Ferroelectric phase transitions in a molecular-like array of quantum dots

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Abstract. A model of a 'molecular' 2D crystal of quantum dots is considered. Each elementary cell contains two dots connected by tunnelling. Such an array of two-level quantum systems with strongly non-linear polarizability demonstrates the ferroelectric (antiferroelectric) phase transitions due to Coulomb interaction. We find the energy of the ground state, spontaneous moment and phase transition temperature in the self-consistent field approximation. Optical manifestations of the phase transitions in the far-infrared absorption are also investigated.

1. Introduction

The possibility of spontaneous polarization of two-dimensional (2D) arrays of quantum dots (QDs) has been discussed in the current literature [1–3]. The simplest models have been considered and the results do not look very encouraging from the viewpoint of experimental realization. Spontaneous polarization has been predicted for quantum dot arrays with isotropic [1] and anisotropic [2] parabolic confinement (the latter case is the so-called 'quantum dashes') and for dipole–dipole interaction between dots. The validity of these approximations can hardly be justified in the recent existing structures. Also, the thermodynamics of the discussed transitions have not been considered in the papers cited above.

In the present paper we consider a different model of a QD array which is free from the above-mentioned limitations of parabolic confinement and dipole interaction. Nonetheless the model allows analytical solution in the framework of self-consistent field approximation (SCFA). In fact, we use the classical idea of a two-well potential from the theory of ferroelectricity and propose a 'molecular' lattice of QDs where each elementary cell contains two dots coupled by tunnelling (figure 1). We hope that the technological difficulties of fabricating such a structure are not insurmountable for modern electronic lithography.

Each 'molecule' is considered as a two-level quantum system described by bound and antibound states. The non-linear polarizability of the system is the main difference between the subject of this paper and that of [1, 2]. We suppose that there is one electron per cell and take into account the Coulomb interaction between 'molecules', but we ignore the intercell tunnelling. We describe the thermodynamic characteristics of the phase transitions, collective excitations and far-infrared (FIR) absorption in the proposed structure.
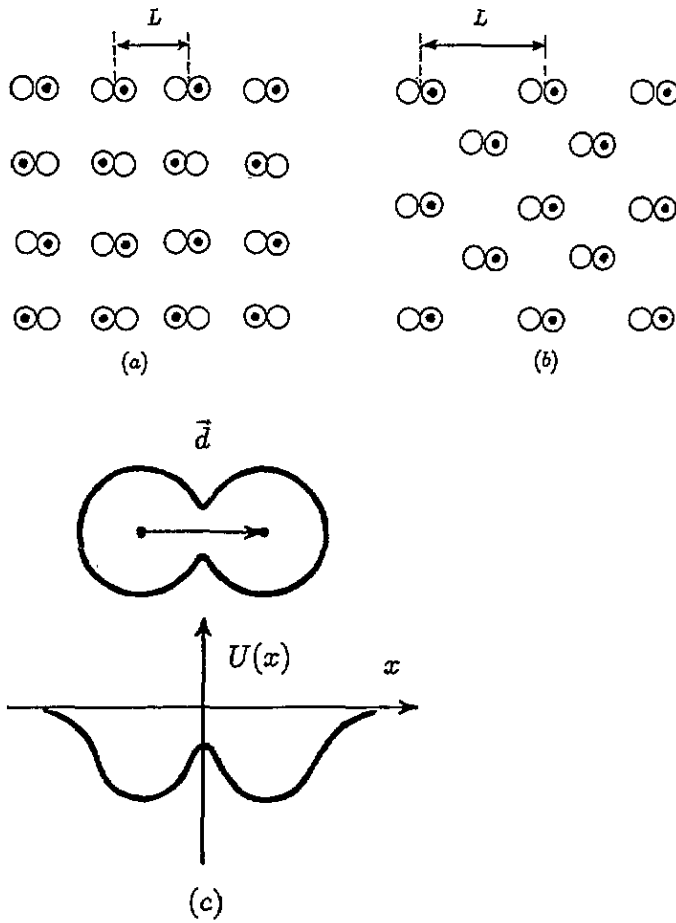
Figure 1. Molecular-like lattices of QDs: (*a*) square lattice with an antiferroelectric arrangement; (*b*) triangular lattice with a ferroelectric arrangement; (*c*) double-well potential of an elementary cell.

2. Phase transitions at $T = 0$

Consider the 2D structure of paired QDs ('molecules') depicted in figure 1(*a*) (square lattice) or figure 1(*b*) (triangular lattice). Within each molecule the electron moves in the double-well potential (figure 1(*c*)):

$$U(r) = u_0(r - d/2) + u_0(r + d/2)$$

where $r = (x, y)$ is the 2D radius vector, d is the distance between QDs in the molecule and $u_0(r)$ is the confining potential of a single dot.

We neglect tunnelling between different molecules and suppose the intra-molecular tunnelling (between the neighbouring dots) to be sufficiently small. This allows us to use the tight-binding approximation to calculate the molecular wavefunction. The electron wavefunction of a single dot at the α-lattice site is $\psi_{j\alpha}(r)$, $j = 1, 2$:

$$\psi_{1\alpha} = \psi_0(r - a_\alpha - d/2) \qquad \psi_{2\alpha} = \psi_0(r - a_\alpha + d/2)$$

where a_α is the lattice vector, α corresponds to the pair of integer numbers n, m ($a_\alpha = e_1 n + e_2 m$, where e_1 and e_2 are basis vectors), j is the number of dots in a molecule and ψ_0 is a single dot wavefunction of the lowest (for simplicity) energy level. In the tight-binding approximation the overlapping integral $S = \langle \psi_{1\alpha} | \psi_{2\alpha} \rangle$ is small: $S \ll 1$.

The Coulomb interaction of the molecules creates an electrostatic potential $\phi_{int}(r)$ that can shift the single-electron energy levels in each dot. We denote these new levels of the αth molecule by $E_{1\alpha}$ and $E_{2\alpha}$, respectively, for dots 1 and 2. These are levels not yet affected by the intra-molecular tunnelling. When the tunnelling is taken into account, we obtain, obviously,

$$E_\alpha^\pm = \tfrac{1}{2}(E_{1\alpha} + E_{2\alpha}) \pm \sqrt{V^2 + \tfrac{1}{4}\Delta_\alpha^2} \qquad \Delta_\alpha = E_{1\alpha} - E_{2\alpha} \tag{1}$$

where V is the tunnelling amplitude between dots 1 and 2. We suppose that V is a constant independent of ϕ_{int} because $\phi_{int} \ll U$ (U is the initial confining potential). In the two-level approximation we have for the wavefunctions

$$\psi_\alpha^\pm = A_\alpha^\pm \psi_{1\alpha} + B_\alpha^\pm \psi_{2\alpha}$$
$$A_\alpha^\pm = [1 + (f_\alpha^\mp)^2/V^2]^{-1/2} \qquad B_\alpha^\pm = \mp[1 + V^2/(f_\alpha^\mp)^2]^{-1/2} \tag{2}$$
$$f_\alpha^\pm = \tfrac{1}{2}\Delta_\alpha \pm \sqrt{V^2 + \tfrac{1}{4}\Delta_\alpha^2}.$$

To find the unknown parameter Δ_α in the SCFA we have to calculate ϕ_{int} in the Hartree form:

$$\phi_{int}(r \simeq a_\alpha) = \sum_{\beta \neq \alpha} \int \psi_\beta^{-*}(r') \frac{e^2}{\epsilon|r - r'|} \psi_\beta^-(r') \, d^2 r'.$$

In this integral we choose functions with the lowest energy ψ_β^- in order to find the ground state of the system. In principle, and this is the essence of the SCFA, one has to find such a distribution Δ_β over the lattice sites $\{a_\alpha\}$ that provides the minimum of the total energy. This programme cannot be exactly realized. Instead, we wish to guess the ground-state structure, to estimate the energy and to demonstrate that under certain conditions the spontaneously polarized state lies energetically lower than the non-polarized paraelectric state. Thus, we find the shifts of energy levels of a two-level system at the αth site due to additional energy ϕ_{int} and we obtain

$$\Delta_\alpha = \sum_{\beta \neq \alpha} A_\beta^2 I_{11}^{\alpha\beta} + 2A_\beta B_\beta I_{12}^{\alpha\beta} + B_\beta^2 I_{22}^{\alpha\beta}$$
$$I_{ij}^{\alpha\beta} = \frac{e^2}{\epsilon} \int \int d^2 r \, d^2 r' \frac{\psi_{i\beta}(r')\psi_{j\beta}(r')}{|r - r'|}[\psi_{1\alpha}^2(r) - \psi_{2\alpha}^2(r)]. \tag{3}$$

The coefficients A_β and B_β depend on Δ_β (see equation (2)); hence, equation (3) is the system of non-linear equations for unknown values Δ_β. In the trivial limiting case $L \to \infty$ (L is the lattice period) the intercell interaction disappears and the structure of the ground state is evident: all electrons occupy the lowest state with $E^- = E_0 - V$, $A_\beta = B_\beta = 1/\sqrt{2}$, $\Delta_\beta \equiv 0$ for all sites. This is the paraelectric non-polarized state. Let us now examine the antiferroelectric state depicted in figure 1(a). Obviously we gain the Coulomb energy at least for $L \gg d$ when the dipole–dipole approximation is applicable. However, localization of an electron in a certain dot results in increasing energy from $E_0 - V$ to E_0. Thus, the net effect has to be estimated. We give such estimations for the square and triangular lattices, where one can expect (see [1]) antiferroelectric and ferroelectric states respectively.

2.1. Square lattice

We look for solution of equation (3) in the form

$$\Delta_\alpha \equiv \Delta(a_\alpha) = \Delta_0(-1)^m \qquad a_\alpha = e_1 n + e_2 m \qquad e_1 \| x \qquad e_2 \| y.$$

In the following we suppose that the condition $d \ll L$ is satisfied, which gives us an opportunity to solve our problem analytically; however, equation (3) is applicable in a general situation when numerical methods should be used. We obtain from equation (3), for $d \ll L$,

$$x = \gamma C_{sq} g(x) \qquad \gamma = \frac{e^2 d^2}{\epsilon L^3 V} \qquad g(x) = 2 \frac{f_+^2(x) - 1}{f_+^2(x) + 1}$$

$$f_+(x) = \tfrac{1}{2}x + \sqrt{\tfrac{1}{4}x^2 + 1} \qquad C_{sq} = \tfrac{1}{4} \sum_{n,m \neq 0} (-1)^m \frac{2n^2 - m^2}{(n^2 + m^2)^{5/2}} \simeq 1.27$$

$$(4)$$

where $x = \Delta_0/V$. Figure 2 demonstrates the graphical solution of equation (4). If the parameter γ does not exceed a critical magnitude $\gamma_{sq} = 1/C_{sq}$, we have only the solution $\Delta_0 = 0$. For $\gamma > \gamma_{sq}$ the second solution appears, which corresponds to the spontaneously polarized state. Note that the dipole–dipole approximation and the condition of the phase transition can be satisfied simultaneously in the case of small tunnelling amplitudes: $V < C_{sq}(e^2/\epsilon L)(d^2/L^2)$, $d \ll L$, $V \ll C_{sq}(e^2/\epsilon L)$.
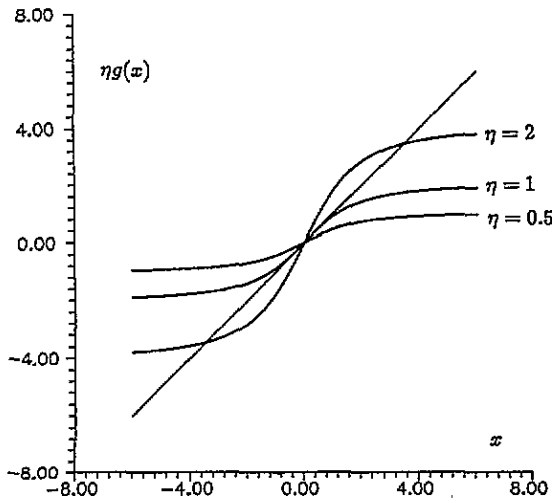

Figure 2. Graphical solution of equation (4), $\eta = C_{sq}\gamma$.

Equation (4) obtained in the dipole–dipole approximation overestimates γ in the situation $L \simeq d$. This unpleasant tendency may be compensated by decreasing the tunnelling amplitude V. The value $(ed)^2/V$ stands for the polarizability of the QD (cf [3]).

The dipole moment and the total energy per elementary cell (the zero energy corresponds to the non-polarized state) are

$$P = \tfrac{1}{4} e d g(x) \qquad E_{tot}/V = 1 - \sqrt{\tfrac{1}{4}x^2 + 1} + \tfrac{1}{8} x g(x). \qquad (5)$$
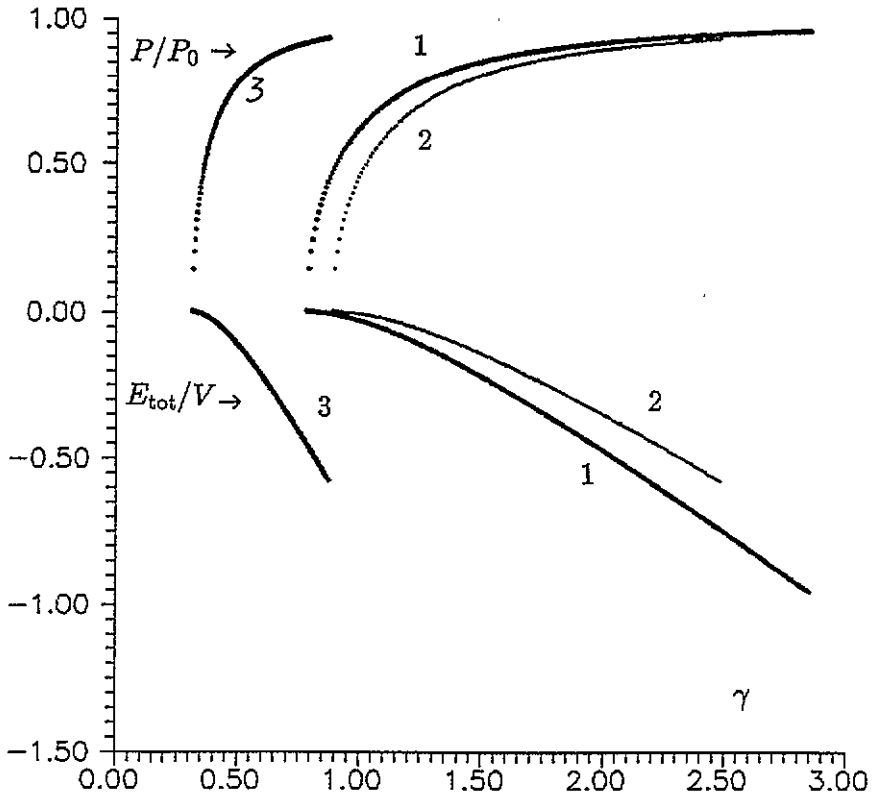
Figure 3. Spontaneous polarization P ($P_0 = \frac{1}{2}ed$) and ground-state energy E_{tot} for the antiferroelectric state (curve 1) and the ferroelectric state (curve 2) of the square lattice, and for the ferroelectric state (curve 3) of the triangular lattice.

At the threshold $\gamma \to \gamma_{sq}$ $P \propto (\gamma - \gamma_{sq})^{1/2}$, $E_{tot} \propto (\gamma - \gamma_{sq})^2$ (figure 3). If we had supposed the ground state to be ferroelectric, i.e. $\Delta_\alpha \equiv \Delta_0$ for any n, m, we would obtain equation (4) with $\bar{C}_{sq} = \frac{1}{8}\sum(n^2 + m^2)^{-3/2} \simeq 1.13$ instead of C_{sq}. In this case the energy is higher than for the antiferroelectric case because $C_{sq} > \bar{C}_{sq}$ (figure 3).

2.2. Triangular lattice

The ground state is ferroelectric. Equation (4) describes the situation with C_{sq} substituted by $C_{tr} = \frac{1}{4}\sum_\beta g_\beta^{-3} \simeq 3.19$ where g_β are the vectors of the triangular lattice. The phase transition occurs at $\gamma > \gamma_{tr} = 1/C_{tr}$ and line 3 in figure 3 qualitatively describes the γ-dependence of the spontaneous momentum. For the antiferroelectric state in the triangular lattice, one obtains $\bar{C}_{tr} < 0$ and the solution with $\Delta_\alpha \neq 0$ does not exist.

3. Influence of an external electric field

In a uniform external electric field F parallel to the vector d the potential $-eF \cdot r$ has to be added to ϕ_{int}. Equation (4) takes the form (for the triangular lattice)

$$x = eFd/V + C_{tr}\gamma g(x). \tag{6}$$

The numerical solution of equation (6) gives the S-shaped curve depicted in figure 4(a) (hysteresis). A more complicated picture arises in the square lattice. The solution has the form $\Delta_\beta = \Delta_1$ for even m (sublattice 1) and $\Delta_\beta = \Delta_2$ for odd m (sublattice 2). For $F = 0$ we have $\Delta_1 = -\Delta_2$ i.e. total compensation of the spontaneous polarization of two sublattices. For $F \neq 0$, two equations for Δ_1 and Δ_2 can be obtained from equation (4):

$$x_1 = \frac{edF}{V} + b^+ \gamma g(x_1) + b^- \gamma g(x_2) \qquad x_2 = \frac{edF}{V} + b^+ \gamma g(x_2) + b^- \gamma g(x_1) \qquad (7)$$

where $x_1 = \Delta_1/V$, $x_2 = \Delta_2/V$, $b^\pm = \frac{1}{2}(\bar{C}_{sq} \pm C_{sq})$. The system (7) can be solved numerically. The spontaneous dipole moment depends on F in a step-like way (see figure 4).
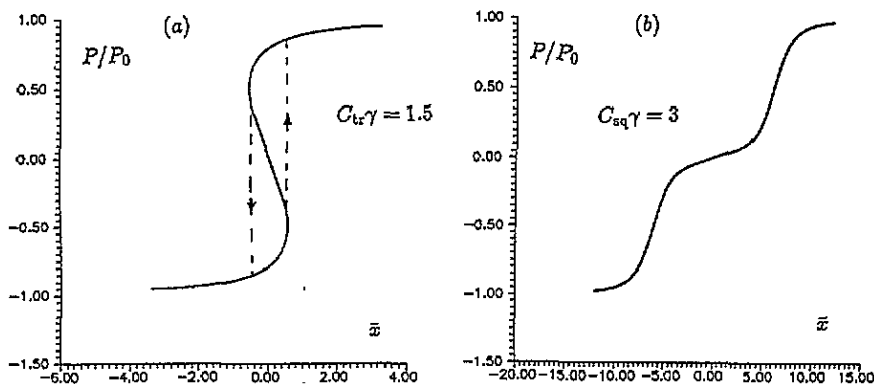

Figure 4. Spontaneous moment in an external electric field ($\bar{x} = eFd/V$): (a) triangular lattice; (b) square lattice.

4. Phase transitions at $T \neq 0$

The free energy can be written in the two-level approximation

$$\mathcal{F} = \frac{2C_i P^2}{L^3} - T \ln \left[\exp\left(\frac{-E_+}{T}\right) + \exp\left(\frac{-E_-}{T}\right) \right] \qquad C_i = C_{sq} \text{ or } C_{tr}. \qquad (8)$$

The first term in equation (8) represents the energy of the Coulomb interaction in the dipole approximation, and P is the electric momentum per elementary cell. Both $E_\pm$ and P depend on Δ but it is more convenient to choose P as an independent variable. In the near vicinity of the transition temperature T_0 we obtain the well known results from the theory of ferroelectricity [4]:

$$\mathcal{F} = \text{constant} + \alpha P^2 + \beta P^4$$

$$\alpha = \frac{2C_i}{L^3} \left[1 - C_i \gamma \tanh\left(\frac{V}{T}\right) \right] \qquad \beta = \left(\frac{edC_i}{L^3}\right)^4 \frac{\Phi(\gamma)}{V^3} \qquad (9)$$

where $\Phi(\gamma)$ is a positive function for $C_i\gamma \geqslant 1$. Spontaneous polarization occurs if $\alpha < 0$: $P^2 = -\alpha/2\beta$. The phase transition temperature and the coefficient α for $T \to T_0$ are

$$T_0 = 2V \Big/ \ln\left(\frac{\gamma C_i + 1}{\gamma C_i - 1}\right) \qquad \alpha = \frac{2C_i}{L^3}\left(\frac{T - T_0}{\Theta}\right) \qquad \Theta = \frac{(T_0^2 \cosh^2 T_0)/V}{V\gamma C_i}.$$

In fact, one can obtain all results for finite T by replacing $C_i \to C_i \tanh(\delta E/2T)$, $\delta E = E_+ - E_- = (4V^2 + \Delta_0^2)^{1/2}$ in the formulae for $T = 0$.

Let us estimate the temperature of the phase transition. Choosing the characteristic parameters $L = 1000$ Å, $d = 200$ Å, $\epsilon = \frac{1}{2}(\epsilon_S + 1)$ and for GaAs $\epsilon_S = 13$, we obtain the estimate $T_0 \simeq 1$ K and 3 K for square and triangular lattices, respectively. These values were obtained in the limit $V \ll e^2 d^2/\epsilon L^3$, when $T_0 \to C_i e^2 d^2/\epsilon L^3$.

5. Far-infrared absorption

We now calculate the absorption of long-wavelength radiation by the collective modes of the QD lattice. If $\tilde{F}_0 \exp(i\omega t)$ is the electric field of the incoming FIR wave, the effective field at each lattice site is $(\tilde{F}_0 + \tilde{F}_{ind}) \exp(i\omega t)$ where $\tilde{F}_{ind}$ takes into account the contribution from surrounding cells. The dipole moment of an elementary cell equals

$$P_\omega = \frac{(ed)^2}{2} \frac{\delta E \tanh(\delta E/2T)}{\delta E^2 - \omega^2} \frac{\tilde{F}_0 + \tilde{F}_{ind}}{1 + \Delta^2/4V^2}. \tag{10}$$

The value $\tilde{F}_{ind}$ can usually be expressed via P as (summation over lattice sites). After substitution in equation (10) we obtain $P_\omega = -\kappa/(\omega^2 - \omega_{res}^2)\tilde{F}_0$, where

$$\kappa = \frac{(ed)^2}{2} \frac{\delta E \tanh(\delta E/2T)}{\Delta^2 + 4V^2} \qquad \omega_{res}^2 = 4V^2 + \Delta^2 - \frac{2C^* e^2 d^2 \delta E \tanh(\delta E/2T)}{L^3\epsilon(1 + \Delta^2/4V^2)}. \tag{11}$$

The last term in ω_{res}^2 is the depolarization shift. For the square lattice we have to substitute into equation (11) the constant $C^* = \bar{C}_{sq}$. At $T > T_0$ (paraelectric state), $\Delta = 0$ and $\omega_{res}^2 = 4V^2[1 - \bar{C}_{sq}\gamma \tanh(V/T)]$. Note that ω_{res} remains finite when $T \to T_0$ because the instability in the square lattice gives rise to the in-plane momentum $q = \pi/L$ (see [1]) while FIR absorption is a process with $q \simeq 0$. Thus, $\omega_{res}^2(T \to T_0) = 4V^2\gamma(C_i - \bar{C}_i) \tanh(V/T_0)$. The temperature dependence of ω_{res}, depicted in figure 5 (curve 1), has a singularity of the type $\omega_{res}(T) - \omega_{res}(T_0) \propto k^{\pm}|T - T_0|$ with k^+ for $T > T_0$ and k^- for $T < T_0$.

In the triangular lattice the instability caused by the Coulomb interaction occurs at $q = 0$. The resonant frequency given by equation (11) ($C^* = C_{tr}$) tends to zero when $T \to T_0$: $(T - T_0)^{1/2}$ (figure 5, curve 2).

6. Sandwich structure with $d\|oz$

A sandwich structure where molecular-like QDs are arranged one under another may be technologically simpler. In this case the dipole moments are parallel to the z direction and the problem is similar to the Ising model but with long-range interaction. It is evident that the antiferroelectric state is energetically preferable. The results follow from equation (4) with a different numerical factor: $C_1 = 0.62$ substituted for C_{sq}.
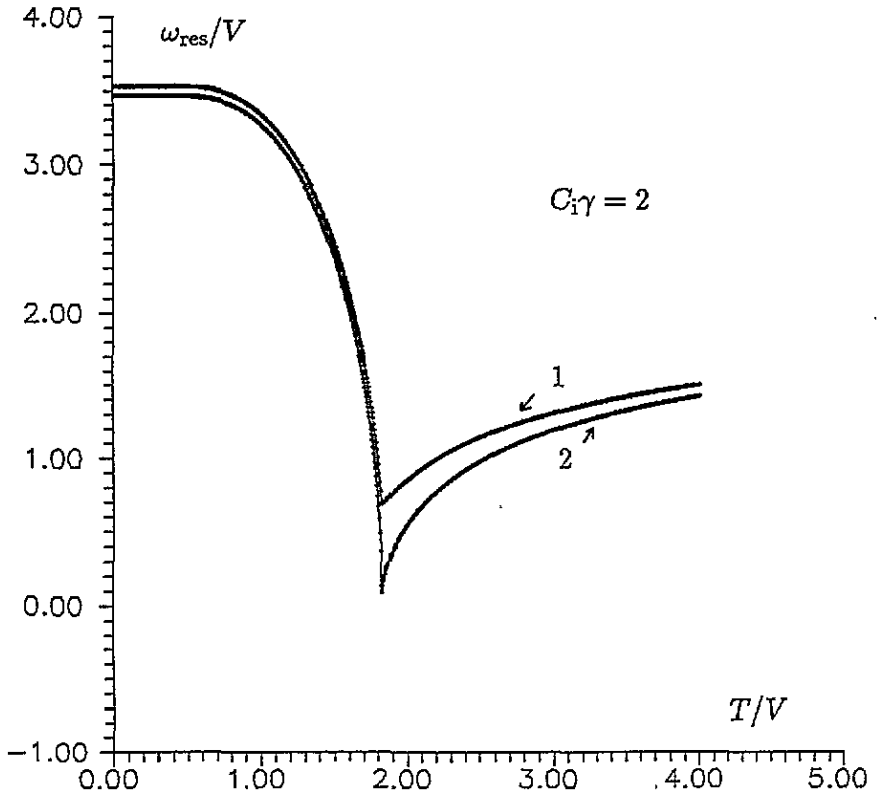
Figure 5. Temperature dependence of the resonant frequencies of the square lattice (curve 1) and the triangular lattice (curve 2).

7. Conclusion

We have considered in the SCFA the possibility of spontaneous polarization in an array of molecular-like quantum dots. Both ferroelectric and antiferroelectric states may occur, depending on the lattice type. One of the optical manifestations of the phase transitions is the T-dependence of the resonant frequency.

Acknowledgment

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