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THEORY OF IMPURITY-INDUCED LATTICE DISTORTIONS IN THE
NORMAL PHASE OF CHARGE-DENSITY-WAVE SYSTEMS

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Theory of Impurity-Induced Lattice Distortions in the Normal Phase of Charge-Density-Wave Systems

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Abstract

A phenomenological Ginzburg-Laundau theory is applied to the *normal* phase of one-dimensional charge-density-wave systems with a finite concentration of impurities. It is found that the interaction between the impurities and the highly polarizable electron gas leads to a strong and oscillatory impurity-impurity interaction, which in turn leads to ordered impurity arrangements and to sizeable periodic lattice distortions. The effect is very strongly dependent on the charge of the impurities, their concentration, and their (interstitial) location in the lattice unit cell. All these factors modify drastically the periodicity associated with the lattice distortion. The theory explains satisfactorily the changing modulation recently observed by Atomic Force Microscopy in the normal (room temperature) phase of NbSe₃ with a variety of impurities.

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Nearly 40 years have passed since Peierls [1] predicted that in a one-dimensional metal the interacting electron-phonon system is unstable towards the creation of a band gap at the Fermi level. Since then several layered [2] and quasi one-dimensional compounds [3–5] – NbSe₃ in particular – that undergo the Peierls transition have been found and investigated in detail. The transition leads, at low temperatures, to a charge-density-wave (CDW) ground state with a wavelength ($2\pi/Q$), where Q is a wavevector very close to that that calipers the quasi-two-dimensional or quasi-one-dimensional Fermi surface. Such a transition also leads to a periodic lattice distortion (PLD) with identical periodicity.

The most interesting and studied effects in these materials are associated with their unique electrical conductivity, and are related to the commensurability of the CDW with the lattice [3–5], to the pinning of the CDW by impurities [6–10], and to the changes in the CDW structure upon the application of high magnetic fields [11]. Recently Coleman *et al.* [12–14] have reported an atomic-force-microscope (AFM) study of an impurity induced PLD in the *normal*, high-temperature phase of NbSe₃. The presence of impurities in crystals grown from powders with concentrations ranging from 0.3 % to 33 % creates well defined periodic modulations of the lattice. It has been observed that the PLD periodicity depends on the kind of impurity (V, Cr, Mn and Gd have been studied, among others) and on its concentration.

In this contribution, the effect of impurities on the PLD in the normal state is investigated based on a phenomenological Ginzburg-Landau formulation [15,16] that has been developed by the authors [17] and previously used to examine the effect of impurities on the structure of the low-temperature, CDW phase. The model describes well also the basic behavior of a normal system on the verge of becoming a CDW state. Even though the formulation does not include explicitly the interaction between the lattice and the impurities, it describes satisfactorily the mutual interactions between impurities and the electron gas, and the effective electric fields acting on the lattice and caused by both, electron gas and impurities.

The total *trial* free energy of a single infinite chain is given as a functional of $n(x)$, the

spatially dependent electronic charge density, and as a function of impurity positions R_l and charges Z_l . The equilibrium value of $n(x)$ is the value which minimizes the trial free energy for a fixed impurity content. The free-energy expression is

$$F_{total} = F_{ee} + F_{ie} + F_{ii} \quad , \quad (1)$$

where

$$F_{ee} = (1/2) \int K_{ee}(x-y) n(x) n(y) dx dy + (C_1/2) \int [dn(x)/dx]^2 dx \\ + (C_2/2) \int n(x)^2 dx + (C_3/4) \int n(x)^4 dx \quad , \quad (2)$$

$$F_{ie} = \sum_l -Z_l \int K_{ie}(x-R_l) n(x) dx \quad , \quad (3)$$

$$F_{ii} = \sum_{l < l'} Z_l Z_{l'} K_{ii}(R_l - R_{l'}) \quad . \quad (4)$$

In these expressions $K_{ee}(x)$, $K_{ie}(x)$, $K_{ii}(x)$ are Coulomb interactions between electrons, between electrons and impurities, and between impurities, respectively. The particle separation along the chain is x , the argument of the functions. The interstitial impurities are assumed to be at a distance x_0 from the axis of the chain. It is also assumed that the electron wave functions have a spatial extent in the direction perpendicular to the chains; that “width” is also assumed to be of the order of x_0 . Therefore

$$K_{ee}(x) = K_{ie}(x) = \frac{C_0}{\sqrt{x_0^2 + x^2}} \quad (5)$$

and

$$K_{ii}(x) = C_0 / |x| \quad . \quad (6)$$

In these equations C_j (with $j = 0$ to 3) are phenomenological constants. In particular C_2 is temperature dependent. Various impurities are distinguished [18] by their effective charge Z_l .

Even though the model uses the electronic charge density as the only order parameter, lattice distortions are taken into account, implicitly, in the free energy expression (1). In

principle the PLD is a unique functional of $n(x)$ and the impurity content and distribution $\{ Z_l, R_l \}$, and can be calculated when and if the *real* $n(x)$ and $\{ Z_l, R_l \}$ are known.

The response of the system to external perturbations, in any phase, is described by a wavevector-dependent inverse susceptibility

$$f(q) = \int K_{ee}(x)e^{iqx}dx + C_1q^2 + C_2 \quad (7)$$

In the normal state $f(q)$ is positive for every q , a necessary condition for stability. In the CDW state $f(q)$ takes negative values in some region in q -space. The temperature-dependent parameter C_2 can be written as $(C_2^{(0)} + B)$, where $C_2^{(0)}$ is the value of C_2 at the CDW transition temperature [19], T_c . The quantity B is taken to be directly proportional to $(T - T_c)$. The wavelength λ of the CDW at the transition point, λ_c , is given as $(2\pi/Q_0)$, where Q_0 is the wavevector where $f(q)$ takes its global minimum value, i.e., Q_0 is the main caliper of the Fermi surface.

In the normal state ($B > 0$) any impurity creates charge-density fluctuations that exhibit Friedel oscillations with wavelengths close to λ_c . In the presence of several impurities, the electrons redistribute themselves on the chain, mostly in the regions around the impurities, screening in the process the effective interaction between impurities. These effects – charge redistribution, resulting electric fields, screened interaction between impurities and the dependence of the total free energy on the impurity distribution $\{ Z_l, R_l \}$ – are the main subject of this investigation.

The (interstitial) impurities are assumed to be in a well-defined location in the unit cell of the crystal. The variables $\{ R_l \}$ refer exclusively to which unit cells contain those impurities. Hence the separation between two impurities on the chain is always an integral multiple of the lattice constant, a . The origin is chosen on the chain such that there is always an impurity at $R_1 = 0$, and all other impurities are located at integral multiples of a ($R_j = m_j a$, where m_j are integers). Equilibrium is achieved for a fixed concentration of impurities when the distribution $\{ R_l \}$ corresponds to the global minimum of the total free energy.

Once the perturbed $n(x)$ and $\{ Z_l, R_l \}$ are known for the global free-energy minimum, it is of interest to determine the PLD. Even though the exact functional dependence of the PLD on $n(x)$ and $\{ Z_l, R_l \}$ are not explicitly written, the elastic characteristics of the crystal will make, in the first approximation, the *local* distortions proportional to the *local* electric fields in that unit cell [20]. The electric field is caused by both the impurities and the electronic charge density, and can be calculated by taking the gradient (derivative) of the total electrostatic potential (as experienced by a test charge)

$$W(x) = \sum_l Z_l K_{ie}(x - R_l) - \int K_{ee}(x - y) n(y) dy \quad . \quad (8)$$

The electric fields are calculated at the midpoints between *possible* impurity locations [$x = (m + 1/2) a$], the assumed positions of the lattice “atoms”. Natural units for the problem were chosen

$$a = 1 \quad , \quad C_0 = 1 \quad , \quad C_3 = 1 \quad ,$$

and the impurity “offset” (and spatial extent of the electron wavefunction) from the chain was taken to be

$$x_0 = a = 1 \quad .$$

The model and its results have the following properties.

(1) The long-range behavior of $K(x)$ implies that the total electronic charge on the chain is

$$\int n(x) dx = \sum_l Z_l \quad ,$$

which means that the chain exhibits charge neutrality, a direct consequence of the model chosen and not a condition imposed externally. The “excess” electrons can be thought of as those introduced by the originally neutral impurities.

(2) For a single isolated impurity the electronic charge redistributes itself around the impurity and displays Friedel oscillations.

(3) As a function of temperature, the response of the electronic charge density to the impurities becomes larger when the system approaches the CDW transition temperature. In

linear-response theory, the electronic charge susceptibility to an impurity potential diverges at T_c .

(4) For an isolated impurity the charge-density response decays return to the bulk value [$n(x) = 0$] with a characteristic healing length ξ ; this healing length increases with decreasing temperature as $(1/\sqrt{B})$.

(5) The wavelength of the Friedel oscillations decreases with decreasing temperature and becomes equal to λ_c at T_c .

(6) The response of the charge density has important implications for the effective interaction between impurities. If the impurity separation is large the interaction is screened and the effective interaction between impurities is much weaker than the bare Coulomb interaction given in equation (6).

(7) If the separation is small compared to the healing length, the effective interaction between impurities is strong and oscillatory. This phenomenon occurs in the vicinity of the transition point.

(8) As a consequence, because of this oscillatory interaction, it is to be expected that the impurities (which are in equilibrium with the solid) order themselves; the characteristic length for this ordering is the wavelength of the Friedel oscillations.

(9) There are three mechanisms which may alter the ordering length to a different value. The first (and weakest) mechanism is the temperature dependence of the wavelength of Friedel oscillations. This mechanism does not produce an appreciable variation in the order, because when the oscillation wavelength is significantly different from λ_c , the healing length ξ is very small and the effective interaction between impurities is quite small.

(10) Close to T_c the susceptibility becomes very large. As a consequence non-linear effects become important in this temperature range. These effects are stronger in the neighborhood of the impurities, where the amount of charge pile-up is large. The non-linearity increases the wavelength of the Friedel oscillation close to the impurities (See Fig. 1). It is therefore essential to include non-linear effects. Away from impurities, where the charge density decays to smaller values, non-linear effects become unimportant and the Friedel-oscillation

wavelength approaches the value given by linear-response theory.

(11) The distance between impurities is an integral multiple of the lattice constant a (the impurities, because of chemical considerations, only occupy well defined locations in the unit cell). Since, λ_c and the lattice constant are in general incommensurable – that is the case in NbSe_3 – the incommensurability may cause “frustration” in the distribution of impurities. Frustration, in general, manifests itself by the presence of a large number of states with essentially the same (or very similar) low free energies.

The numerical results presented here were obtained by applying periodic boundary conditions to a finite chain of length $37a$. The wavenumber of the CDW, Q_0 was assumed to be $(9/37) \cdot (2\pi/a)$, corresponding to a wavelength $\lambda_c = 4.11a$, a value close to the CDW wavevector of NbSe_3 for the high-temperature transition. The temperature of the chain is chosen to be infinitesimally above the transition temperature ($B = 0^+$), where the healing length ξ is infinite. To this chain N identical impurities ($1 \leq N \leq 18$; a single value of $Z_l = Z$, the same for all impurities) are added and minimum value of the trial free energy was determined as a function of the positions $\{R_l\}$ for all concentrations $\nu = N/37$ and various Z . Results are given in Figs. 2 and 3.

For small values of the concentration it is obvious that the typical impurity separations are the distances that correspond to L_{min} , the minima [21] of the curve shown in Fig. 1. When the concentration is increased slowly, a point is reached when the impurities cannot be separated by the most favorable distances of Fig. 1. Therefore a decrease in the characteristic separation of the impurities occurs, with a corresponding change in the charge-density (and electric field) oscillations.

The calculations of Figs. 2 and 3 correspond to four different impurity charges ($Z = 1$, $Z = 2$, $Z = 3$ and $Z = 5$). The nearest-neighbor separation (lowest free-energy minima) for $N = 2$ is different in all cases. They correspond to values of $6a$, $15a$, $16a$, and $17a$ respectively. In each case the absolute minimum is not for the first local minimum (closest separation). For large N the number of possible configurations is very high, and many of those have similar free energies. Finding the global minimum of the free energy for a given

N is therefore difficult. The approach used here consists of two steps. The first step was to approximate the total energy of the system by the sum of two-impurity (pair) potentials (as shown in Fig. 1) between all impurity pairs. Distributions that correspond to local minima in this approximation were then used to calculate, from equations (1)-(6), the exact free energy. The distribution (within this small set) with the minimum exact energy was taken to be the solution of the problem, and all physical properties were then determined for that case. Even assuming that one might have missed, occasionally, the true free-energy minimum, the distributions reported here should nonetheless display all the correct physical properties.

The behavior of the system, in particular the PLD, as a function of the impurity concentration can be analyzed by studying the maxima of the square of the Fourier transform $|E(q)|^2$ of the electric field, $E(x) = dW/dx$. The wave vector at the maximum is an indication of the dominant periodicity of the distorted lattice. It should be expected that:

(A) Whenever possible the impurities will distribute themselves so that the separation between pairs are at the minima L_{min} of the two-impurity potential shown in Fig. 1. This is usually the case for low impurity concentrations when frustration effects are negligible. The impurity distribution in these cases is not uniform, but shows a well defined quasi-periodic pattern.

(B) However, when the impurity concentration gets higher this picture breaks down. In that case, because of the mutual Coulomb repulsion, the impurities tend to be evenly spaced, at separations smaller than L_{min} . For those (high) concentrations the period is solely determined by the value of ν .

(C) Therefore the electronic structure of the electron gas, dominated by λ_c , and the nature of the impurity (as given here by Z) are relevant only for low-impurity concentrations.

(D) The transition takes place, essentially, at a concentration ν_t such that $\nu_t = a/L_{min}$.

(E) The results of AFM studies [12-14] on crystals of $NbSe_3$ with various concentrations of V, Cr, Mn, and Gd exhibit all the features predicted in the above analysis. Long-range modulations with wavelengths up to ten unit cells have been observed. The modulation

wavelengths are multiples of the unit cell, and decrease through a series of monotonically shorter wavelengths as the impurity concentration increases above certain critical values. The wavelength series observed for each impurity is different, as expected for the different impurity charges Z_i . The characteristics have all been measured in the dilute interstitial-impurity range, where the fundamental CDW structure below the transition temperature remains essentially unchanged from that of pure NbSe₃.

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- [18] One may want to distinguish further between impurities by adding to the Coulomb term (5) of the impurity-electron interaction K_{ie} , a short-range potential; this approach is not followed here.
- [19] The constant $C_2^{(0)}$ is such that the inverse susceptibility (7) has a global minimum at $f(q) = 0$ when $B = 0$.
- [20] The AFM, in fact, measures the *local forces* at the surface of the sample, i.e., a locally averaged electric field.
- [21] It should be remembered that periodic boundary conditions impose spurious periodicities; in particular any impurity separation given by λ becomes also an impurity separation ($37a - \lambda$).

FIGURES

FIG. 1. The total free energy $F(R)$ for two impurities as a function of their separation R and for various values of impurity charge Z . The temperature is $B = 0^+$ and periodic boundary conditions (period $37a$) are applied to the sample. At $B = 0^-$ a CDW of period $\lambda = (37a/9)$ sets in. The leftmost curve corresponds to $Z = 1$. The others, in increasingly monotonic order, are for $Z = 2$, $Z = 3$, $Z = 4$, and $Z = 5$ (rightmost curve).

FIG. 2. Distribution of impurities on a chain of period $37a$ for various values of N and Z . The black dots represent the position of impurities. The energy of each distribution is invariant under arbitrary lattice translations. For clarity, a convention has been adopted such that there is always an impurity at site 0.

FIG. 3. Most significant contributions to the Fourier series of the electric field at the lattice sites. Those wavevectors for which the square of the Fourier transform is a maximum are shown by full circles. Wavevectors for which the square of the Fourier transform is not the maximum, but it is at least 70 % of the maximum value are shown by open circles.

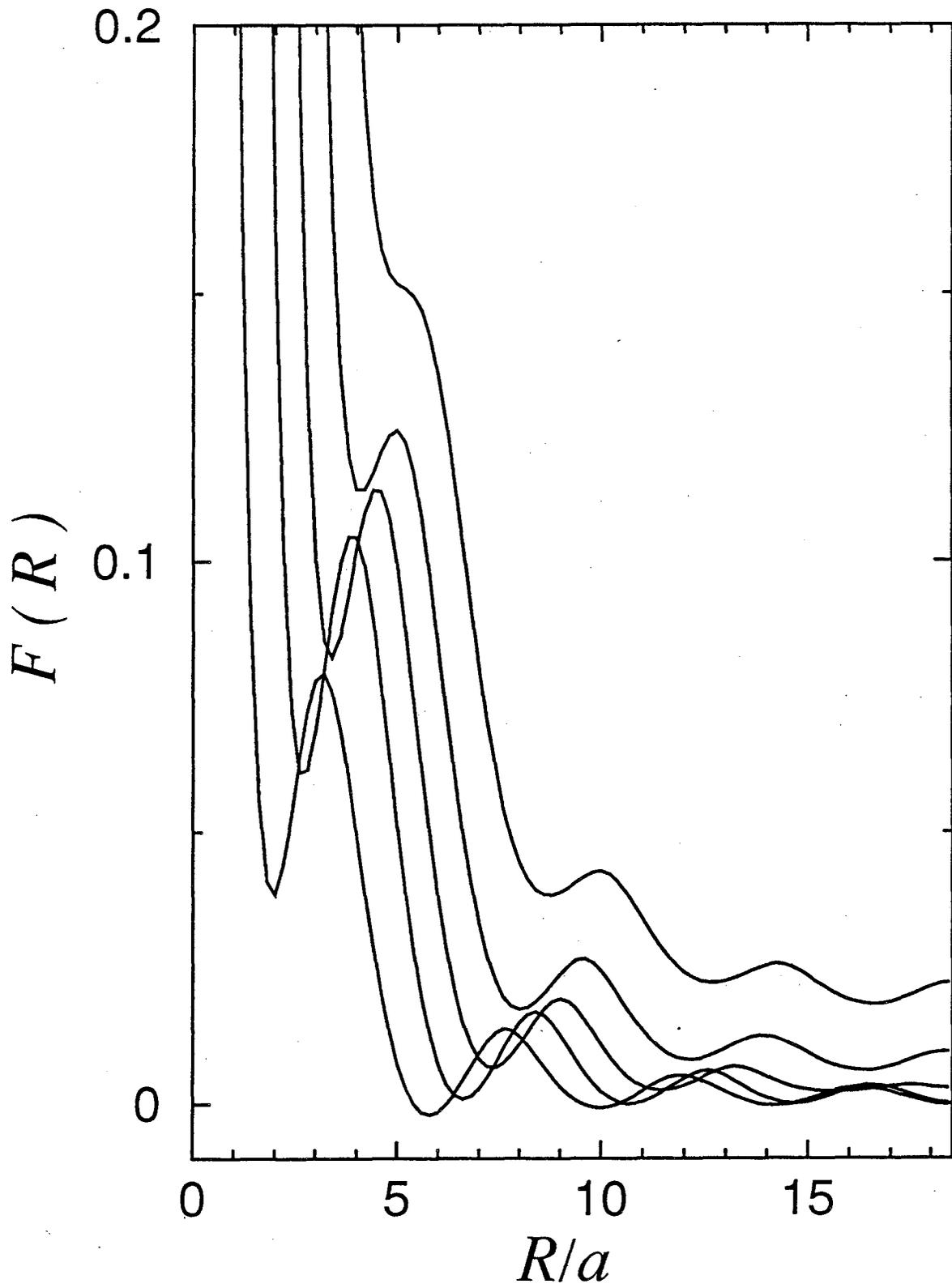


FIGURE 1

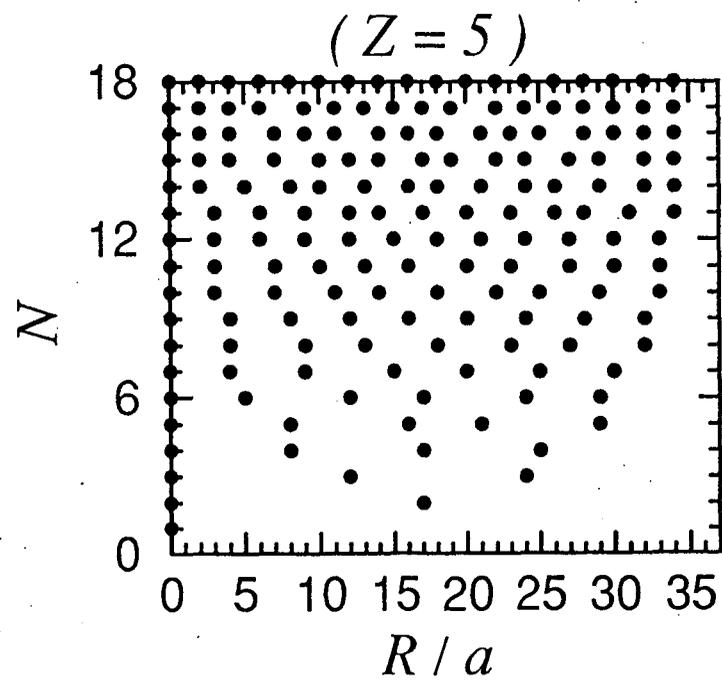
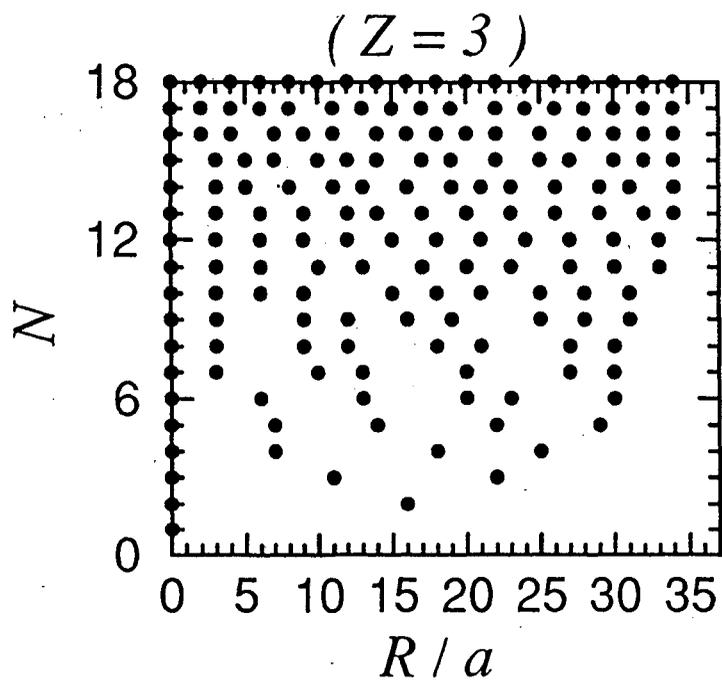
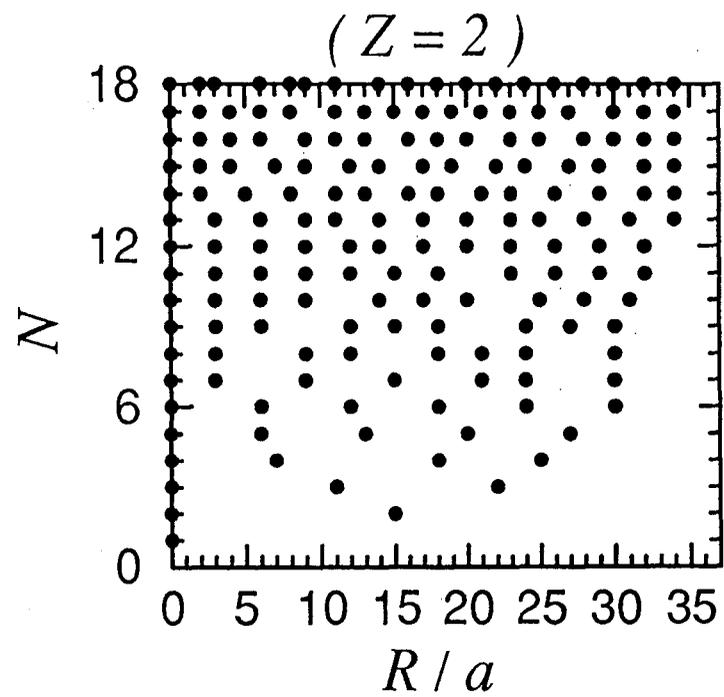
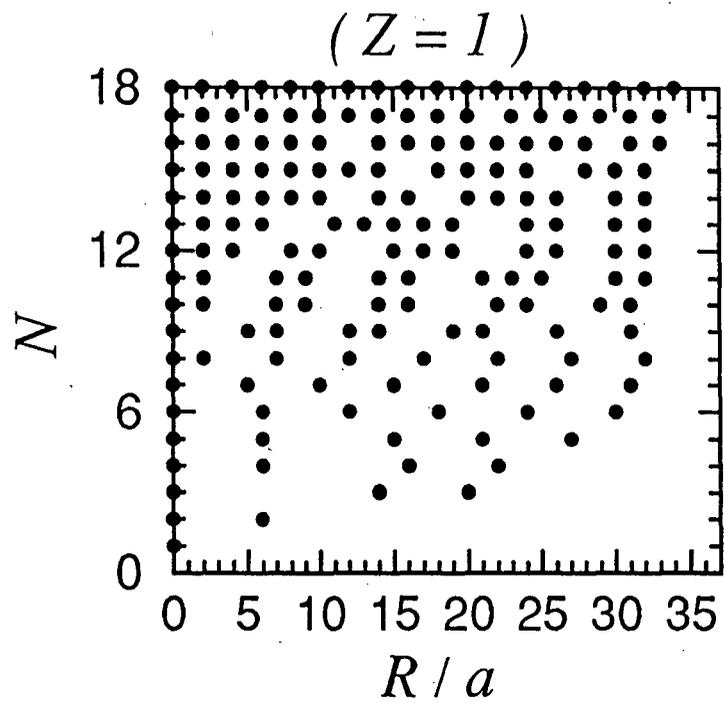


FIGURE 2

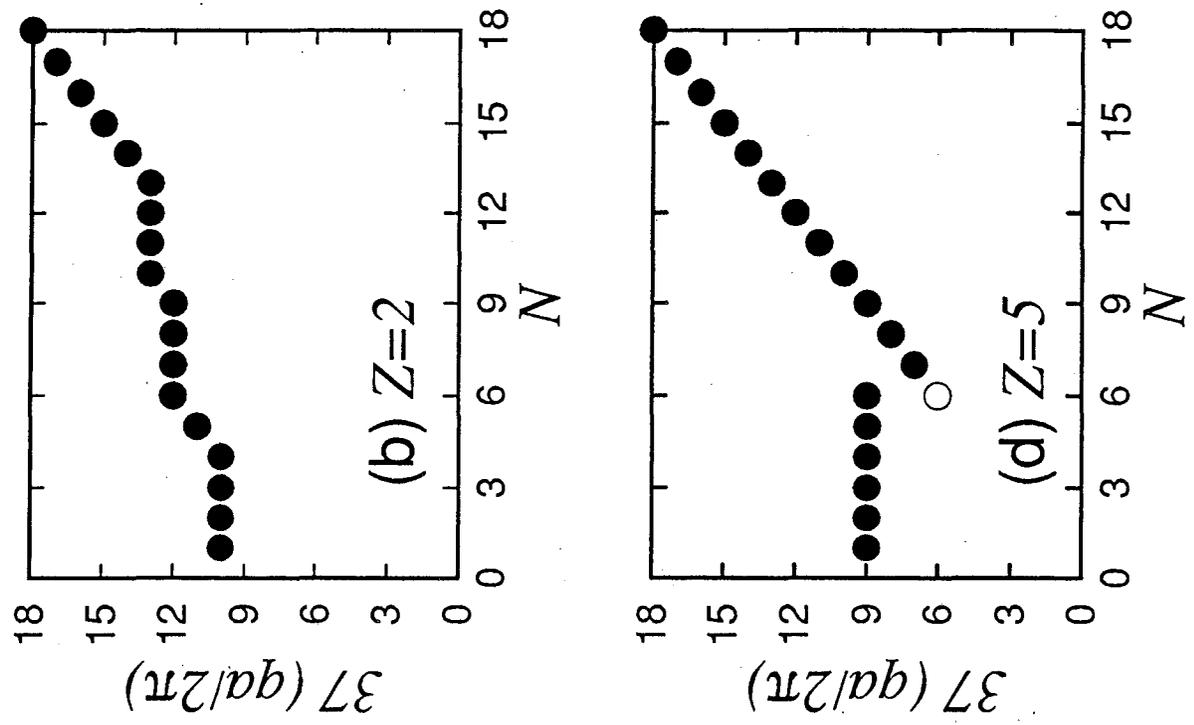


FIGURE 3

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