_{\text{tot}} = \Big(\sum_i s_i\Big)^2 \tag{2.2}$$

with s_i representing the spin at the site i. The application of a uniform magnetic field h in the z-direction gives rise to the total Hamiltonian

$$H_T = H_0 + H_1 \quad \text{and} \quad [H_T, S^2_{\text{tot}}] = 0 \tag{2.3}$$

with

$$H_1 = g\mu h \sum_{j=i}^{N} s_j{}^z \tag{2.4}$$

where μ is the Bohr magneton and g the gyromagnetic ratio. Then the partition function for such system is

$$Z = \sum_{S}^{N/2} \sum_{M=-S}^{S} \sum_{F=1}^{f^S} \exp\{-\beta E(F, S) - \beta g\mu h M\} \tag{2.5}$$

where $\beta = 1/kT$, F distinguishes among the f^S states with the same S, and M is the eigenvalue of S^z_{tot} in this subspace. Let

$$\gamma_S = \sum_{F=1}^{f^S} \exp\{-E(F, S)/kT\} \tag{2.6}$$

We call γ_S, the sub-partition function. Defining the activity variable

$$z = \exp(\alpha/2) \tag{2.7}$$

with $\alpha = \beta g\mu h$, the partition function (2.5) takes the form

$$Z(z) = \sum_{S}^{n=N\ 2} \gamma_S [z^{2S} + z^{2S-2} + \ldots + z^{-2S}] \tag{2.8}$$

This can be written in the form:

$$Z(z) = \sum_{S}^{n=N/2} \gamma_S \frac{\sinh(S+1/2)\alpha}{\sinh \alpha/2} \tag{2.9}$$

Thus Z is a symmetric function in the activity variable z with the coefficients γ_S which depend exclusively on the spectrum of the system at zero magnetic field. Since the $\gamma_S > 0$ by definition (2.6) [and since $z > 0$ by definition (2.7)], we see that $Z(z)$ has no real positive zeros, and thus Z is analytic in β and z for all finite N. However, in the limit as $N \to \infty$ these complex roots may coalesce into a 'line' of finite density that pinches the real positive z-axis for some value of temperature. If this happens, then by the Yang-Lee theorem this indicates the existence of a phase transition.

We want to consider the behaviour of the system at zero magnetic field ($z = 1$) and we notice that for $z = 1$, Z reduces to $\Sigma \gamma_S (2S + 1)$. So we allow the magnetic field to take on complex values and then let $\mathrm{Re}(h) \to 0^+$. Thus we introduce a variable y by $= z^{iy}$. Since the Re h is zero, $y \in [0, 2\pi]$. With this variable the partition function can be written as

$$Z(y) = \frac{1}{\sin y} \sum_{S}^{n} \gamma_S \sin(2S+1)y \tag{2.10}$$

Let

$$\hat{Z}(y) = \Sigma\, \gamma_S \sin(2S+1)y \tag{2.11}$$

Let us assume that the system undergoes a phase transition at some temperature T_c and that Yang-Lee's criterion is also a necessary condition. (This may not be so, since it has not been shown that if the system undergoes a phase transition then there is a finite density of roots in an arbitrarily small neighbourhood of the real activity axis). Then we know that the free energy per spin is non-analytic at that value $z = z_c$ where the line of zeros cuts the real activity axis and that there are two distinct analytic pieces for real positive values of interest, one to the left of z_c and the other to the right of z_c. Below this temperature any region R containing the real activity axis is free of zeros and therefore the free energy per spin is completely analytic. This is again true for $T > T_c$. But the functional form of the free energy per spin in general is different from the functional form below $T = T_c$. However, the limiting value of the free energy per spin as $T \to T_c^+$ and $T \to T_c^-$ with Re h fixed at Re $h_c + \epsilon$ (where ϵ is arbitrarily small and real), can be expected to be the same. Since the free energy per spin is a function of γ_s and since we expect the functional form of the free energy per spin to be different below and above T_c, we should expect the relation between γ_s and $\gamma_{s'}$ to change across $T = T_c$. Further, at $T = T_c$ we expect that all the γ_s to be the same up to a multiplicative factor which is positive and independent of S and which will be determined later on (*see* Appendix A). (Since we expect the values of free energy per spin for $T > T_c$ and $T < T_c$ to coincide at $T = T_c$).

Thus we are led to consider the following hypotheses.

$$\frac{1}{N}\log\frac{\gamma_S}{\gamma_{S-1}} > \frac{1}{N}\log A_n \qquad \forall\, S \tag{2.12 a}$$

with $\quad A_n > 0 \quad$ for $\quad T < T_c'$

$$-\lim_{n\to\infty}\frac{(E_F - E_A)}{2nkT_c} > -\frac{3}{4}\log n - \frac{1}{4n}\log 2\pi + \log 2$$

or

$$E_F - E_A > -\frac{JN\log 2}{\theta_c} \tag{3.8}$$

Of course $\theta_c = J/kT_c$ differs from crystal to crystal, depending on the lattice structure and dimensionality of the lattice. Thus, by using the critical conditions we are able to obtain an expression for the bounds of the spectrum. For the case of one dimension this result is not meaningful since we know that there is no phase transition. However, if we take the values of θ_c for the F.C.C. the B.C.C. and the S.C. that are estimated from the high temperature expansion, namely, $\theta_c \sim 0{\cdot}24$, $0{\cdot}4$ and $0{\cdot}6$, respectively, we obtain:

$$\frac{E_A - E_F}{N} > \begin{cases} 4J\log 2 & \text{for the F.C.C.} \\ 2{\cdot}5J\log 2 & \ldots \text{B.C.C.} \\ 1{\cdot}666\log 2 & \ldots \text{S.C.} \end{cases} \tag{3.9}$$

4. Summary and discussion

To summarize, we have considered a class of Hamiltonians with S_{tot} as a good quantum number. The partition function for such a system under a uniform applied magnetic field can be written as a symmetric function in z. Since we were interested in the zero magnetic field situation, we let the magnetic field take on complex values and the real part approach zero. By introducing a hypothesis relating the subpartition functions with different values of S we were able to show that when the equality holds, given an arbitrary small neighbourhood about $z = 1$, the number of zeros indefinitely increases in the limit as $N \to \infty$, thus indicating that the system undergoes a phase transition. We then obtained an estimate of the bounds on the spectrum of the Heisenberg Hamiltonian. Unfortunately we are unable to find a model which satisfies our hypothesis.

Thus we have succeeded in using the Yang-Lee's theorem on the mechanism of phase transition. It may be argued that the quantities obtained, namely, γ_s are quite complicated so that not much reduction has been obtained. For this we remark that the main purpose of the analysis is not very much to obtain any reduction of the difficulties involved in the computation of Z (which is altogether a different problem), but to be able to use Yang-Lee theorem to obtain some information about the system. The analysis of the problem may be well appreciated if it is recalled that the Yang-Lee theorem has not been used since its publication (to the best of our knowledge). Further, the analysis of the present problem does indicate how it may be possible to use a similar approach for other problems of the same nature. In addition, if one considers a sequence of groups which commute among themselves and with the Hamiltonian, then depending on the number of Casimir invariants the reduction of Z into quantities similar to γ_s would be greatly enhanced. (A possible example would be a Hamiltonian which is invariant under unitary group in N-dimensions.)

If one wants to consider proving the necessity for the hypothesis one meets with the following formidable problem. Since there are several orders of phase transition, these, in the spirit of the present problem, will have to be related to the

density of zeros at the point where they close onto the real activity axis. This problem is quite open and so the problem of obtaining both necessary and sufficient conditions appears to be quite hard.

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Appendix A

By using the hypothesis and the form of y_1, we will prove that $\bar{Z}$ in an upper bound function of $\hat{Z}$. It is obvious that the sum in (2.11) changes sign as the argument of the sine function increases from zero to k, where k is some integer. Accordingly we split the sum (2.11) into two sets of sums, one of which is positive and the other is negative. Due to the form of y_1 we use, the sine function changes sign at approximate intervels of S characterized by the integer value of $m = (2n+1)/r$, which we denote by m_i. Let the number of such m_i's be l. [For simplicity we will assume l to be even. Slight modification is necessary when l is odd and for that case $\hat{Z} > \gamma_0 \sum A_n^S \sin(2S+1)y_1$.] Rewriting (2.11) we have

$$\begin{aligned}\hat{Z}(y_1) = &\sum_{S=0}^{m_1=(1)} \gamma_S \sin(2S+1)y_1 + \sum_{(1)+1}^{m_1+m_2=(2)} \gamma_S \sin(2S+1)y_1 \\ &+ \ldots\ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots\ldots \\ &+ \sum_{S=(k-1)+1}^{(k)} \gamma_S \sin(2S+1)y_1 + \sum_{(k)+1}^{(k+1)} \gamma_S \sin(2S+1)y_1 \\ &+ \ldots\ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots\ldots \\ &+ \sum_{S=(l-2)+1}^{(l-1)} \gamma_S \sin(2S+1)y_1 + \sum_{(l-1)+1}^{(l)=n} \gamma_S \sin(2S+1)y_1 \qquad (A.1)\end{aligned}$$

where $(k) = \sum_{i=1}^{k} m_i$. The odd terms are positive and even terms are negative. Using the hypothesis (2.12 *a*) we replace each term by its upper bound. Thus we have

$$\begin{aligned}\hat{Z}(y_1) < &\frac{\gamma_{(1)}}{A_n^{(1)}} \sum_{S=0}^{(1)} A_n^S \sin(2S+1)y_1 + \frac{\gamma_{(1)}}{A_n^{(1)}} \sum_{(1)+1}^{(2)} A_n^S \sin(2S+1)y_1 \\ &+ \ldots\ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots\ldots \\ &+ \frac{\gamma_{(k)}}{A_n^{(k)}} \sum_{(k-1)+1}^{(k)} A_n^S \sin(2S+1)y_1 + \frac{\gamma_{(k)}}{A_n^{(k)}} \sum_{(k)+1}^{(k+1)} A_n^S \sin(2S+1)y_1 \\ &+ \ldots\ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots\ldots \\ &+ \frac{\gamma_{(l-1)}}{A_n^{(l-1)}} \sum_{(l-2)+1}^{(l-1)} A_n^S \sin(2S+1)y_1 + \frac{\gamma_{(l-1)}}{A_n^{(l-1)}} \sum_{(l-1)+1}^{n} A_n^S \sin(2s+1)y_1 \qquad (A.2)\end{aligned}$$

It is easy to show that

$$\sum_{S=0}^{m} A_n^S \sin(2S+1)y$$

$$= \frac{A_n^{m+2}\sin(2m+1)y - A^{m+1}\sin(2m+3)y + (1+A_n)\sin y}{A_n^2 - 2A_n\cos 2y + 1} \quad \text{(A.3)}$$

The denominator of (A.3) is positive for any $y\epsilon\ (0, 2\pi)$ and finite N because

$$A_n^2 - 2A_n\cos 2y + 1 = (A_n - 1)^2 + 4A_n\sin^2 y > 0$$

(Note that $A_n > 0$). The m_i's can at the most differ by unity. Thus $m_1 + m_2 = 2m$ or $2m+1$. Consider

$$\sum_{S=0}^{2m} A_n^S \sin(2S+1)y_1.$$

Using (A.3), the form of y_1 and $m = (2n+1)/r$, [apart from a denominator which is exactly the same as in (A.3)], we have

$$A_n^{2m+2}\sin\left(2\pi + \frac{r\pi}{2(2n+1)}\right) - A_n^{2m+1}\sin\left(2\pi + \frac{3r\pi}{2(2n+1)}\right)$$
$$+ (1+A_n)\sin y_1$$

(For convenience we have used $m = (2n+1)/r$ instead of its integer value. The result that follows from this is equally true even when the integer value of m is used). When n is large and $r \ll n$, we can use $\sin y = y$, Using this we have

$$\frac{r\pi}{2(2n+1)}\left[A_n^{2m+1}(A_n - 3) + 1 + A_n\right].$$

This quantity is less than or equal to zero for $1 \leqslant A_n < 3$. In particular the form of A_n we use is $A_n = 1 + B/(2n+1)$. This choice follows from the discussion given in Appendix B. The equality holds at $A_n = 1$. [These results hold even if we drop the restriction that $r \ll n$ for $A_n = 1 + B/(2n+1)$ and $y\epsilon\ (0, \pi/2)$.]

Thus we have

$$\sum_{S=0}^{2m} A_n^S \sin(2S+1)y_1 < 0.$$

Similarly, we can show that

$$\sum_{S=(k)+1}^{(k)+2m+1} A_n^S \sin(2S+1)y_1 < 0. \quad \text{(A.4)}$$

[Although eq. (A.4) was shown to hold when $(k+2) - (k) = 2m$, it holds even when $(k+2) - (k) = 2m+1$]. Using (A.4) and $\gamma_0 < \gamma_{(k)}/A_n^{(k)}$ for $k > 0$ we obtain

$$\hat{Z} < \gamma_0 \sum_{S=0}^{n} A_n^S \sin(2S+1)y_1 = \bar{Z}$$

Then $\bar{Z}$ has the form given in (A.3) with $m = n$ except for the multiplicative factor γ_0. Thus we have obtained $\bar{Z}$ to be the upper bound of the function $\hat{Z}$.

Similarly, using (2.12 *b*) it can be shown that (2.14 *b*) follows. Although, these relations have been proved for a specific choice of y_1, clearly they hold for any choice of y which satisfies the conditions that the total number of changes in sign is even,

Appendix B

Consider the function $\tilde{Z}$ given in (2·14 *c*). Since γ_0 is positive (for $0 > \beta > \infty$) it is sufficient to show that $\sum_{S=0}^{n} A_n^S \sin(2S+1)\, y_1$ alternates in sign for successive values of $r/2$. From (A.3) it is clear that it is sufficient to show that the numerator of (A.3) alternates in sign (with $n = m$) for successive values of $r/2$. Rewriting the numerator of (A.3) with $m = n$ and $y_1 = r\pi/2(2n+1)$, we get

$$f(A_n, y_1) = A_n^{n+2} \sin\frac{r\pi}{2} - A_n^{n+1} \sin\frac{r\pi}{2} \cos\frac{r\pi}{2n+1} - A_n^{n+1} \cos\frac{r\pi}{2} \sin\frac{r\pi}{2n+1} + (A_n+1) \sin\frac{r\pi}{2(2n+1)} \tag{B.1}$$

Case 1: r and $r/2$ are even

$$f_1(A_n, y_1) = -A_n^{n+1} \sin\frac{r\pi}{2n+1} + (A_n+1) \sin\frac{r\pi}{2(2n+1)}$$

The choice of A_n we use is $A_n = 1 + B/(2n+1)$. For all those values of r for which $r\pi/(2n+1)$ is within the first quadrant, $\sin r\pi/(2n+1) > \sin r\pi/2(2n+1)$. (Note that it is sufficient to consider small angles in the first quadrant, since in the limit as $n \to \infty$ there are infinitely many such values.) Thus, $f_1(A_n, y_1)$ is negative for all finite n. In the limit $n \to \infty$, $A_n^n \to e^{B/2}$ and $\sin r\pi/(2n+1) \sim r\pi/(2n+1)$. Using these limits, we have

$$f_1(A_n, y_1) \to (-e^{B/2} 2A_n + A_n + 1) \frac{r\pi}{2(2n+1)} \tag{B.2}$$

Thus $f_1(A_n, y_1)$ approaches zero from the negative side.

Case 2: r is even and $r/2$ is odd.

In this case, we have

$$f_2(A_n, y_1) = A_n^{n+1} \sin\frac{r\pi}{2n+1} + (A_n+1) \sin\frac{r\pi}{2(2n+1)}.$$

For such values of r, and $\frac{r\pi}{2n+1} \in (0, \pi/2)$, $f_2(A_n, y_1)$ is always positive for all finite n. Thus in the limit of large n, we have

$$f_2(A_n, y_1) \to (2A_n e^{B/2} + A_n + 1) \frac{r\pi}{2(2n+1)} \tag{B.3}$$

This approaches zero from the positive side. (Note that these results hold even when the restriction that $r \ll n$ is dropped for $A_n = 1 + B/(2n+1)$ and $y \in (0, \pi/2)$)

Thus, given an arbitrarily small neighbourhood about $y = 0$, the number of zeros of $f(A_n, y_1)$ indefinitely increases in the limit as $n \to \infty$.

Some remarks on the choice of A_n are in order. The constant A_n which is a function of N only relates γ_S to γ_{S-1}. These relations imply that γ_S is an increasing function of S. Since only the constant relates γ_S to γ_{S-1} one must expect to eliminate the constant in the calculation (as was seen in the example considered). At the first sight, it appears that there is a considerable amount of arbitrariness in the

choice of A_n. However this is only in the choice of B $A_n = 1 + B/(2n + 1)$. All those choice of A_n that alternate the sign of (B.1) for successive values of $y_1 = r\pi/2\,(2n + 1)$ are permitted. From equation (B.1) [or (B.2) and (B.3)] it is clear that A_n infinitesimally close to unity is the best choice. If A_n is very much larger than unity and less than 3, then $A_n^{n+1} \to \infty$. Though this choice alternates the sign, the function is not well behaved in the limit as $N \to \infty$. Thus there is not much arbitrariness in the choice of A_n.

Appendix C

We argue in the following that $(1/N) \log \gamma_s$ is intensive. In the limit of large N the free energy per particle, $(1/N) \log Z$, is an intensive quantity (*see* Griffiths 1964). Then it can easily be seen that $(1/N) \log \gamma_s$ cannot have any dependence on N, N^2, etc. By choosing a proper scale, the following relation holds $\infty > Z > \gamma_s > 1$. Thus

$$\frac{1}{N} \log Z > \frac{1}{N} \log \gamma_s > 0$$

$\log \gamma_s$ can be expanded in powers of N.

$$A'N + B'N^2 + C'N^3 + \ldots$$

Then it is clear that all constants except A' should be zero, otherwise, the inequality breaks down (The choice of A' is also restricted to $A' < (1/N) \log Z$). Thus we see that $(1/N) \log \gamma_s$ is intensive. Thus it is clear that the quantities $(1/N) \log \gamma_s$ and $(1/N) \log \gamma_s$ differ from their limiting values by terms of order of $(1/N)$ and higher.

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Compressive energy of ions in ionic crystals

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Abstract. The possibility of writing the repulsive energy in the Born model of binary ionic crystals as a sum of two separate contributions from the two ions has been investigated. Such an approach leads to two identities, one connecting the lattice spacings of a family of ionic crystals and the other connecting their compressibilities. These identities have been tested on the alkali halide crystals over a range of pressures. The agreement is found to be quite satisfactory. Some further predictions with respect to crystals which exist as two polymorphs have also been tested. In all cases, the deviations of the experimental values from the exact identities can be traced to the fact that second neighbour repulsions in the crystals have been neglected. It is hence concluded that individual compressive energies for ions in ionic crystals is a very attractive possibility.

Keywords. Alkali halides; atomic compression; Born model; ionic crystals; repulsive energy.

Introduction

The introduction of concepts like ionic radius, ionic polarisability, etc., that are dependent on individual ions has proved of immense value in the development of the theory of ionic crystals. In this context it seems relevant to ask whether one could extend these ideas to more complicated properties like compressibility. The concept of ionic compressibility would require two postulates: (*a*) the internal energy of an ion is a function of its size, and (*b*) the repulsive energy in an ionic crystal arises from the increase in the internal energy of the ions when they are compressed. The repulsive energy would then have to be written as the sum of contributions from the two ions as in eq. (1) below. This is a classical picture which would not get theoretical support from the quantum mechanical approach where repulsion is caused by the overlap of neighbouring electron clouds. But then one must note that even the concept of the ionic radius for which there is definite experimental evidence cannot really be justified from the overlap theory. The full quantum mechanical treatment, in fact, leads to very messy numerical computation which has only been carried out approximately for a few compounds, and does not appear to lead to any physical insight. There seems therefore to be some need for postulating empirical functions for the form of the repulsive energy. Almost all earlier workers have tried either the function A/r^n or $b \exp(-r/\rho)$ where r is the interionic distance and have succeeded to some extent in explaining the behaviour of ionic crystals. In this paper, we investigate the consequence of postulating a function of the type in eq. (1). All functions

proposed are only attempted approximations to the true repulsive function. However, the function we have proposed, if found acceptable, has some advantages. Firstly, this would directly lead to a kind of inverse additivity rule for the compressibilities of ions. Further, if we consider a family of binary ionic crystals made up of all combinations of m positive ions and n negative ions, whereas all the earlier approaches mentioned above would require mn functions to be determined, the present alternative would require only $(m + n)$ functions.

In this paper, we test this postulate [(eq. (1)] on the alkali halides. The various attractive forces between the ions have been treated as in the Born model [for a good review of the Born model, *see* Tosi (1964)].

Just from the functional form of the repulsive potential assumed, we are able to derive two identities which have to be satisfied by certain experimentally determinable quantities in sets of crystals. These identities have been tested on the alkali halides. The agreement appears to be satisfactory implying that the concept of individual compressive energy for ions is an attractive possibility worthy of further investigation and evaluation.

Theory

In this paper we investigate the possibility of the repulsive energy being completely separated out into the *sum of contributions from the two ions*. Thus

$$W_{\text{rep}} = W_+(r_+) + W_-(r_-) \tag{1}$$

where, W_+ and W_- are functions of r_+ and r_-, the radii of the two ions. The functions W_+ and W_- are presumed to be unique for a given ion and hence transferable from one crystal to another. Geometrically, we can visualize an ion as a soft fluffy sphere, the repulsive energy being produced by compression and distortion at the points of contact with its neighbours. *The repulsive energy in this formulation does not depend on the agency causing the distortion.* It should be noted that in the present formulation r_+ and r_- are *variables* which can vary for a given ion from crystal to crystal and also with pressure in the same crystal.

To keep the discussion as general as possible, we do not specify any particular functional form for W_+ and W_-. We thus write the total lattice energy per molecule of a binary ionic crystal as

$$W = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{8} + W_+(r_+) + W_-(r_-) \tag{2}$$

where the first three terms on the right hand side give respectively the Madelung electrostatic energy, the van der Waals dipole-dipole interaction energy and the van der Waals dipole-quadrupole interaction energy. As it stands, W is a function of three variables—r, the nearest neighbour distance, r_+, the radius of the positive ion, and r_-, the radius of the negative ion.

Now, in our geometrical picture of the crystal, the nearest neighbours are in contact with one another, so that we immediately have the relation

$$r = r_+ + r_- \tag{3}$$

In addition, we have one further relation expressing the internal equilibrium of the lattice. This arises from the minimisation of the energy of the crystal with