FEDERAL UNIVERSITY OF CEARÁ
SCIENCE CENTER
PHYSICS DEPARTMENT
GRADUATE PROGRAM IN PHYSICS
ACADEMIC MASTER'S DEGREE IN PHYSICS

FRANCISCO GIOVANI PEREIRA MONTEIRO

THERMODYNAMIC PROPERTIES OF SYSTEMS WITH STRONG LIGHT-MATTER COUPLING

FORTALEZA
2024

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Dissertation submitted to the Graduate Program in Physics of the Science Center of the Federal University of Ceará, as a partial requirement for obtaining the title of Master in Physics. Concentration Area: Condensed Matter Physics.

Advisor: Prof. Dr. Eduardo Bedê Barros

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Dados Internacionais de Catalogação na Publicação
Universidade Federal do Ceará
Sistema de Bibliotecas
Gerada automaticamente pelo módulo Catalog, mediante os dados fornecidos pelo(a) autor(a)

M776t Monteiro, Francisco Giovani Pereira.
Thermodynamic properties of systems with strong light-matter coupling / Giovani Monteiro. – 2024.
59 f. : il. color.

Dissertação (mestrado) – Universidade Federal do Ceará, Centro de Ciências, Programa de Pós-Graduação em Física, Fortaleza, 2024.
Orientação: Prof. Dr. Eduardo Bedê Barros.

1. Oscillator. 2. Light-matter coupling. 3. Dipole. 4. Thermodynamics. I. Título.
CDD 530

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Approved on: 19/02/2024

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To my family, mother, father and sister, and my girlfriend. Without them I would never achieve what I achieved, they were fundamental in the most difficult time of my life.

ACKNOWLEDGEMENTS

To God for the opportunity to make this dream come true.

Especially, to my parents, Edilene Pereira Maia Monteiro and Querginaldo Soares Monteiro, my sister, Suzana Maia Monteiro, and my girlfriend, Liane Lima da Cunha, for all the affection, assistance and trust placed in me.

To Prof. Dr. Eduardo Bedê Barros for guiding me in my master's thesis, and for his attention and commitment.

To the PhD student in Electrical Engineering, Ednardo Moreira Rodrigues, and his assistant, Alan Batista de Oliveira, undergraduate student in Electrical Engineering, for adapting the *template* used in this work so that it complies with the standards of the library of Federal University of Ceará (UFC).

To all the teachers who have passed through my academic career, for the knowledge acquired and for being the people I am inspired by, both as a human being and as a professional; especially Francisco Carlos de Oliveira, Francisca Daniele Costa de Lima Beserra and Marcelo Nobre dos Santos Beserra.

To my undergraduate friend Raul Victor, for all the times he helped me with the organization of this work in overleaf, being fundamental to its completion.

To the university where I graduated, UECE/FAFIDAM, where I realized the dream of one day completing a master's degree and to my current university, UFC, for granting me the honor of being taught by such qualified teachers.

To all the friends that Physics gave me the pleasure of meeting, for the great conversations (especially about Physics), especially Anderson Pitombeira, Matheus Nunes and Eduardo Melo.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

“I was an ordinary person who studied hard. There are no miracle people. It happens they get interested in this thing and they learn all this stuff, but they’re just people.”(Feynman, 1983)

ABSTRACT

We consider an lattice of isotropic simple harmonic oscillators, with charge, immersed in a dielectric background, which will couple strongly with the light traveling in the medium. Neglecting quadrupoles, the oscillators have an electric dipole moment and interact with each other through an instantaneous Coulombian interaction. Starting from a quantum formalism, we obtain the dispersion relation, leading to the quantization of the Hamiltonian of the coupled system, in terms of the bosonic operators of creation and annihilation. From the eigenstates and energy eigenvalues of the polaritons, we obtained the canonical partition function, through which the connection with thermodynamics is established, allowing us to determine physical quantities of interest, such as the Helmholtz free energy, internal energy, specific heat, and pressure. In this work, we analyze and discuss the effect of light-matter interaction on such physical properties.

Keywords: oscillator; light-matter coupling; dipole; light; matter; thermodynamics.

RESUMO

Consideramos uma rede de osciladores harmônicos simples isotrópicos, com carga, imersos em um fundo dielétrico, que irão acoplar fortemente com a luz que viaja no meio. Desprezando os quadrupolos, os osciladores possuem um momento dipolo elétrico, e interagem entre si através de uma interação Coulombiana instantânea. Partindo de um formalismo quântico, obtemos a relação de dispersão, levando à quantização da Hamiltoniana do sistema acoplado, em termos dos operadores bosônicos de criação e aniquilação. A partir dos autoestados e das auto-energias dos polaritons, obtivemos a função canônica de partição, através da qual se estabelece a conexão com a termodinâmica, permitindo-nos determinar grandezas físicas de interesse, como a energia livre de Helmholtz, energia interna, calor específico e pressão. Neste trabalho, analisamos e discutimos o efeito da interação luz-matéria em tais propriedades físicas.

Palavras-chave: oscilador; acoplamento luz-matéria; dipolo; luz; matéria; termodinâmica.

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BZ	Brillouin zone
DSC	deep strong coupling
GS	ground-state
SHO	simple harmonic oscilatlator
USC	ultra strong coupling

CONTENTS

1 INTRODUCTION

In most cases, when trying to describe the physical properties of materials, the light is usually considered an external perturbation and is ignored due to the weak interaction with the material. This is a reasonable approximation for many cases, but when light and matter interact strongly, the physical and chemical properties of the material change, and the electromagnetic modes cannot be neglected. These coupling regimes are referred to as ultra strong coupling (USC) and deep strong coupling (DSC) and are defined by the relationship between the Rabi frequency and the excitation frequencies of the material. In the USC regime, the Rabi frequency is smaller and of the order of the excitation frequencies, while in the DSC regime it is larger (Anappara *et al.*, 2009).

Strong coupling can be used to generate phase singularities for use in sensing and optoelectronics, in nanophotonic structures, following the concept of cavity-free strong coupling, because the electromagnetic modes maintained by the material are strong enough to strongly couple to the material's own molecular resonance (Thomas *et al.*, 2022).

Extreme regimes of light-matter coupling can be achieved by plasmonic crystals of metallic and semiconducting nanoparticles, applicable to nonlinear optics, the search for cooperative effects and ground states, and polariton chemistry (Mueller *et al.*, 2020). Other examples of applications utilizing USC and DSC regimes are superconducting circuits, semiconductor quantum wells, novel quantum optical phenomena, quantum simulation, and quantum computation (Forn-Diaz *et al.*, 2019).

Given such applicability and interest in the USC and DSC regimes, it may be necessary to develop physical models that consider the strong interaction between light and matter. The study of such systems gave rise to the description of a new quasiparticle, the polariton, first studied by Fano (1956) and Hopfield (1958), associated with any coupling between an electromagnetic wave and a polarization wave within a medium.(Cardona; Peter, 2005).

In general, polarization in materials has three different origins: due to phonons (quantized modes of vibration) in diatomic ionic crystals, whose ionic pairs have a dipole moment (Simon, 2013; Huang, 1951); by excitons, the quasiparticles formed by the electron-hole pair (Cardona; Peter, 2005); and plasmons (plasma oscillation quantum (Kittel; Mceuen, 2018)). Despite their conceptual differences, these three represent the same physical problem of dipole excitation on a periodic material.

In this work, we consider a dielectric isotropic three-dimensional system consisting of a lattice of identical charged oscillators (dipoles) in a dielectric medium, where we consider that dipoles interact via the instantaneous Coulomb force, which consequently produces polarization modes. We will use the Coulomb gauge (Craig; Thirunamachandran, 1998), where the scalar potential is due only to charge distributions.

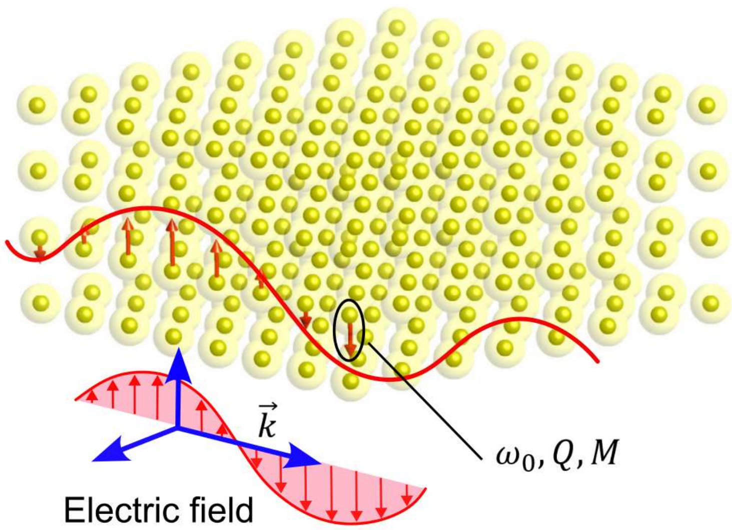
The temperature generates vibrations in the medium that mix with electromagnetic waves, resulting in a light-matter coupling Hamiltonian, diagonalized by a Bogoliubov transformation, from which we extract the polariton dispersion relation. Considering the context of the canonical ensemble, one can explore the statistics of the system taking into account all degrees of freedom, to find the thermal properties from our theoretical model. Our objective is to study and discuss the effect of the strong light-matter interaction on the thermodynamic properties of such systems.

2 THEORETICAL FOUNDATION

2.1 Model

We consider that material excitations can be effectively described as a lattice of identical and isotropic simple harmonic oscillators, with charge Q, mass M and natural oscillation frequency ω_0 uniformly distributed in space, with density $N = 1/V$, where V is the volume of the unit cell $-$*i.e.*, one oscillator per primitive cell$-$ immersed in a background of dielectric constant ε_∞. The simple harmonic oscilatlator (SHO) oscillates around its equilibrium position with a displacement $\mathbf{u}$. In addition, the charge is displaced relative to another charge with a different sign; therefore, this SHO will have a dipole moment, which will interact with the electric field of the electromagnetic waves propagating in the medium. The described model is schematized in figure 1.

Figure 1 – Schematic model.



Source: Elaborated by the author (2024).

This work focuses on cases where the quadruple moment (and higher order multiple moments) can be neglected (Barros *et al.*, 2021). This model of coupled oscillators is convenient for treating certain cases of different natures; for example, in nanoparticle supercrystals, the center of mass of the electronic cloud of each nanoparticle is displaced due to an external electric field and thus undergoes a restoring electric force due to a fixed positive charge (Moores; Goettmann, 2006). This force is linear to the displacement of the center of mass (Jackson, 2021) and thus we can return to the model of SHOs. Another example is ionic diatomic crystals, where within each unit cell there are two different ionized atoms bound by a restoring force. In this case, we replace the displacement of the SHO by the relative displacement of the two ions inside the primitive cell and the mass by the effective mass of the two particles (Cardona; Peter, 2005):

$$M\mathbf{u} \rightarrow \mu(\mathbf{u}_+ - \mathbf{u}_-). \tag{2.1}$$

2.2 Noninteracting dipoles

Consider an electromagnetic plane wave traveling in a medium with an electric field

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \tag{2.2}$$

where $\mathbf{E}_0$ is the amplitude of the electric wave polarized along $\hat{\lambda}_\mathbf{k}$: $\mathbf{E}_0 = E_0\hat{\lambda}_\mathbf{k}$. Thus, in addition to the restoring force $-M\omega_0^2\mathbf{u}$, the SHO will also feel a force due to the macroscopic electric field $Q\mathbf{E}$. We could also consider the force due to the field caused by the dipole moment of each SHO of the array, but we will ignore this effect for now, such that each SHO is independent of the each other SHO in the lattice. Given these considerations, the equation of motion for a dipole in $\mathbf{r}$ oscillating around this position is

$$M\frac{d^2}{dt^2}\mathbf{u} = -M\omega_0^2\mathbf{u} + Q\mathbf{E}. \tag{2.3}$$

To solve this equation, we can propose

$$\mathbf{u} = \mathbf{u}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{2.4}$$

When inserting it into the equation of motion, the amplitude $\mathbf{u}_0$ must be

$$\mathbf{u}_0 = \frac{Q\mathbf{E}_0}{M(\omega_0^2 - \omega^2)}. \tag{2.5}$$

Knowing that the dipole moment of each SHO is $Q\mathbf{u}$, the macroscopic polarization due to the SHO will be

$$\mathbf{P}_{SHO} = NQ\mathbf{u}. \tag{2.6}$$

Replacing eq.(2.5) by eq.(2.6) we get

$$\mathbf{P}_{SHO} = \frac{NQ^2}{M(\omega_0^2 - \omega^2)}\mathbf{E}. \tag{2.7}$$

For an isotropic medium, the equation of the displacement vector is

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon(\omega) \mathbf{E}, \tag{2.8}$$

where $\varepsilon(\omega)$ is the scalar dielectric function and $\mathbf{P}$ is the total polarization, which is not just $\mathbf{P}_{SHO}$ because the valence electrons of the surrounding medium also produce polarization, so $\mathbf{P} = \mathbf{P}_{SHO} + \mathbf{P}_b$; where $\mathbf{P}_b$ is the background polarization related to the macroscopic field by

$$\mathbf{P}_b = \varepsilon_0 \chi_b \mathbf{E} = \varepsilon_0 (\varepsilon_b - 1) \mathbf{E}. \tag{2.9}$$

The background dielectric function ε_b usually depends on ω, but we will focus on cases where the frequency ω is much smaller than the resonance frequency of the valence electrons. In this case, it is common to write $\varepsilon_b(0) = \varepsilon_\infty$, which is called the high-frequency dielectric constant (Smith; Shiles, 1978; Cardona; Peter, 2005), and $\mathbf{P}_b = \varepsilon_0(\varepsilon_\infty - 1)\mathbf{E}$. Therefore eq.(2.8) becomes

$$\mathbf{D} = \varepsilon_0 \left[\varepsilon_\infty + \frac{NQ^2}{\varepsilon_0 M(\omega_0^2 - \omega^2)} \right] \mathbf{E} = \varepsilon_0 \varepsilon \mathbf{E} \tag{2.10}$$

and we obtain the dielectric function

$$\varepsilon(\omega) = \varepsilon_\infty \left[1 + \frac{NQ^2}{\varepsilon_0 \varepsilon_\infty M(\omega_0^2 - \omega^2)} \right], \tag{2.11}$$

which, written in terms of the coupling frequency

$$\Omega = \frac{NQ^2}{4M\varepsilon_0 \varepsilon_\infty \omega_0}, \tag{2.12}$$

will be

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 + \frac{4\Omega\omega_0}{\omega_0^2 - \omega^2} \right). \tag{2.13}$$

Since there are no free charges, $\nabla \cdot \mathbf{D} = 0$, and by substituting $\mathbf{D} = \varepsilon \mathbf{E}$, we get

$$\varepsilon(\omega)(\mathbf{k} \cdot \mathbf{E}_0) = 0. \tag{2.14}$$

Two cases arise from this equation: when $\mathbf{k} \cdot \mathbf{E}_0 = 0$ or the special case when $\varepsilon = 0$. In the first case, the electric field must be perpendicular to the propagation direction and the nonzero response of the SHOs is described by the dielectric function. On the other hand, if $\varepsilon = 0$, we can conclude, from the Maxwell equations for a non-magnetic medium, that the electric field is longitudinal (for any $\mathbf{k}$ other than zero) and the ω frequency, which eq.(2.13) solves for $\varepsilon = 0$, is

$$\omega_L = \sqrt{\omega_0^2 + 4\Omega\omega_0}. \tag{2.15}$$

This is the frequency at which the field is longitudinal, characterized by the upper horizontal line in figure 2.

For a transverse field, from Maxwell's equations in a dielectric medium, we get

$$k^2 = \frac{\omega^2 \varepsilon}{c^2}, \tag{2.16}$$

where substituting $\varepsilon(\omega)$ results in

$$k^2 = \frac{\omega^2 \varepsilon_\infty}{c^2} \left(1 + \frac{4\Omega\omega_0}{\omega_0^2 - \omega^2} \right). \tag{2.17}$$

By isolating ω from eq.(2.17), we obtain the two branches of the dispersion relation for the coupled regime

$$\omega_\pm = \sqrt{\frac{\omega_{ph,\mathbf{k}}^2 + \omega_0^2 + 4\Omega\omega_0}{2}} \left[1 \pm \sqrt{1 - \frac{4\omega_{ph,\mathbf{k}}^2 \omega_0^2}{(\omega_{ph,\mathbf{k}}^2 + \omega_0^2 + 4\Omega\omega_0)^2}} \right]^{1/2}, \tag{2.18}$$

where $\omega_{ph,\mathbf{k}}$ is the uncoupled photon dispersion in the medium, $kc/\sqrt{\varepsilon_\infty}$. In units of ω_0, eq.(2.2) is plotted below as a function of $kc/\sqrt{\varepsilon_\infty}\omega_0$, for the coupling frequency $\Omega = 0.5\omega_0$. Note that at the long wavelength limit ($k \to 0$), the upper branch tends to the longitudinal frequency eq.(2.15), which is expected because at long wavelengths the transverse and longitudinal waves are identical and thus are expected to be degenerate. The two transverse branches correspond to the polariton states discussed in the quantum model below.

2.3 Interaction dipoles: quantum approach

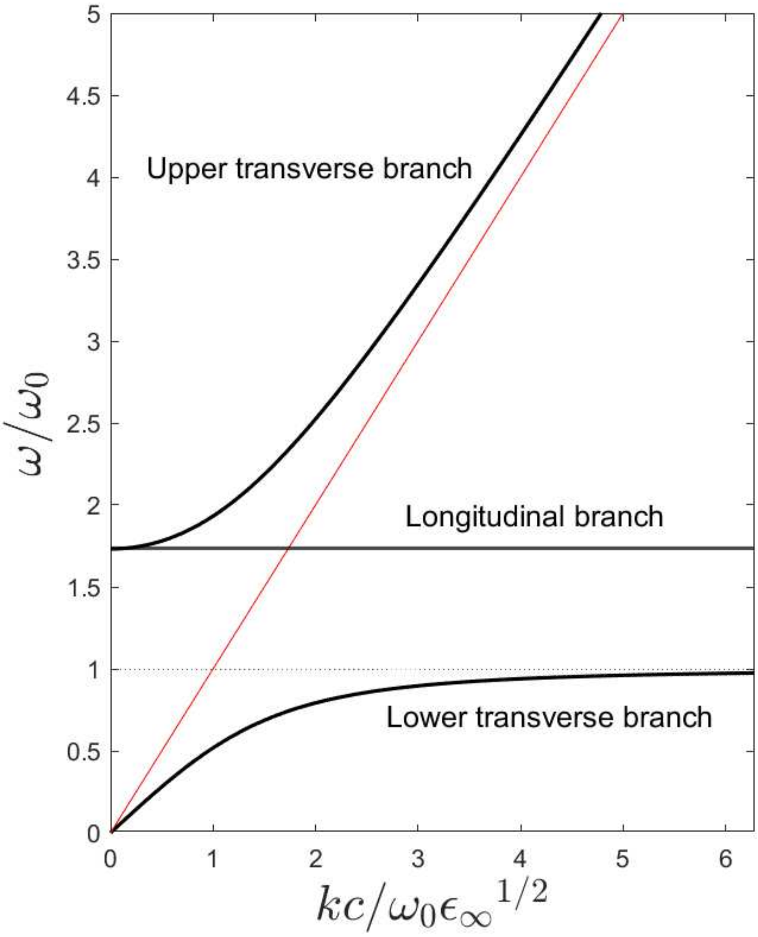
We now introduce a quantum formalism to describe the same system. Let us consider again a lattice of dipoles in a medium with dielectric constant ε_∞, where each dipole is considered as an SHO with mass M, charge Q and natural frequency ω_0. For the quantum approach, we will describe the system by obtaining the Hamiltonian in the Heisenberg formalism, *i.e.*, in terms of creation and annihilation operators. For this, we consider the energy of each SHO, the interaction energy between dipoles and dipoles with light, and the energy of the photons.

2.3.1 Dipole Hamiltonian

Let us start with what does not depend on light: the part for the total energy due only to the dipoles. The dipole Hamiltonian H_{dip} will have two parts: the term corresponding to the individual energy of each oscillator H_0 and the interaction energy between the dipoles H_{int},

$$H_{dip} = H_0 + H_{int}. \tag{2.19}$$

Figure 2 – Dispersion relation for non-interacting dipoles.



Source: Elaborated by the author (2024).

For H_0, we have

$$H_0 = \sum_l \left[\frac{\mathbf{\Pi}^2(\mathbf{r}_l)}{2M} + \frac{M\omega_0^2}{2}\mathbf{h}^2(\mathbf{r}_l) \right] \tag{2.20}$$

where $\mathbf{h}(\mathbf{r}_l)$ is the shift of the SHO charge Q at site l and $\mathbf{\Pi}(\mathbf{r}_l)$ is the conjugate canonical moment at $\mathbf{h}(\mathbf{r}_l)$. When we sum in components,

$$H_0 = \sum_l \sum_{\hat{i}=\hat{x},\hat{y},\hat{z}} \left[\frac{\Pi^{\hat{i}^2}(\mathbf{r}_l)}{2M} + \frac{M\omega_0^2}{2}h^{\hat{i}^2}(\mathbf{r}_l) \right]. \tag{2.21}$$

Now, let us introduce the bosonic operators:

$$b^{\hat{i}}_{\mathbf{r}_l} = \sqrt{\frac{M\omega_0}{2\hbar}}h^{\hat{i}}(\mathbf{r}_l) + i\frac{\Pi^{\hat{i}}(\mathbf{r}_l)}{\sqrt{2M\hbar\omega_0}}; \tag{2.22}$$

$$b^{\hat{i}\,\dagger}_{\mathbf{r}_l} = \sqrt{\frac{M\omega_0}{2\hbar}}h^{\hat{i}}(\mathbf{r}_l) - i\frac{\Pi^{\hat{i}}(\mathbf{r}_l)}{\sqrt{2M\hbar\omega_0}}. \tag{2.23}$$

By writing $h^{\hat{i}}(\mathbf{r}_l)$ and $\Pi^{\hat{i}}(\mathbf{r}_l)$ in terms of them, we have

$$h^{\hat{i}}(\mathbf{r}_l) = \sqrt{\frac{\hbar}{2M\omega_0}}\left({b^{\hat{i}}_{\mathbf{r}_l}}^{\dagger} + b^{\hat{i}}_{\mathbf{r}_l}\right) \tag{2.24}$$

and

$$\Pi^{\hat{i}}(\mathbf{r}_l) = i\sqrt{\frac{M\hbar\omega_0}{2}}\left({b^{\hat{i}}_{\mathbf{r}_l}}^{\dagger} - b^{\hat{i}}_{\mathbf{r}_l}\right), \tag{2.25}$$

that, when replacing it into H_0, we get

$$H_0 = \hbar\omega_0 \sum_{\hat{i},l}\left({b^{\hat{i}}_{\mathbf{r}_l}}^{\dagger} b^{\hat{i}}_{\mathbf{r}_l} + \frac{1}{2}\right). \tag{2.26}$$

Using the representation of bosonic operators in reciprocal space $b^{\hat{i}}_{\mathbf{r}_l} = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_l} b^{\hat{i}}_{\mathbf{k}}$, eq.(2.26) becomes

$$H_0 = \hbar\omega_0 \sum_{\hat{i},\mathbf{k}}\left({b^{\hat{i}}_{\mathbf{k}}}^{\dagger} b^{\hat{i}}_{\mathbf{k}} + \frac{1}{2}\right). \tag{2.27}$$

Where $b^{\hat{i}}_{\mathbf{k}}$ (${b^{\hat{i}}_{\mathbf{k}}}^{\dagger}$) annihilates (creates) a boson of wave vector $\mathbf{k}$ and oscillation mode $\hat{i}$; as discussed in the introduction, this boson can be, for example, a plasmon, an exciton, or a phonon.

Since all the retardation effects will be accounted for within the light-matter coupling, for the interaction Hamiltonian, we can consider the instantaneous Coulombian interaction between dipoles $V_{dip} = \frac{1}{4\pi\varepsilon_0\varepsilon_\infty}\frac{\mathbf{p}\cdot\mathbf{p}' - 3(\mathbf{p}\cdot\hat{n})(\mathbf{p}'\cdot\hat{n})}{|\mathbf{r}'-\mathbf{r}|^3}$, where $\hat{n} = \frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|}$. This leads to

$$H_{int} = \frac{1}{8\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r^3_{ll'}} - 3\frac{r^{\hat{i}}_{ll'} r^{\hat{j}}_{ll'}}{r^5_{ll'}}\right) p^{\hat{i}}_l p^{\hat{j}}_{l'}. \tag{2.28}$$

Again, replacing $p^{\hat{i}}_l$ with $Qh^{\hat{i}}(\mathbf{r}_l)$ and using eq.(2.24), we have

$$\begin{aligned} H_{int} = {} & \frac{\hbar Q^2}{16\pi M\varepsilon_0\varepsilon_\infty\omega_0}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r^3_{ll'}} - 3\frac{r^{\hat{i}}_{ll'} r^{\hat{j}}_{ll'}}{r^5_{ll'}}\right)\left[{b^{\hat{i}}_{\mathbf{r}_l}}^{\dagger}{b^{\hat{j}}_{\mathbf{r}_{l'}}}^{\dagger} + {b^{\hat{i}}_{\mathbf{r}_l}}^{\dagger} b^{\hat{j}}_{\mathbf{r}_{l'}}\right. \\ & \left. + b^{\hat{i}}_{\mathbf{r}_l}{b^{\hat{j}}_{\mathbf{r}_{l'}}}^{\dagger} + b^{\hat{i}}_{\mathbf{r}_l} b^{\hat{j}}_{\mathbf{r}_{l'}}\right]. \end{aligned} \tag{2.29}$$

Replacing the creation and annihilation operators by their respective representations in reciprocal space, $b^{\hat{i}}_{\mathbf{r}_l} = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_l} b^{\hat{i}}_{\mathbf{k}}$, we get

$$\begin{aligned} H_{int} = {} & \frac{\hbar Q^2}{16\pi M\varepsilon_0\varepsilon_\infty\omega_0}\sum_{\hat{i},\hat{j}}\sum_{\mathbf{k}}\left\{-\left[\sum_{\boldsymbol{\rho}}\left(3\frac{\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^2} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}\right]\left({b^{\hat{i}}_{\mathbf{k}}}^{\dagger}{b^{\hat{j}}_{-\mathbf{k}}}^{\dagger} + {b^{\hat{i}}_{\mathbf{k}}}^{\dagger} b^{\hat{j}}_{\mathbf{k}}\right)\right. \\ & \left. - \left[\sum_{\boldsymbol{\rho}}\left(3\frac{\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^2} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{-i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}\right]\left(b^{\hat{i}}_{\mathbf{k}}{b^{\hat{j}}_{\mathbf{k}}}^{\dagger} + b^{\hat{i}}_{\mathbf{k}} b^{\hat{j}}_{-\mathbf{k}}\right)\right\}. \end{aligned} \tag{2.30}$$

The term in the first square bracket is the matrix element $D^{\hat{i},\hat{j}}(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}}\left(3\frac{\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^2} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}$ (except for a factor $\frac{1}{N\pi}$) and the second is it's conjugate complex $D^{\hat{i},\hat{j}*}(\mathbf{k})$. Let us now write the Hamiltonian in terms of the coupling frequency, defined in the classical formalism (see eq.(2.12)), $\Omega = \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty\omega_0}$. The interaction Hamiltonian is then simply

$$H_{int} = -\frac{\hbar\Omega}{4}\sum_{\hat{i},\hat{j}}\sum_{\mathbf{k}}\left[D^{\hat{i},\hat{j}}(\mathbf{k})\left(b_{\mathbf{k}}^{\hat{i}\dagger}b_{-\mathbf{k}}^{\hat{j}\dagger} + b_{\mathbf{k}}^{\hat{i}\dagger}b_{\mathbf{k}}^{\hat{j}}\right) + D^{\hat{i},\hat{j}*}(\mathbf{k})\left(b_{\mathbf{k}}^{\hat{i}}b_{\mathbf{k}}^{\hat{j}\dagger} + b_{\mathbf{k}}^{\hat{i}}b_{-\mathbf{k}}^{\hat{j}}\right)\right]. \tag{2.31}$$

2.3.2 Coupling to light

To treat the coupling of matter to light, it is suitable to use the quantization of electromagnetic modes in a cavity with the dimensions of the crystal (Weick; Mariani, 2015; Hopfield, 1958). Consequently, the energy between the two subsystems (matter and light) is exchanged without loss. Thus, the Hamiltonian for the photonic subsystem of the cavity is

$$H_{ph} = \sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}}\hbar\omega_{ph,\mathbf{k}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}, \tag{2.32}$$

where $c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}$ ($c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\dagger}$) annihilates (creates) a photon of wavevector $\mathbf{k}$ and transverse polarization $\hat{\lambda}_{\mathbf{k}}$ ($\hat{\lambda}_{\mathbf{k}}\cdot\mathbf{k} = 0$), and $\omega_{ph,\mathbf{k}} = kc/\sqrt{\varepsilon_\infty}$ is the dispersion of the uncoupled photon in the medium.

Finally, for the Coulomb gauge, the dipole and light interact through the following Hamiltonian:

$$H_{dip-ph} = \sum_l\left[\frac{Q}{M}\mathbf{\Pi}(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) + \frac{Q^2}{2M}\mathbf{A}^2(\mathbf{r}_l)\right], \tag{2.33}$$

where $\mathbf{A}(\mathbf{r}_l)$ is the potential vector at position $\mathbf{r}_l$. As just mentioned, the crystal is seen as a cavity with quantized modes, where we can use the quantization of the electromagnetic field (HUTTNER; BARNETT, 1992), from which we write the fields in terms of photonic annihilation and creation operators, and hence $\mathbf{A}(\mathbf{r}_l)$ is given by

$$\mathbf{A}(\mathbf{r}_l) = \sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}}\hat{\lambda}_{\mathbf{k}}\sqrt{\frac{N\hbar}{2\varepsilon_0\varepsilon_\infty\mathcal{N}\omega_{ph,\mathbf{k}}}}\left(c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}e^{i\mathbf{k}\cdot\mathbf{r}_l} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\dagger}e^{-i\mathbf{k}\cdot\mathbf{r}_l}\right). \tag{2.34}$$

Substituting $\mathbf{\Pi}(\mathbf{r}_l)$ for eq.(2.25) and the potential vector by eq.(2.34), the first term on the right becomes

$$\begin{aligned}\frac{Q}{M}\sum_l\mathbf{\Pi}(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) = i\hbar\omega_0\sqrt{\frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty\omega_0}}\mathcal{N}^{-1/2}\sum_{\hat{\lambda}_{\mathbf{k}},\hat{i},l,\mathbf{k}}\frac{\hat{i}\cdot\hat{\lambda}_{\mathbf{k}}}{\sqrt{\omega_{ph,\mathbf{k}}}}\left(b_{\mathbf{r}_l}^{\hat{i}\dagger} - b_{\mathbf{r}_l}^{\hat{i}}\right)\\ \times\left(c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}e^{i\mathbf{k}\cdot\mathbf{r}_l} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\dagger}e^{-i\mathbf{k}\cdot\mathbf{r}_l}\right)\end{aligned} \tag{2.35}$$

and if we change the bosonic operators for the reciprocal space, we get

$$\frac{Q}{M}\sum_{l}\mathbf{\Pi}(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) = i\hbar\omega_0 \sum_{\hat{\imath},\hat{\lambda}_{\mathbf{k}},\mathbf{k}} (\hat{\imath}\cdot\hat{\lambda}_{\mathbf{k}})\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}\left(b_{\mathbf{k}}^{\hat{\imath}\,\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + b_{\mathbf{k}}^{\hat{\imath}\,\dagger}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} - b_{\mathbf{k}}^{\hat{\imath}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} - b_{\mathbf{k}}^{\hat{\imath}}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}\right). \tag{2.36}$$

Doing the same for the second term on the right:

$$\frac{Q^2}{2M}\sum_{l}\mathbf{A}^2(\mathbf{r}_l) = \hbar\omega_0 \sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}} \frac{\Omega}{\omega_{ph,\mathbf{k}}}\left(c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}\right). \tag{2.37}$$

Therefore, the coupled Hamiltonian is

$$\begin{aligned} H_{dip-ph} = \hbar\omega_0 \Bigg\{ &\sum_{\hat{\imath},\hat{\lambda}_{\mathbf{k}},\mathbf{k}} (\hat{\imath}\cdot\hat{\lambda}_{\mathbf{k}})\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}\left(b_{\mathbf{k}}^{\hat{\imath}\,\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + b_{\mathbf{k}}^{\hat{\imath}\,\dagger}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} - b_{\mathbf{k}}^{\hat{\imath}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} - b_{\mathbf{k}}^{\hat{\imath}}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}\right) \\ &+ \sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}} \frac{\Omega}{\omega_{ph,\mathbf{k}}}\left(c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}\right)\Bigg\}. \end{aligned} \tag{2.38}$$

The total Hamiltonian is the sum

$$H = H_0 + H_{int} + H_{ph} + H_{dip-ph}, \tag{2.39}$$

whose terms are given by eq.(2.26), eq.(2.31), eq.(2.32) and eq.(2.38). Note that crystal momentum is conserved; for example, the operation $b_{\mathbf{k}}^{\hat{\imath}\,\dagger}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}$ creates a boson of the material excitations of wavevector $\mathbf{k}$ (*e.g.*, $b_{\mathbf{k}}^{\hat{\imath}\,\dagger}$ creates a plasmon or phonon), but it also annihilates a photon of the same wavevector, and so the total variation of the momentum of this process is zero.

2.3.3 Diagonalization

Using the Bogoliubov transformation, we can find a base of operators that diagonalizes the Hamiltonian; *i.e.*, an operator $\eta_{\mathbf{k}}$ such that

$$H = \sum_{\mathbf{k}} \hbar\omega_{pol,\mathbf{k}}\eta_{\mathbf{k}}^{\dagger}\eta_{\mathbf{k}} \tag{2.40}$$

and must satisfy Heisenberg's equation of motion

$$[\eta_{\mathbf{k}}, H] = \hbar\omega_{pol,\mathbf{k}}\eta_{\mathbf{k}} \tag{2.41}$$

for the polariton frequency $\omega_{pol,\mathbf{k}}$. The operator $\eta_{\mathbf{k}}$ represents the strong coupling regimes where light and matter form a polariton (*e.g.*, plasmon-polariton, phonon-polariton, or exciton-polariton) and must consist of a hybrid state of both:

$$\eta_{\mathbf{k}} = \sum_{\hat{\imath}=\hat{x},\hat{y},\hat{z}}\left(u_{\mathbf{k}}^{\hat{\imath}}b_{\mathbf{k}}^{\hat{\imath}} + v_{\mathbf{k}}^{\hat{\imath}}b_{-\mathbf{k}}^{\hat{\imath}\,\dagger}\right) + \sum_{\hat{\lambda}_{\mathbf{k}}}\left(m_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}} + n_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}c_{-\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\,\dagger}\right). \tag{2.42}$$

If we use eq.(2.42) along with the total Hamiltonian in eq.(2.39) on the dynamical equation eq.(2.41), we get a set of ten equations obtained from the known commutation relations.

$$\left[b_{\mathbf{k}'}^{\hat{i}}, b_{\mathbf{k}}^{\hat{j}\dagger}\right] = \delta_{\hat{i},\hat{j}}\delta_{\mathbf{k}',\mathbf{k}} \tag{2.43}$$

and

$$\left[c_{\mathbf{k}'}^{\hat{\lambda}'_{\mathbf{k}'}}, c_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}\dagger}\right] = \delta_{\hat{\lambda}'_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}\delta_{\mathbf{k}',\mathbf{k}}. \tag{2.44}$$

By organizing them in a matrix 10×10:

$$\begin{pmatrix} \omega_0\mathbb{I}_3-\frac{1}{2}\Omega F_{\mathbf{k}} & \frac{1}{2}\Omega F_{\mathbf{k}} & -i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}} \\ -\frac{1}{2}\Omega F_{\mathbf{k}} & -\omega_0\mathbb{I}_3+\frac{1}{2}\Omega F_{\mathbf{k}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}} & -i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}} \\ i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}}^{\mathrm{T}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}}^{\mathrm{T}} & \left(\omega_{ph,\mathbf{k}}+2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}}\right)\mathbb{I}_2 & -2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}}\mathbb{I}_2 \\ i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}}^{\mathrm{T}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}}P_{\mathbf{k}}^{\mathrm{T}} & 2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}}\mathbb{I}_2 & -\left(\omega_{ph,\mathbf{k}}+2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}}\right)\mathbb{I}_2 \end{pmatrix}\begin{pmatrix}\mathbf{u_k}\\ \mathbf{v_k}\\ \mathbf{m_k}\\ \mathbf{n_k}\end{pmatrix} = \omega_{pol,\mathbf{k}}\begin{pmatrix}\mathbf{u_k}\\ \mathbf{v_k}\\ \mathbf{m_k}\\ \mathbf{n_k}\end{pmatrix}. \tag{2.45}$$

Where $\mathbf{u_k}$, $\mathbf{v_k}$, $\mathbf{m_k}$ and $\mathbf{n_k}$ are the vectors consisting of components $u_{\mathbf{k}}^{\hat{i}}$, $v_{\mathbf{k}}^{\hat{i}}$, $m_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}$ and $n_{\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}$. $F_{\mathbf{k}}$ is the matrix 3×3 whose elements are

$$D^{\hat{i},\hat{j}}(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}}\left(\frac{3\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^2} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}, \tag{2.46}$$

and $P_{\mathbf{k}}$ is

$$P_{\mathbf{k}} = \begin{pmatrix} \hat{x}\cdot\hat{\lambda}_{1,\mathbf{k}} & \hat{x}\cdot\hat{\lambda}_{2,\mathbf{k}} \\ \hat{y}\cdot\hat{\lambda}_{1,\mathbf{k}} & \hat{y}\cdot\hat{\lambda}_{2,\mathbf{k}} \\ \hat{z}\cdot\hat{\lambda}_{1,\mathbf{k}} & \hat{z}\cdot\hat{\lambda}_{2,\mathbf{k}} \end{pmatrix}, \tag{2.47}$$

where $\hat{\lambda}_{1,\mathbf{k}}$ and $\hat{\lambda}_{2,\mathbf{k}}$ represent the two transverse polarization states, which are transverse to each other, where we may orient as $\hat{\lambda}_{2,\mathbf{k}} = \hat{k}\times\hat{\lambda}_{1,\mathbf{k}}$.

The choice of axes $\hat{x}$, $\hat{y}$ and $\hat{z}$ is arbitrary, and considering a photon with wave vector $\mathbf{k}$ and transverse polarization directions $\hat{\lambda}_{1,\mathbf{k}}$ and $\hat{\lambda}_{2,\mathbf{k}}$ we can do $\hat{z} = \hat{k}$, $\hat{x} = \hat{\lambda}_{1,\mathbf{k}}$ and $\hat{y} = \hat{\lambda}_{2,\mathbf{k}}$, which simplifies our matrix $P_{\mathbf{k}}$. Furthermore, in this work we are mainly interested in the overall physical behavior of these types of systems, so we will consider the continuum limit, where the details of the crystal structure are not relevant, and we can observe that the lattice sum factor is different from zero only for diagonal terms; this implies that the matrix $F_{\mathbf{k}}$ is simply diagonal (thus, the nonzero elements are $D^{\hat{\lambda}_{1,\mathbf{k}},\hat{\lambda}_{1,\mathbf{k}}}(\mathbf{k})$, $D^{\hat{\lambda}_{2,\mathbf{k}},\hat{\lambda}_{2,\mathbf{k}}}(\mathbf{k})$ and $D^{\hat{k},\hat{k}}(\mathbf{k})$). By assuming these considerations, we simplify the problem because the equations for each direction do not mix terms from other directions, and then we have two independent matrices of dimension 4×4 for transverse modes, and one of dimension 2×2 for longitudinal modes:

$$\begin{pmatrix} \omega_0-\frac{1}{2}\Omega D(\mathbf{k}) & \frac{1}{2}\Omega D(\mathbf{k}) & -i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} \\ -\frac{1}{2}\Omega D(\mathbf{k}) & -\omega_0+\frac{1}{2}\Omega D(\mathbf{k}) & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & -i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} \\ i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & \omega_{ph,\mathbf{k}}+2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}} & -2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}} \\ i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & i\omega_0\sqrt{\frac{\Omega}{\omega_{ph,\mathbf{k}}}} & 2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}} & -\left(\omega_{ph,\mathbf{k}}+2\frac{\omega_0\Omega}{\omega_{ph,\mathbf{k}}}\right) \end{pmatrix} \begin{pmatrix} u^T_{\mathbf{k}} \\ v^T_{\mathbf{k}} \\ m_{\mathbf{k}} \\ n_{\mathbf{k}} \end{pmatrix} = \omega_{pol,\mathbf{k}} \begin{pmatrix} u^T_{\mathbf{k}} \\ v^T_{\mathbf{k}} \\ m_{\mathbf{k}} \\ n_{\mathbf{k}} \end{pmatrix}; \quad (2.48)$$

$$\begin{pmatrix} \omega_0+\frac{1}{2}(4-D(\mathbf{k}))\Omega & -\frac{1}{2}(4-D(\mathbf{k}))\Omega \\ \frac{1}{2}(4-D(\mathbf{k}))\Omega & -\omega_0-\frac{1}{2}(4-D(\mathbf{k}))\Omega \end{pmatrix} \begin{pmatrix} u^L_{\mathbf{k}} \\ v^L_{\mathbf{k}} \end{pmatrix} = \omega_{L,\mathbf{k}} \begin{pmatrix} u^L_{\mathbf{k}} \\ v^L_{\mathbf{k}} \end{pmatrix}. \quad (2.49)$$

or more compactly:

$$(M_T-\omega_{pol,\mathbf{k}}\mathbb{I}_4)\begin{pmatrix} u^T_{\mathbf{k}} \\ v^T_{\mathbf{k}} \\ m_{\mathbf{k}} \\ n_{\mathbf{k}} \end{pmatrix} = 0; \quad (2.50)$$

$$(M_L-\omega_{L,\mathbf{k}}\mathbb{I}_2)\begin{pmatrix} u^L_{\mathbf{k}} \\ v^L_{\mathbf{k}} \end{pmatrix} = 0. \quad (2.51)$$

Where

$$D(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}}\left[3\frac{\left(\rho^{\hat{\lambda}_{\mathbf{k}}}\right)^2}{\rho^2}-1\right]\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}. \quad (2.52)$$

For non-trivial solutions, this matrix equation is satisfied only if the determinant of $M_T-\omega_{pol,\mathbf{k}}\mathbb{I}_4$ is zero. By imposing it, we obtain the secular equation

$$\omega^2_{ph,\mathbf{k}}\left(\omega_0^2-\omega_0\Omega D(\mathbf{k})\right)-\left[\omega^2_{ph,\mathbf{k}}+\omega_0^2+\omega_0\Omega(4-D(\mathbf{k}))\right]\omega^2_{pol,\mathbf{k}}+\omega^4_{pol,\mathbf{k}}=0. \quad (2.53)$$

From the equations of classical electrodynamics, for a transverse plane wave, the relation eq.(2.16) must be valid and the dielectric function can be obtained from

$$\varepsilon = \frac{k^2c^2}{\omega^2} = \varepsilon_\infty\frac{\omega^2_{ph,\mathbf{k}}}{\omega^2_{pol,\mathbf{k}}}. \quad (2.54)$$

Thus, by isolating $\omega^2_{ph,\mathbf{k}}/\omega^2_{pol,\mathbf{k}}$ in eq.(2.53) and substituting it in eq.(2.54), we get the dielectric function

$$\varepsilon(\mathbf{k},\omega_{pol,\mathbf{k}}) = \varepsilon_\infty\left(1+\frac{4\omega_0\Omega}{\omega_0^2-\omega_0\Omega D(\mathbf{k})-\omega^2_{pol,\mathbf{k}}}\right). \quad (2.55)$$

The dispersion relation is determined by solving the biquadratic equation for $\omega^2_{pol,\mathbf{k}}$:

$$\omega_{pol,\mathbf{k}\pm} = \sqrt{\frac{\omega_0^2+\omega^2_{ph,\mathbf{k}}+\omega_0\Omega\,(4-D(\mathbf{k}))}{2}}\left\{1\pm\sqrt{1-\frac{4\omega^2_{ph,\mathbf{k}}\left(\omega_0^2-\omega_0\Omega D(\mathbf{k})\right)}{\left[\omega_0^2+\omega^2_{ph,\mathbf{k}}+\omega_0\Omega\,(4-D(\mathbf{k}))\right]^2}}\right\}^{1/2}. \quad (2.56)$$

If we do the same for the longitudinal equation, we get

$$\omega_{L,\mathbf{k}} = \sqrt{\omega_0^2+(4-D(\mathbf{k}))\,\omega_0\Omega}. \quad (2.57)$$

These three bands are shown in figure 3, for the first Brillouin zone (BZ). The extra bands are obtained by folding the photon states with large **k** into the first BZ which also couple to material excitations. If we include the Umklapp processes in our Hamiltonian, we have a sum in **G** for the photon annihilation operators $c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}+\mathbf{G}}$, where we get a dispersion relation for each primitive wavevector **G**, as shown in figure 3.

It is interesting to note that for $D(\mathbf{k})\to 0$, this reproduces perfectly the obtained results in the classical approach when the dipole-dipole interaction is disregarded. Furthermore, we can use the same classical approach taken in section 2.2 and obtain exactly the same dispersion relation. This interesting result is shown in Appendix A, where we demonstrate the equivalence between the quantum and classical formalisms for both one and two SHO per unit cell. In this work, we have chosen to apply the quantum formalism because it provides us with more physical information and a more detailed description of our system than classical formalism, as we will study below.

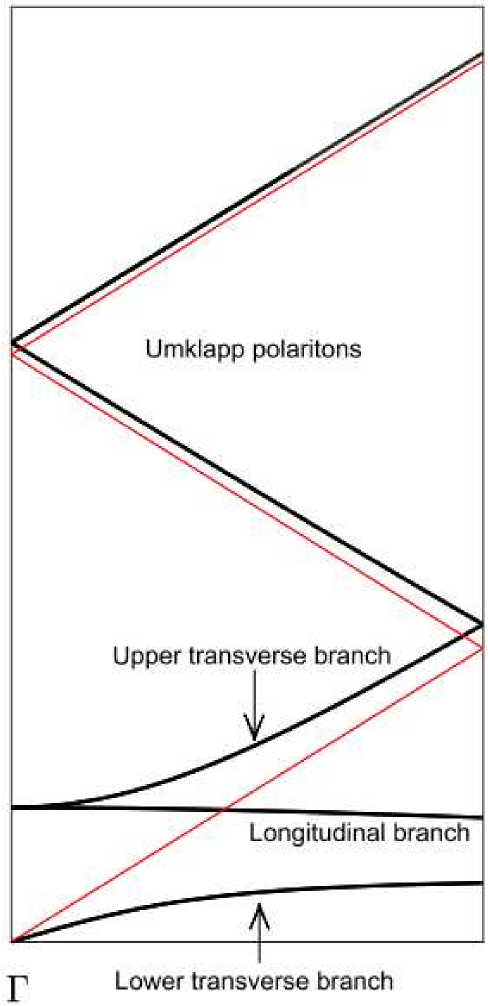
2.4 Thermodynamic analysis: uncoupled system

If the dipole-light interaction does not exist, $\Omega = 0$, and therefore the system is said to be uncoupled. Thus we have a system with matter oscillation modes with constant dispersion $\omega(\mathbf{k}) = \omega_0$ (Einstein solid) and free photons with dispersion $\omega_{ph,\mathbf{k}} = c|\mathbf{k}|/\sqrt{\varepsilon_\infty}$, where the total Hamiltonian consists only of H_0 and H_{ph} (see eq.(2.27) and eq.(2.32)). From the total Hamiltonian of the free system, the canonical partition function can be obtained, but we will not go into details now, as this will be discussed in detail later in the text, when we consider a more general case, taking into account the coupling.

Analyzing first the matter part, as in the Einstein solid, the canonical function partition will be

$$Z_{mat} = \prod_{\substack{\mathbf{k}\\|\mathbf{k}|\le\pi/a}} \frac{1}{8}\mathrm{csch}^3\left(\frac{\hbar\omega_0}{2k_BT}\right). \quad (2.58)$$

Figure 3 – Dispersion relation.



Source: Elaborated by the author (2024).

In the thermodynamic limit, the Helmholtz free energy is related to the partition function, resulting in

$$F_{mat} = k_B T \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| \leq \pi/a}} \ln\left[\frac{1}{8}\sinh^3\left(\frac{\hbar\omega_0}{2k_B T}\right)\right], \tag{2.59}$$

where F_{mat} is the Helmholtz free energy of the free excitations of the SHOs. We consider the first BZ to be approximately a sphere of radius π/a, where a is the size of the unit cell. The table 1 shows some of its experimental values. At continuum limit we have

$$F_{mat} = \frac{4Vk_B T}{\pi^2}\int_0^{\pi/a} \ln\left[\frac{1}{8}\sinh^3\left(\frac{\hbar\omega_0}{2k_B T}\right)\right] k^2 dk = \frac{4\pi}{3} N k_B T \ln\left[\frac{1}{8}\sinh^3\left(\frac{\hbar\omega_0}{2k_B T}\right)\right]. \tag{2.60}$$

Free photons coexist with the material excitations inside the crystal, whose dispersion

Table 1 – Brillouin zone size for different materials. The values used are found in (Drick-Amer *et al.*, 1967), (Bryksin *et al.*, 1972), (Perumal; Mahadevan, 2005), (Torabi *et al.*, 2014), (Wang; Herron, 1990), (Fryar *et al.*, 2005),(Cardona; Peter, 2005), and (Mueller *et al.*, 2020).

Material excitation	Phonons			Excitons		Plasmons
Material	NaCl	LiF	CdF_2	CdS	ZnO	Gold nanoparticle
$\frac{\pi}{a}$ (units of $\frac{\omega_0\sqrt{\varepsilon_\infty}}{c}$)	$8{,}24\times10^5$	$7{,}72\times10^5$	$8{,}40\times10^5$	$2{,}24\times10^2$	$1{,}02\times10^2$	$0{,}43-1{,}14$

Source: Elaborated by the author.

is $\omega_{ph,\mathbf{k}} = c|\mathbf{k}|/\sqrt{\varepsilon_\infty}$. Thus, the free photon canonical function partition is

$$Z_{ph} = \prod_{\mathbf{k}}^{\infty} \frac{1}{4}\mathrm{csch}^2\left(\frac{\hbar\omega_{ph,\mathbf{k}}}{2k_BT}\right), \tag{2.61}$$

leading to

$$F_{ph} = k_BT\sum_{\mathbf{k}}^{\infty}\ln\left[\frac{1}{4}\sinh^2\left(\frac{\hbar\omega_{ph,\mathbf{k}}}{2k_BT}\right)\right]. \tag{2.62}$$

Therefore, the total Helmholtz free energy of the free system is

$$F^{free} = k_BT\left\{\sum_{\substack{\mathbf{k}\\|\mathbf{k}|\le\pi/a}}\ln\left[\frac{1}{8}\sinh^3\left(\frac{\hbar\omega_0}{2k_BT}\right)\right]+\sum_{\mathbf{k}}^{\infty}\ln\left[\frac{1}{4}\sinh^2\left(\frac{\hbar\omega_{ph,\mathbf{k}}}{2k_BT}\right)\right]\right\}. \tag{2.63}$$

Considering a free photon cavity, the photon wave functions must be zero at the contours, which leads to a discretization of the wave vectors. Thus, in the continuum limit ($V\to\infty$), the discrete sum can be replaced by an integral, which allows us to determine F_0 by

$$F^{free} = \frac{4Vk_BT}{\pi^2}\left\{\int_0^{\pi/a}\ln\left[\frac{1}{8}\sinh^3\left(\frac{\hbar\omega_0}{2k_BT}\right)\right]k^2dk+\int_0^{\infty}\ln\left[\frac{1}{4}\sinh^2\left(\frac{\hbar ck}{2k_BT\sqrt{\varepsilon_\infty}}\right)\right]k^2dk\right\}. \tag{2.64}$$

Or separating the ground state terms from the excited terms

$$\begin{aligned}F^{free} &= \frac{4Vk_BT}{\pi^2}\left\{\int_0^{\pi/a}\ln\left[\left(1-e^{-\hbar\omega_0/k_BT}\right)^3\right]k^2dk+\int_0^{\infty}\ln\left[\left(1-e^{-\hbar ck/k_BT\sqrt{\varepsilon_\infty}}\right)^2\right]k^2dk\right\}\\ &+\frac{4V}{\pi^2}\left(3\int_0^{\pi/a}\frac{\hbar\omega_0}{2}k^2dk+2\int_0^{\infty}\frac{\hbar ck/\sqrt{\varepsilon_\infty}}{2}k^2dk\right)=\\ &\frac{4Vk_BT}{\pi^2}\left\{\int_0^{\pi/a}\ln\left[\left(1-e^{-\hbar\omega_0/k_BT}\right)^3\right]k^2dk+\int_0^{\infty}\ln\left[\left(1-e^{-\hbar ck/k_BT\sqrt{\varepsilon_\infty}}\right)^2\right]k^2dk\right\}+E_{GS}^{free}.\end{aligned} \tag{2.65}$$

We can now see that there is a problem in calculating the photon energy; the part coming from the ground state tends to infinity. As this contribution is independent of temperature, being only a constant energy, it is usual to omit this contribution and focus on the excited components. We will follow this trend in this work and leave the discussion on the ground-state contributions to the thermodynamics of these systems to a later work.

The Helmholtz free energy of the excited states is then

$$F_{exc}^{free} = \frac{4Vk_BT}{\pi^2}\left\{\int_0^{\pi/a} \ln\left[\left(1-e^{-\hbar\omega_0/k_BT}\right)^3\right]k^2dk + \int_0^{\infty} \ln\left[\left(1-e^{-\hbar ck/k_BT\sqrt{\varepsilon_\infty}}\right)^2\right]k^2dk\right\}, \quad (2.66)$$

which solving the integrals we obtain

$$F_{exc}^{free} = -4\pi Nk_BT\ln\left(\frac{e^{\hbar\omega_0/k_BT}}{e^{\hbar\omega_0/k_BT}-1}\right) - \frac{8\pi^2}{45}\frac{\varepsilon_\infty^{3/2}k_B^4V}{\hbar^3c^3}T^4. \quad (2.67)$$

Where the first term corresponds to the contribution from the matter-like states, while the second contribution is that of the free photon gas.

3 RESULTS

We now turn our attention to the coupled light-matter system.

3.1 Ground-state

As we have done so far, we have obtained the dispersion relation for each mode; $\omega_{\pm,\mathbf{k}}$ for transverse and $\omega_{L,\mathbf{k}}$ for longitudinal vibrations. Thus, the energy is given by $\hbar\omega_{\mathbf{k}}\left(n_{\mathbf{k}}+\frac{1}{2}\right)$, where $n_{\mathbf{k}}$ is the number of polaritons for a wave vector $\mathbf{k}$. The ground-state (GS) corresponds to the quantum vacuum of polaritons ($n_{\mathbf{k}}=0$) whose quantum states are at the lowest energy; each state $\mathbf{k}$ yields two transverse terms of energy $\frac{\hbar\omega_{+,\mathbf{k}}}{2}$ and $\frac{\hbar\omega_{-,\mathbf{k}}}{2}$, and one longitudinal of energy $\frac{\hbar\omega_{L,\mathbf{k}}}{2}$. Therefore, the GS energy is calculated as follows:

$$E_{GS}=\frac{\hbar}{2}\left[\sum_{\substack{\mathbf{k}\\|\mathbf{k}|\leq k_c}}2\omega_{+,\mathbf{k}}+\sum_{\substack{\mathbf{k}\\|\mathbf{k}|\leq\pi/a}}\left(2\omega_{-,\mathbf{k}}+\omega_{L,\mathbf{k}}\right)\right], \tag{3.1}$$

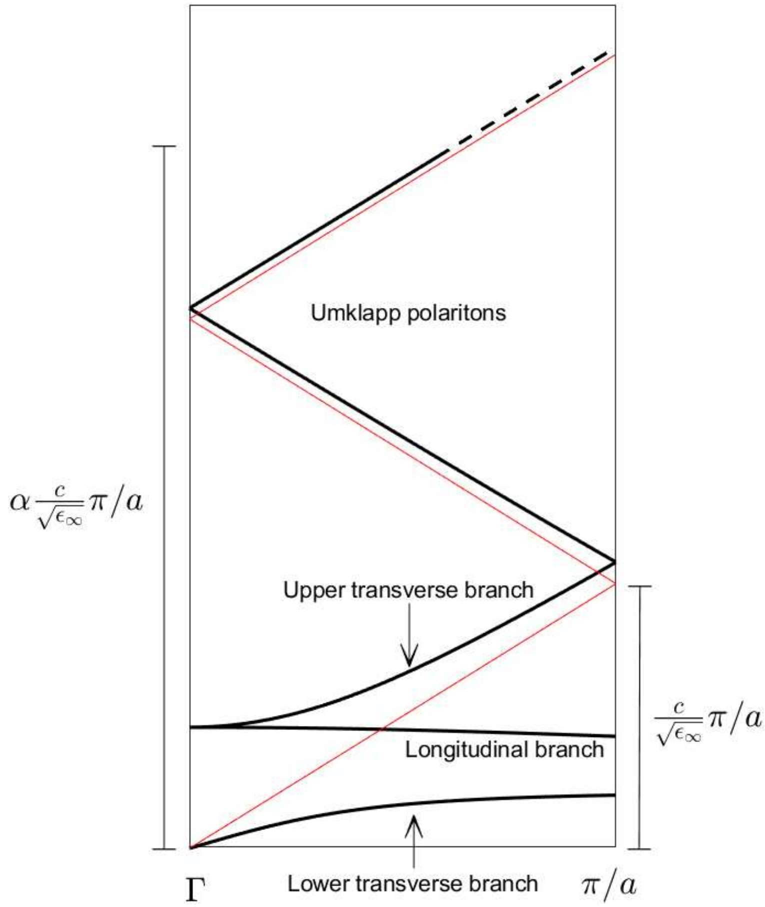
where π/a is the size of the BZ, with a being the lattice constant. Note also that we impose a cutoff k_c on the summation for the upper polaritons; this is because, in reality, wavelengths of the order of the dimensions of the centers of oscillation will not induce relevant dipole moments, and thus the photons beyond this limit will not couple. For example, in nanoparticle supercrystals, the electric field fluctuating in nanoparticle-like dimensions does not induce an effective dipole moment. Therefore, since u_0 is the dimension of the centers of oscillation, the cutoff must be of the order of $k_c=\pi/u_0$. Therefore, we rewrite $k_c=\alpha\pi/a$, where α is another parameter describing the properties of our system; it can range from values close to 1 to very high values. Figure 4 shows the interesting energies.

Considering a cubic crystal of size L, the contour conditions of electrodynamics impose that the photon wave functions must vanish in the surfaces, and hence the components of the wave vector must be multiples of π/L. Therefore, in the limit $L\to\infty$, we can change the summation to an integral: $\sum_{\mathbf{k}}f(\mathbf{k})\to\frac{4L^3}{\pi^2}\int d^3kf(\mathbf{k})$. In this case, the ground-state energy is calculated by doing

$$E_{GS}=\frac{\hbar L^3}{2\pi^3}\left[\int_{|\mathbf{k}|\leq\alpha\pi/a}2\omega_{+,\mathbf{k}}d^3k+\int_{|\mathbf{k}|\leq\pi/a}\left(2\omega_{-,\mathbf{k}}+\omega_{L,\mathbf{k}}\right)d^3k\right], \tag{3.2}$$

Now we notice that the vector dependence on the frequencies is only given by $D(\mathbf{k})$. As we are mainly interested, in this work, in the continuum limit, we can exchange $D(\mathbf{k})$ by a mean

Figure 4 – The considered excitation energies for the summation of the total energy of the system; α denotes the cutoff in the contributions of the photon energy for the coupling.



Source: Elaborated by the author (2024).

structure parameter $D(\mathbf{k}) \to s$ such that the frequencies have a fully spherical symmetry at $\mathbf{k}$ and we can solve the integral by

$$E_{GS} = \frac{2\hbar L^3}{\pi^2}\left[\int_0^{\alpha\pi/a} 2\omega_+ k^2 dk + \int_0^{\pi/a} (2\omega_- + \omega_L)k^2 dk\right], \tag{3.3}$$

where

$$\omega_\pm(k) = \sqrt{\frac{\omega_L^2 + c^2k^2/\varepsilon_\infty}{2}}\left\{1 \pm \sqrt{1 - \frac{4\omega_T^2 c^2k^2/\varepsilon_\infty}{\left[\omega_L^2 + c^2k^2/\varepsilon_\infty\right]^2}}\right\}^{1/2}; \tag{3.4}$$

$$\omega_L = \sqrt{\omega_0^2 + (4-s)\omega_0\Omega}; \tag{3.5}$$

$$\omega_T = \sqrt{\omega_0^2 - s\omega_0\Omega}. \tag{3.6}$$

Again, we note that for $\alpha \to \infty$, the integration in the upper band should be of the order of k^4 and must diverge. To avoid this problem, we consider a finite α. Taking the difference of the ground-state of the coupled system with respect to the free system

$$\Delta E_{GS} = \frac{2\hbar L^3}{\pi^2}\left[\int_0^{\alpha\pi/a} 2\left(\omega_+ - \frac{ck}{\sqrt{\varepsilon_\infty}}\right)k^2dk + \int_0^{\pi/a}(2\omega_- + \omega_L - 3\omega_0)\,k^2dk\right]. \tag{3.7}$$

Is convenient to rearrange the integration of the following form

$$\Delta E_{GS} = \frac{2\hbar L^3}{\pi^2}\left\{\int_0^{\pi/a}\left[2(\omega_+ + \omega_-) + \omega_L - 2\frac{ck}{\sqrt{\varepsilon_\infty}} - 3\omega_0\right]k^2dk + 2\int_{\pi/a}^{\alpha\pi/a}\left(\omega_+ - \frac{ck}{\sqrt{\varepsilon_\infty}}\right)k^2dk\right\}. \tag{3.8}$$

Let us first focus on the first integral. It is easy to prove the relation

$$\omega_+ \pm \omega_- = \sqrt{\frac{c^2k^2}{\varepsilon_\infty} \pm 2\omega_T\frac{ck}{\sqrt{\varepsilon_\infty}} + \omega_L^2}, \tag{3.9}$$

and so we have

$$\int_0^{\pi/a}(\omega_+ - \omega_-)\,k^2dk = \int_0^{\pi/a}\sqrt{\frac{c^2k^2}{\varepsilon_\infty} \pm 2\omega_T\frac{ck}{\sqrt{\varepsilon_\infty}} + \omega_L^2}k^2dk. \tag{3.10}$$

This equation can be solved analytically by using trigonometric integration. However the final expression is long and confusing, so we omit it. We can simplify this expression by assuming that π/a is very large ($\pi/a \gg \omega_0\sqrt{\varepsilon_\infty}/c$), where we can take the expansion:

$$\begin{gathered}\sqrt{\frac{c^2(\pi/a)^2}{\varepsilon_\infty} \pm 2\omega_T\frac{c\pi/a}{\sqrt{\varepsilon_\infty}} + \omega_L^2} = \\ \frac{ck}{\sqrt{\varepsilon_\infty}}\left\{1 + \frac{\omega_T\sqrt{\varepsilon_\infty}}{c\pi/a} + \frac{1}{2}\frac{\left(\omega_L^2 - \omega_T^2\right)\varepsilon_\infty}{c^2(\pi/a)^2} - \frac{1}{3}\frac{\left(\omega_L^2 - \omega_T^2\right)\omega_T\varepsilon_\infty^{3/2}}{c^3(\pi/a)^3} + O\left[\left(\frac{\omega_0\sqrt{\varepsilon_\infty}}{c\pi/a}\right)^4\right]\right\}.\end{gathered} \tag{3.11}$$

Taking this limit, in the result of eq.(3.10), the dominant term will be

$$\begin{gathered}\sqrt{\frac{c^2k^2}{\varepsilon_\infty} \pm 2\omega_T\frac{ck}{\sqrt{\varepsilon_\infty}} + \omega_L^2}\left[-\frac{1}{8}(\pi/a + \omega_T)(\omega_L^2 - 5\omega_T^2)\right. \\ \left.+\frac{1}{4}\left((\pi/a)^2 + 2\omega_T\pi/a + \omega_L^2\right)(\pi/a - 5\omega_T/3)\right],\end{gathered} \tag{3.12}$$

and, by using the expansion eq.(3.11) and grouping in powers of π/a, and joining with the other trivial integrations of the parts on ω_L, ω_0 and $ck/\sqrt{\varepsilon_\infty}$ in eq.(3.8), we will get

$$\begin{gathered}\Delta E_{GS} = \frac{4\varepsilon_\infty^{3/2}\hbar L^3}{\pi^2c^3}\left[\left(\omega_T + \frac{\omega_L}{2} - \frac{3\omega_0}{2}\right)\frac{c^3(\pi/a)^3}{3\varepsilon_\infty^{3/2}} + \left(\frac{\omega_L^2 - \omega_T^2}{4}\right)\frac{c^2(\pi/a)^2}{\varepsilon_\infty}\right] + \\ \frac{4\hbar L^3}{\pi^2}\int_{\pi/a}^{\alpha\pi/a}\left(\omega_+ - \frac{ck}{\sqrt{\varepsilon_\infty}}\right)k^2dk + O\left[\left(\frac{\omega_0\sqrt{\varepsilon_\infty}}{c\pi/a}\right)^2\right].\end{gathered} \tag{3.13}$$

For the second integration, as we are considering $\pi/a \gg \omega\sqrt{\varepsilon_\infty}/c$, let us take the expansion $\omega_+ - \frac{ck}{\sqrt{\varepsilon_\infty}} = \frac{\omega_L^2 - \omega_T^2}{2ck/\sqrt{\varepsilon_\infty}} + O\left[\left(\frac{\omega_0\sqrt{\varepsilon_\infty}}{ck}\right)^2\right]$ to obtain

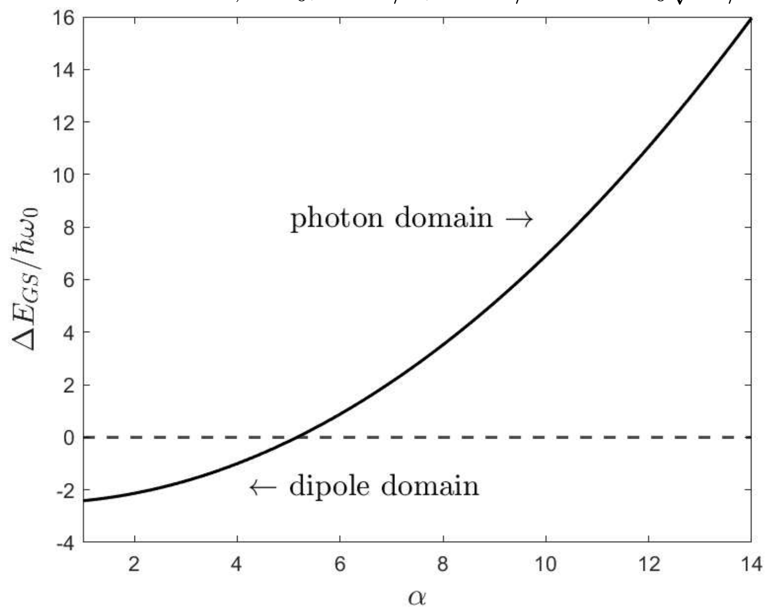
$$\int_{\pi/a}^{\alpha\pi/a}\left(\omega_+ - \frac{ck}{\sqrt{\varepsilon_\infty}}\right)k^2dk = \frac{4\hbar L^3}{\pi^2}\left(\frac{\omega_L^2 - \omega_T^2}{4}\right)\frac{\sqrt{\varepsilon_\infty}(\pi/a)^2}{c}\left(\alpha^2 - 1\right) + O\left[\left(\frac{\pi L}{a}\right)^3\right]. \tag{3.14}$$

Therefore, ignoring the remaining powers, we get the expression for the GS difference per unit cell of the crystal

$$\frac{\Delta E_{GS}}{N} = \frac{4\pi}{3}\hbar\left(\omega_T + \frac{\omega_L}{2} - \frac{3\omega_0}{2}\right) + 4\pi\hbar\omega_0\Omega\frac{\sqrt{\varepsilon_\infty}}{c\pi/a}\alpha^2, \tag{3.15}$$

where we use $a^3 = V/N$ and $\omega_L^2 - \omega_T^2 = 4\omega_0\Omega$. Let us be careful not to confuse this N with what we named in section 2.2; now, N is the total number of unit cells. The dependence of the ground-state energy difference on α is shown in figure 5, by solving numerically the integration given by eq.(3.7).

Figure 5 – Energy ground-state relative to the free system for $\Omega = 0{,}75\omega_0$, $s = 4/3$, and $\pi/a = 100\omega_0\sqrt{\varepsilon_\infty}/c$.

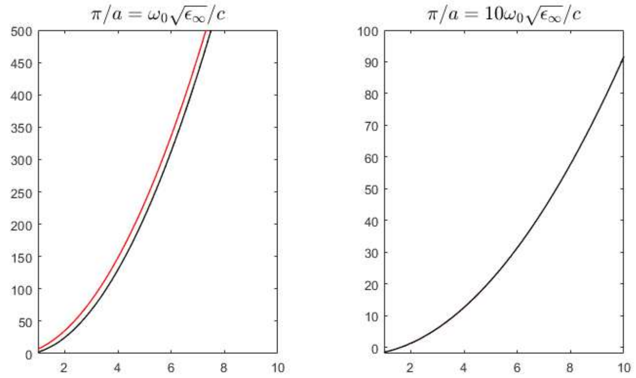


Source: Elaborated by the author (2024).

For small values of α, the contribution from the dipole-dipole interaction dominates and the GS energy decreases with increasing light-matter coupling. However, as α increases, the photon terms dominate and ΔE_{GS} becomes positive.

From figure 6 we see that the approximation made has an excellent agreement; the red curve is the predicted behavior in eq.(3.15) and the black curve is the numerical calculation. For $\pi/a = 10\omega_0\sqrt{\varepsilon_\infty}/c$ the two curves practically overlap, so we cannot visualize their separation. figure 7 shows the dependence of the GS energy with respect to the coupling intensity Ω, ranging the structure parameter s. It is interesting to highlight that $s = 2/3$ is obtained for a face-centered cubic lattice in the limit $k \to 0$. The increase of s causes a reduction of the transverse frequency ω_T and, as we have already commented, the effect is that the GS energy difference becomes negative and therefore, as s is larger, we have a wider range of values for which ΔE_{GS} is negative,

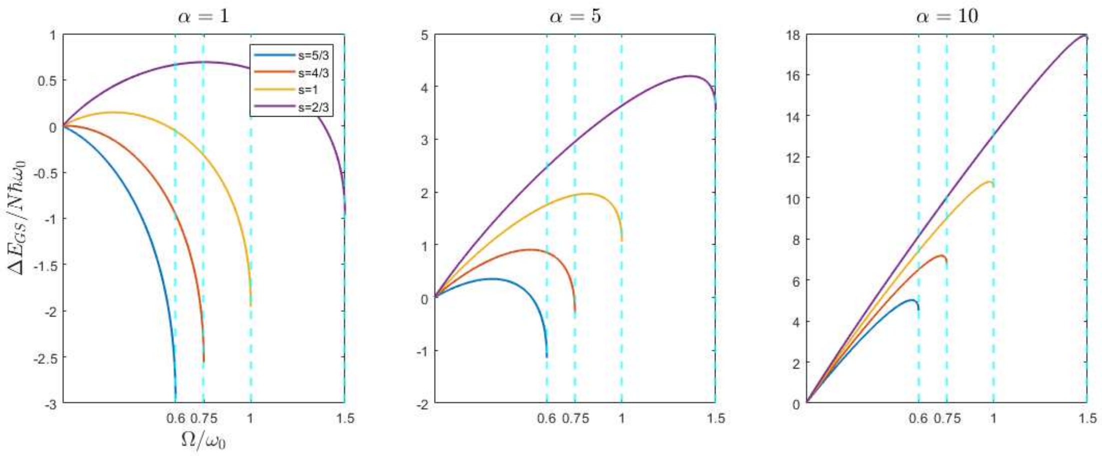
Figure 6 – Approximation taken for the ground-state energy.



Source: Elaborated by the author (2024).

as we see in figure 7. Furthermore, we note that as the coupling parameter approaches $1/s$, the curve becomes steep with a negative derivative. As we will see later, this behavior leads to interesting results and we will refer to this condition $\Omega/\omega_0 = 1/s$ the collapse condition, for reasons which will become clearer below.

Figure 7 – Ground-state energy for $\pi/a = 100\omega_0\sqrt{\varepsilon_\infty}/c$.



Source: Elaborated by the author (2024).

3.2 Thermodynamic properties of the coupled light-matter system

The diagonalization of the Hamiltonian leads to the well-known treatment of a unidimensional harmonic oscillator. Each $\mathbf{k}$ supports an quantum oscillator of frequency $\omega_{\mathbf{k}}$—which we have already determined: $\omega_{\pm,\mathbf{k}}$ and $\omega_{L,\mathbf{k}}$— with energy operator $\hbar\omega_{\mathbf{k}}\left(\eta_{\mathbf{k}}{}^{\dagger}\eta_{\mathbf{k}} + \frac{1}{2}\right)$, whose eigenstates are $|n_{\mathbf{k}}\rangle$ with engenvalues of energy $E_{n_{\mathbf{k}}} = \hbar\omega_{\mathbf{k}}\left(n_{\mathbf{k}} + \frac{1}{2}\right)$. In the bosons statistics, $|n_{\mathbf{k}}\rangle$ represents a single state particle, occupied with $n_{\mathbf{k}}$ quanta (in our case, polaritons), which is obtained by acting successively the creation operator $\eta_{\mathbf{k}}{}^{\dagger}$ in the ground-state: $\eta_{\mathbf{k}}{}^{\dagger}|0\rangle = \frac{1}{\sqrt{n_{\mathbf{k}}!}}|n_{\mathbf{k}}\rangle$.

Our total Hamiltonian is

$$H = \sum_{\substack{\mathbf{k} \\ |\mathbf{k}|\leq\alpha\pi/a}} \sum_{\hat{\lambda}_{\mathbf{k}}=\hat{\lambda}_{\mathbf{k},1},\hat{\lambda}_{\mathbf{k},2}} \hbar\omega_{+,\mathbf{k}}\left(\eta_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}{}^{\dagger}\eta_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}+\frac{1}{2}\right)+\sum_{\substack{\mathbf{k} \\ |\mathbf{k}|\leq\pi/a}}\left[\sum_{\hat{\lambda}_{\mathbf{k}}=\hat{\lambda}_{\mathbf{k},1},\hat{\lambda}_{\mathbf{k},2}} \hbar\omega_{-,\mathbf{k}}\left(\eta_{-,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}{}^{\dagger}\eta_{-,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}+\frac{1}{2}\right)\right.$$
$$\left.+\hbar\omega_{L,\mathbf{k}}\left(\eta_{L,\mathbf{k}}{}^{\dagger}\eta_{L,\mathbf{k}}+\frac{1}{2}\right)\right], \tag{3.16}$$

where the eigenstates will be denominated by the ensemble of occupation numbers $\{n\}$, and are given by the direct product

$$|\psi_{\{n\}}\rangle = \prod_{|\mathbf{k}|\leq\alpha\pi/a}\prod_{\hat{\lambda}_{\mathbf{k}}}|n_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}\rangle\otimes\prod_{|\mathbf{k}'|\leq\pi/a}|n_{L,\mathbf{k}'}\rangle\otimes\prod_{\hat{\lambda}_{\mathbf{k}'}}|n_{-,\mathbf{k}'}^{\hat{\lambda}_{\mathbf{k}'}}\rangle\,, \tag{3.17}$$

which constitutes the Fock space. The canonical partition function is obtained by doing

$$Z = \mathrm{Tr}\left[\exp\left(-\beta H\right)\right] = \sum_{\{n\}}\exp\left(-\beta\left\{\sum_{|\mathbf{k}|\leq\alpha\pi/a}\sum_{\hat{\lambda}_{\mathbf{k}}}\hbar\omega_{+,\mathbf{k}}\left(n_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}+\frac{1}{2}\right)\right.\right.$$
$$\left.\left.+\sum_{|\mathbf{k}|\leq\pi/a}\sum_{\hat{\lambda}_{\mathbf{k}}}\left[\hbar\omega_{-,\mathbf{k}}\left(n_{-,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}+\frac{1}{2}\right)+\hbar\omega_{L,\mathbf{k}}\left(n_{L,\mathbf{k}}+\frac{1}{2}\right)\right]\right\}\right), \tag{3.18}$$

where $\beta = 1/k_BT$. Since there are no restrictions on the number of polaritons, we can use the factoring:

$$Z = \prod_{|\mathbf{k}|\leq\alpha\pi/a}\prod_{\hat{\lambda}_{\mathbf{k}}}\left\{\sum_{n_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}=0}^{\infty}\exp\left[-\beta\hbar\omega_{+,\mathbf{k}}\left(n_{+,\mathbf{k}}^{\hat{\lambda}_{\mathbf{k}}}+\frac{1}{2}\right)\right]\right\}$$
$$\times\prod_{|\mathbf{k}'|\leq\pi/a}\left\{\sum_{n_{L,\mathbf{k}'}=0}^{\infty}\exp\left[\hbar\omega_{L,\mathbf{k}'}\left(n_{L,\mathbf{k}'}+\frac{1}{2}\right)\right]\right\}\prod_{\hat{\lambda}_{\mathbf{k}'}}\left\{\sum_{n_{-,\mathbf{k}'}^{\hat{\lambda}_{\mathbf{k}'}}=0}^{\infty}\exp\left[-\beta\hbar\omega_{-,\mathbf{k}'}\left(n_{-,\mathbf{k}'}^{\hat{\lambda}_{\mathbf{k}'}}+\frac{1}{2}\right)\right]\right\}. \tag{3.19}$$

By using the geometric series, we get the final form for the canonical partition function

$$Z = \prod_{\substack{\mathbf{k} \\ |\mathbf{k}|\leq\alpha\pi/a}}\frac{1}{4}\mathrm{csch}^2\left(\frac{\beta\hbar\omega_{+,\mathbf{k}}}{2}\right)\left[\prod_{\substack{\mathbf{k} \\ |\mathbf{k}|\leq\pi/a}}\frac{1}{8}\mathrm{csch}^2\left(\frac{\beta\hbar\omega_{-,\mathbf{k}}}{2}\right)\mathrm{csch}\left(\frac{\beta\hbar\omega_{L,\mathbf{k}}}{2}\right)\right], \tag{3.20}$$

with the average occupancy numbers given by

$$\langle n_{\pm,\mathbf{k}}\rangle = \frac{1}{e^{\beta\hbar\omega_{\pm,\mathbf{k}}}-1}; \tag{3.21}$$

$$\langle n_{L,\mathbf{k}}\rangle = \frac{1}{e^{\beta\hbar\omega_{L,\mathbf{k}}}-1}. \tag{3.22}$$

3.2.1 Helmholtz free energy

The connection with thermodynamics in the canonical ensemble is established by the Helmholtz free energy

$$F = -\frac{1}{\beta}\ln(Z), \tag{3.23}$$

leading to

$$F = \frac{1}{\beta}\left\{\sum_{\substack{\mathbf{k}\\ |\mathbf{k}|\leq\alpha\pi/a}} \ln\left[\frac{1}{4}\sinh^2\left(\frac{\beta\hbar\omega_{+,\mathbf{k}}}{2}\right)\right] + \sum_{\substack{\mathbf{k}\\ |\mathbf{k}|\leq\pi/a}} \ln\left[\frac{1}{8}\sinh^2\left(\frac{\beta\hbar\omega_{-,\mathbf{k}}}{2}\right)\sinh\left(\frac{\beta\hbar\omega_{L,\mathbf{k}}}{2}\right)\right]\right\}. \tag{3.24}$$

Separating the parts corresponding to the ground-state and the excited states,

$$F = \frac{1}{\beta}\left\{\sum_{\substack{\mathbf{k}\\ |\mathbf{k}|\leq\alpha\pi/a}} 2\ln\left(1-e^{-\beta\hbar\omega_{+,\mathbf{k}}}\right) + \sum_{\substack{\mathbf{k}\\ |\mathbf{k}|\leq\pi/a}}\left[2\ln\left(1-e^{-\beta\hbar\omega_{-,\mathbf{k}}}\right)+\ln\left(1-e^{-\beta\hbar\omega_{L,\mathbf{k}}}\right)\right]\right\} + E_{GS}. \tag{3.25}$$

As already mentioned, the zero point energy must diverge for $\alpha\to\infty$, and for now, we will be concerned only with studying the thermal properties coming from the excited states, that is, of the boson gas. For the excited states, it is actually convenient to take $\alpha\to\infty$. Again, assuming the periodicity conditions in the three-dimensional cavity and taking the continuum limit, the difference of the Helmholtz free energy in comparison with the ground-state is calculated from

$$\begin{aligned} F - E_{GS} = \frac{4Vk_BT}{\pi^2}\Bigg\{&\int_0^\infty 2\ln\left(1-e^{-\hbar\omega_+/k_BT}\right)k^2dk + \int_0^{\pi/a}\Bigg[2\ln\left(1-e^{-\hbar\omega_-/k_BT}\right) \\ &+\ln\left(1-e^{-\hbar\omega_L/k_BT}\right)\Bigg]k^2dk\Bigg\}. \end{aligned} \tag{3.26}$$

3.2.2 Internal energy and specific heat

The average of the total energy is

$$U = 2\sum_{\mathbf{k}}^{\infty}\hbar\omega_{+,\mathbf{k}}\left(\langle n_{+,\mathbf{k}}\rangle+\frac{1}{2}\right) + \sum_{|\mathbf{k}|\leq\pi/a}\left[2\hbar\omega_{-,\mathbf{k}}\left(\langle n_{-,\mathbf{k}}\rangle+\frac{1}{2}\right)+\hbar\omega_{L,\mathbf{k}}\left(\langle n_{L,\mathbf{k}}\rangle+\frac{1}{2}\right)\right], \tag{3.27}$$

leading to

$$U = 2\sum_{\mathbf{k}}^{\infty}\frac{\hbar\omega_{+,\mathbf{k}}}{e^{\hbar\omega_{+,\mathbf{k}}}-1} + \sum_{|\mathbf{k}|\leq\pi/a}\left[2\frac{\hbar\omega_{-,\mathbf{k}}}{e^{\beta\hbar\omega_{-,\mathbf{k}}}-1}+\frac{\hbar\omega_{L,\mathbf{k}}}{e^{\beta\hbar\omega_{L,\mathbf{k}}}-1}\right] + E_{GS}, \tag{3.28}$$

which, by exchanging the summation for integration, leads to

$$U = \frac{4V}{\pi^2}\left\{2\int_0^\infty \frac{\hbar\omega_+}{e^{\hbar\omega_+/k_BT}-1}k^2dk + \int_0^{\pi/a}\left[2\frac{\hbar\omega_-}{e^{\hbar\omega_-/k_BT}-1}+\frac{\hbar\omega_L}{e^{\hbar\omega_L/k_BT}-1}\right]k^2dk\right\} + E_{GS}. \tag{3.29}$$

For high temperatures, high-energy polaritons are dominant and, using the approximation $\omega_+ \simeq \omega_{ph} + \frac{\omega_L^2-\omega_T^2}{2\omega_{ph}} = \omega_{ph} + \frac{2\omega_0\Omega}{\omega_{ph}}$, and expanding in Taylor series the distribution

$$\frac{1}{\exp\left[\beta\hbar\omega_{ph}\left(1+\frac{2\omega_0\Omega}{\omega_{ph}^2}\right)\right]-1} = \frac{1}{e^{\beta\hbar ck/\sqrt{\varepsilon_\infty}}-1} - \beta\hbar\frac{e^{\beta\hbar\omega_{ph}}}{\left(e^{\beta\hbar\omega_{ph}}-1\right)^2}\frac{2\omega_0\Omega}{\omega_{ph}} + O\left[\left(\frac{2\omega_0\Omega}{\omega_{ph}^2}\right)^2\right], \tag{3.30}$$

disregarding the powers $\left(\frac{2\omega_0\Omega}{\omega_{ph}}\right)^2$ and further, we can get

$$U - E_{GS} = \frac{8V}{\pi^2}\int_0^\infty \frac{\omega_{ph}k^2dk}{e^{\beta\hbar\omega_{ph}}-1} + \frac{16V}{\pi^2}\frac{\varepsilon_\infty^{3/2}\omega_0\Omega}{\hbar c^3\beta^2}\int_0^\infty \frac{e^x(1-x)-1}{(e^x-1)^2}xdx. \tag{3.31}$$

We have that $\int_0^\infty \frac{e^x(1-x)-1}{(e^x-1)^2}xdx = -\pi^2/6$, and therefore

$$U - E_{GS} = \frac{8V}{\pi^2}\int_0^\infty \frac{\omega_{ph}k^2dk}{e^{\beta\hbar\omega_{ph}}-1} - \frac{8}{3}\frac{\varepsilon_\infty^{3/2}k_B^2\omega_0\Omega V T^2}{\hbar c^3}, \tag{3.32}$$

by noting that the first term of the right hand is the energy of the free photons minus the respective ground-state, we rewrite

$$U - E_{GS} = U^{free} - E_{GS}^{free} - \frac{8}{3}\frac{\varepsilon_\infty^{3/2}k_B^2\omega_0\Omega V T^2}{\hbar c^3}. \tag{3.33}$$

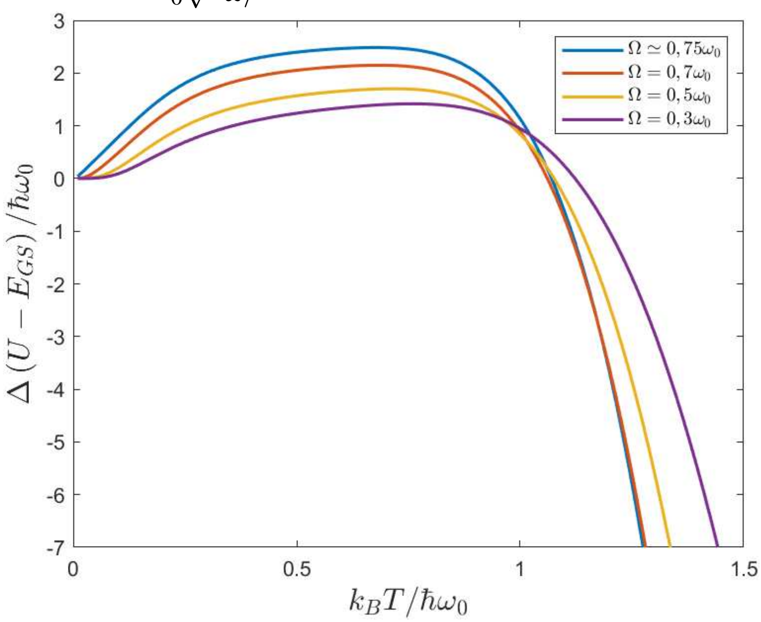
The behavior for low temperatures can also be obtained, but we will make a very detailed analysis later in the calculation of the specific heat for this limit. To understand the effect of coupling, it is interesting to study physical quantities by comparing them with the free system. Thus, the change in the energy of the boson gas caused by the coupling will be

$$\begin{aligned}\Delta(U-E_{GS}) = \frac{4V}{\pi^2}\Bigg\{&2\int_0^\infty\left[\frac{\hbar\omega_+}{e^{\hbar\omega_+/k_BT}-1} - \frac{\hbar\omega_{ph}}{e^{\hbar\omega_{ph}/k_BT}-1}\right]k^2dk \\ &+\int_0^{\pi/a}\left[2\frac{\hbar\omega_-}{e^{\hbar\omega_-/k_BT}-1} + \frac{\hbar\omega_L}{e^{\hbar\omega_L/k_BT}-1} - 3\frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}-1}\right]k^2dk\Bigg\},\end{aligned} \tag{3.34}$$

where $\Delta(U-E_{GS})$ is the energy difference between the excited states of the coupled and free systems. If $T\to\infty$, the energy will tend to the third term on the right of eq.(3.33).

By numerical solution of the integral in eq.(3.34), we plot the dependence on temperature for different coupling magnitudes in figure 8, by noticing the transition in the signal of $\Delta(U-E_{GS})$ with the increase of T, as expected in eq.(3.33). This negative value is because the occupation number of the upper polaritons is smaller than the occupation number of the free photons, despite having greater energy.

Figure 8 – Energy difference between the excited states of the coupled and free system, taking $\pi/a = \omega_0\sqrt{\varepsilon_\infty}/c$.



Source: Elaborated by the author (2024).

The specific heat at constant volume can be obtained from the definition $c_v = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_{V,N}$, from eq.(3.29):

$$c_V = \frac{8\pi k_B}{(\pi/a)^3}\Bigg\{\int_0^\infty \left(\frac{\hbar\omega_+}{k_BT}\right)^2 \frac{e^{\hbar\omega_+/k_BT}}{\left(e^{\hbar\omega_+/k_BT}-1\right)^2}k^2dk + \int_0^{\pi/a}\left[\left(\frac{\hbar\omega_-}{k_BT}\right)^2 \frac{e^{\hbar\omega_-/k_BT}}{\left(e^{\hbar\omega_-/k_BT}-1\right)^2} + \frac{1}{2}\left(\frac{\hbar\omega_L}{k_BT}\right)^2 \frac{e^{\hbar\omega_L/k_BT}}{\left(e^{\hbar\omega_-/k_BT}-1\right)^2}\right]k^2dk\Bigg\}. \tag{3.35}$$

At small temperatures, the distributions will tend to zero, except the low polaritons, which for small k's, will be dominant, as ω_- tends to zero, and becomes highly populated. Therefore, let us use the approximation $\omega_- \simeq v_gk$ ($v_g = \frac{\omega_T}{\omega_L\sqrt{\varepsilon_\infty}}c$ is the group velocity) to solve the integration, obtaining

$$c_V = \frac{8}{\pi^2}\frac{Vk_B}{N\hbar^3v_g^3\beta^3}\int_0^\infty \frac{e^x x^4}{(e^x-1)^2}dx = \frac{32\pi^2}{15}\frac{Vk_B}{N\hbar^3v_g^3\beta^3}. \tag{3.36}$$

By introducing the Debeye temperature $T_D = \frac{\hbar v_g k_D}{k_B}$ (k_D is the Debeye wavevector defined as $k_D = \left(\frac{3}{4\pi}\right)^{1/3}\pi/a$), we get the asymptotic behavior for small temperatures

$$c_V = \frac{8\pi^4}{5}k_B\left(\frac{T}{T_D}\right)^3. \tag{3.37}$$

The same result was predicted by Debeye (Gopal, 2012) for the solids, but with the difference that v_g is the sound velocity in the crystals. In our model, v_g must be much larger, because it is proportional to the light velocity (as we can see in Table 1, in ionic crystals, the BZ is large; $\pi/a \sim 10^5\omega_0\sqrt{\varepsilon_\infty}/c$). For this reason, in regular crystals, the phonon contribution to the specific heat is much larger than that of the polaritons and these can be readily disregarded when discussing the thermodynamical properties. This may cease to be true as the coupling strength becomes larger, lowering the group velocity of the polaritons.

For high temperatures, it is sufficient to derivate eq.(3.33) with respect to T, to obtain the expression

$$c_V = c_V^{free} - \frac{16}{3}\frac{\varepsilon_\infty^{3/2}k_B^2\omega_0\Omega VT}{N\hbar c^3}, \tag{3.38}$$

where c_V^{free} is the specific heat of the photon gas. By numerically solving the integral, we plot the specific heat, taking $\pi/a = \omega_0\sqrt{\varepsilon_\infty}/c$ and $s = 4/3$, for different coupling strengths, as shown in figure 9. We observe the expected cubic dependence for low temperatures and also, as the coupling approaches its maximum value, c_V becomes more expressive; the reason is that the excitation frequency ω_T becomes small, strongly increasing the population of lower polaritons, where this can be seen mathematically from the reduction of the group velocity, corresponding to the coefficient of T^3.

We also analyze the change with the size of the BZ, given in figure 10. For $\pi/a = 100\omega_0\sqrt{\varepsilon_\infty}/c$, the behavior with T^3 is seen only for temperatures outside the grid of the graph. Looking at the same curve, we notice two temperature ranges where c_V is almost constant, corresponding to regions where the dipole-dipole interaction will dominate; in the first, ω_T, and the second, both ω_T and ω_L.

3.2.3 Pressure

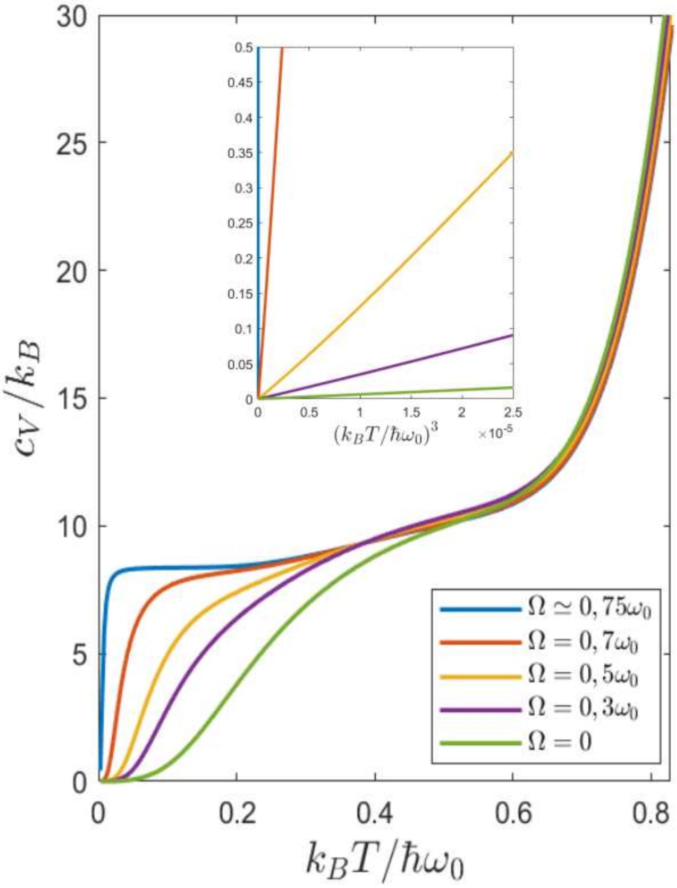
The pressure is related to F by $P = -\left(\partial F/\partial V\right)_{T,N}$. But its value will also diverge due to the GS energy, and once again, we have decided to leave these terms aside. The pressure corresponding to the polariton gas is

$$P = \frac{1}{V}\left(\Omega\frac{\partial}{\partial\Omega} - 1\right)F_{exc} + \frac{4\pi}{3}\frac{Nk_BT}{V}\ln\left[\left(1 - e^{\frac{\hbar\omega_-(k=\pi/a)}{k_BT}}\right)^2\left(1 - e^{-\hbar\omega_L/k_BT}\right)\right], \tag{3.39}$$

where F_{exc} is the component of the free energy coming from the excited states

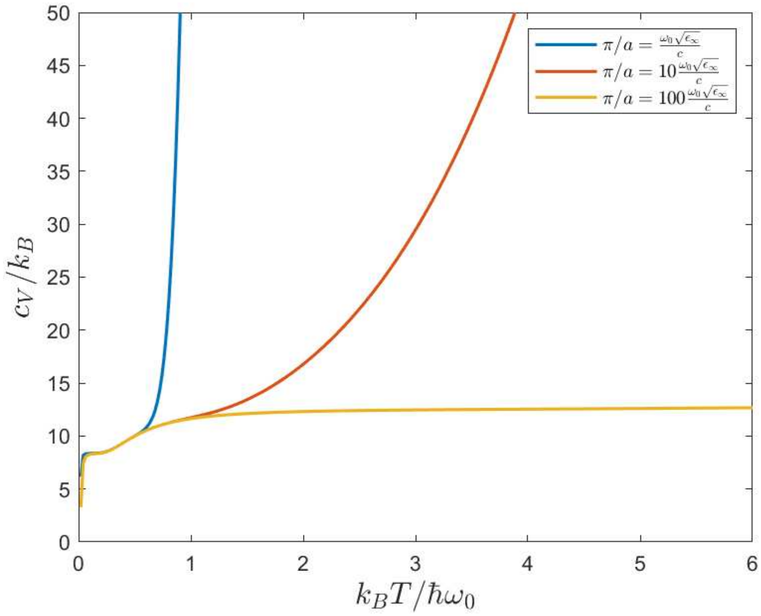
$$\begin{aligned} F_{exc} = \frac{4Vk_BT}{\pi^2}\Bigg\{ &\int_0^\infty \ln\left[\left(1 - e^{-\hbar\omega_+/k_BT}\right)^2\right]k^2dk \\ &+ \int_0^{\pi/a}\ln\left[\left(1 - e^{-\hbar\omega_-/k_BT}\right)^2\left(1 - e^{-\hbar\omega_L/k_BT}\right)\right]k^2dk\Bigg\}. \end{aligned} \tag{3.40}$$

Figure 9 – Specific heat for $\pi/a = \omega_0\sqrt{\varepsilon_\infty}/c$ and $s = 4/3$, ranging the magnitude of the coupling.



Source: Elaborated by the author (2024).

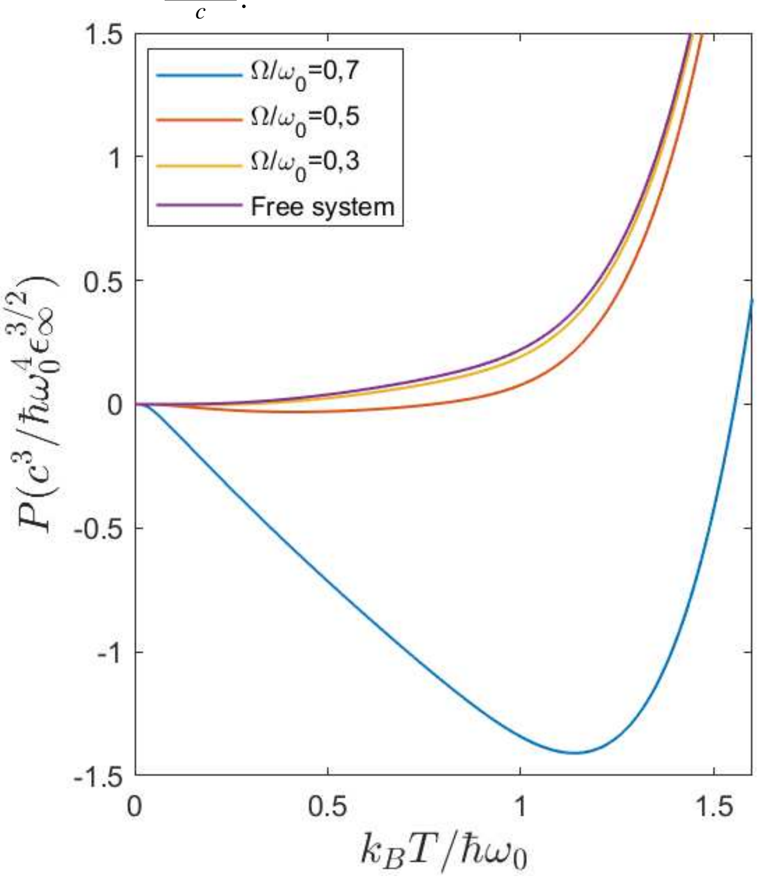
Figure 10 – Specific heat ranging π/a, for $\Omega \simeq 0{,}75\omega_0$ and $s = 4/3$.



Source: Elaborated by the author (2024).

The behavior of P with respect to T is shown in figure 11, for different coupling values.

Figure 11 – Pressure of the excitation states for $\pi/a = \frac{\omega_0\sqrt{\varepsilon_\infty}}{c}$.

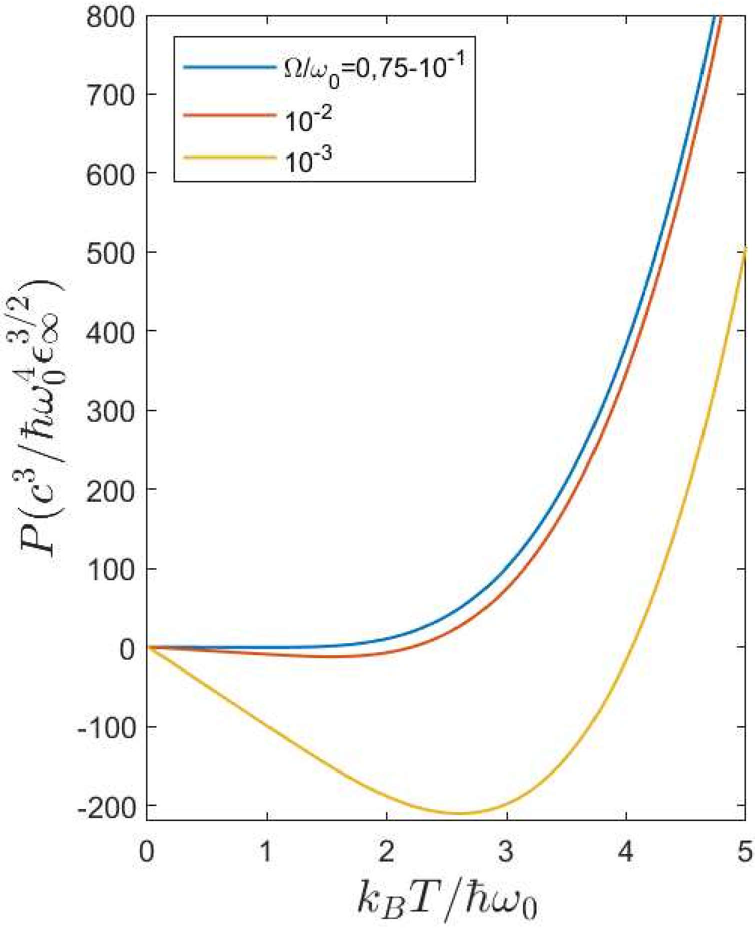


Source: Elaborated by the author (2024).

To better visualize the dependence of the pressure on the coupling strength, we also show in figure 12 the $P \times T$ plot for coupling parameters $\Omega/\omega_0 = 0.75 - d$, with $d = 0.1$, 0.01 and 0.001. We see that the negative pressure effect only becomes relevant as the relative coupling parameter approaches the collapse condition $\Omega/\omega_0 = 1/s = 0.75$. This is because the lower polaritons get the domain at certain temperatures; the derivative with respect to Ω produces a term proportional to $1/\omega_T$. But it will not prevail, as we can see in figure 11 and figure 12, because this contribution has a linear dependence with respect to T, and inevitably the high energy polaritons will dominate the expression, having a behavior proportional to T^4, as we will now show.

At high temperatures, the photon-like polaritons will predominate, and we can again

Figure 12 – Pressure ranging coupling in logarithmic scale.



Source: Elaborated by the author (2024).

use the approximation $\omega_+ \simeq \frac{ck}{\sqrt{\varepsilon_\infty}} + \frac{\omega_L^2-\omega_T^2}{2ck/\sqrt{\varepsilon_\infty}}$ to obtain

$$\begin{aligned} P &\simeq \frac{8}{\pi^2\beta}\int_0^\infty \left(\Omega\frac{\partial}{\partial\Omega}-1\right)\ln\left(1-e^{-\frac{\beta\hbar ck}{\sqrt{\varepsilon_\infty}}}e^{-\frac{\beta\hbar(\omega_L^2-\omega_T^2)}{2ck/\sqrt{\varepsilon_\infty}}}\right)k^2dk \\ &\simeq \frac{8}{\pi^2}\Bigg[\underbrace{\frac{2\hbar\omega_0\Omega}{c/\sqrt{\varepsilon_\infty}}\int_0^\infty \frac{1}{e^{\frac{\beta\hbar ck}{\sqrt{\varepsilon_\infty}}}-1}kdk}_{\text{coupling contribution}}\underbrace{-\frac{1}{\beta}\int_0^\infty \ln\left(1-e^{-\frac{\beta\hbar ck}{\sqrt{\varepsilon_\infty}}}\right)k^2dk}_{\text{uncoupled photons}}\Bigg] \\ &= \frac{8}{\pi^2}\left[\frac{2\varepsilon_\infty^{3/2}\omega_0\Omega}{\hbar c^3\beta^2}\int_0^\infty \frac{1}{e^x-1}xdx+\frac{\varepsilon_\infty^{3/2}}{c^3\hbar^3\beta^4}\int_0^\infty \ln\left(\frac{e^x}{e^x-1}\right)x^2dx\right], \end{aligned} \tag{3.41}$$

and thus, knowing that $\int_0^\infty \frac{1}{e^x-1}xdx = \frac{\pi^2}{6}$, and $\int_0^\infty \ln\left(\frac{e^x}{e^x-1}\right)x^2dx = \frac{\pi^4}{45}$, we get the approximate equation for the pressure at high temperatures

$$P = \frac{8\varepsilon_\infty^{3/2}k_B^2\omega_0\Omega}{3\hbar c^3}T^2 + P^{free}, \tag{3.42}$$

where P^{free} is the pressure of the free photon gas

$$P^{free} = \frac{8\pi^2}{45}\frac{k_B^4\varepsilon_\infty^{3/2}}{\hbar^3c^3}T^4, \tag{3.43}$$

noting that the coupling effect has a dependence on T^2.

Now let us get the pressure at low temperatures. In the limit $T \to 0$, as in the same analysis done for the specific heat, the high-energy polaritons and the longitudinal bosons become irrelevant in comparison with the low-energy polaritons. The Helmholtz's free energy can be approximately written as

$$F_{exc} \simeq -\frac{8V}{\pi^2\beta}\int_0^{\pi/a}\ln\left(\frac{e^{\beta\hbar\omega_-}}{e^{\beta\hbar\omega_-}-1}\right)k^2dk. \tag{3.44}$$

Again, let us take the approximation $\omega_- \simeq \frac{\omega_T}{\omega_L\sqrt{\varepsilon_\infty}}ck = v_gk$, and apply the variables transformation, to obtain

$$F_{exc} \simeq -\frac{8V}{\pi^2(\hbar v_g)^3}\frac{1}{\beta^4}\int_0^{\infty}\ln\left(\frac{e^x}{e^x-1}\right)x^2dx. \tag{3.45}$$

Substituting the integral $\int_0^\infty \ln\left(\frac{e^x}{e^x-1}\right)x^2dx = \frac{\pi^4}{45}$, and introducing the Debeye temperature, we get

$$F_{exc} = -\frac{2\pi^4}{15}\left(\frac{T}{T_D}\right)^3 Nk_BT. \tag{3.46}$$

From eq.(3.39), we can obtain the approximated pressure for regimes of low temperatures, knowing that $\frac{\partial T_D}{\partial\Omega} = -\frac{T_D}{2\omega_0}\left[s\frac{\omega_0^2}{\omega_T^2}+s(4-s)\frac{\omega_0^2}{\omega_L^2}\right]$:

$$P = \frac{2\pi^4}{15}\left\{1-\frac{3\Omega}{2\omega_0}\left[s\frac{\omega_0^2}{\omega_T^2}+(4-s)\frac{\omega_0^2}{\omega_L^2}\right]\right\}\left(\frac{T}{T_D}\right)^3\frac{Nk_BT}{V}. \tag{3.47}$$

Therefore, the final expression is

$$P = \frac{8\pi^2}{45}\left\{\frac{\omega_T^2\omega_L^2}{\omega_0^4}-\frac{3}{2}\frac{\Omega}{\omega_0}\left[s\frac{\omega_L^2}{\omega_0^2}+(4-s)\frac{\omega_T^2}{\omega_0^2}\right]\right\}\frac{\omega_0^4\omega_L}{\omega_T^5}\frac{\varepsilon_\infty^{3/2}k_B^4}{\hbar^3c^3}T^4, \tag{3.48}$$

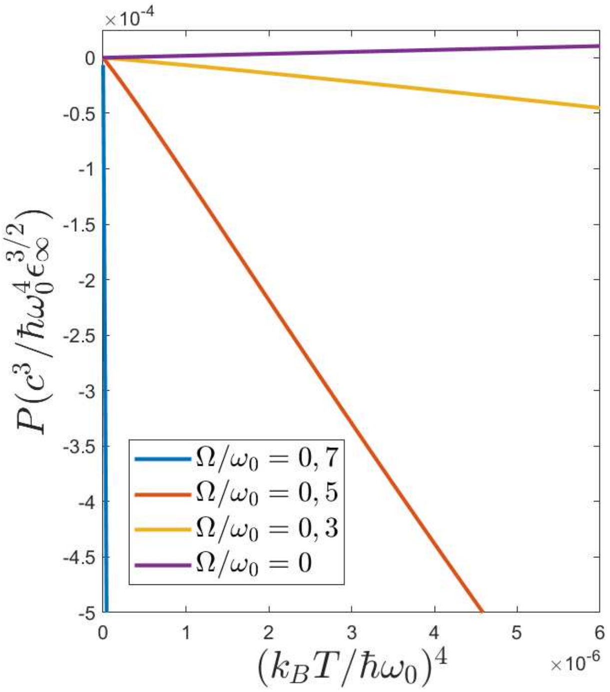
which we can rewrite as the form

$$P = \frac{8\pi^2}{45}\left\{\left[1-(1+s)\frac{\Omega}{\omega_0}\right]^2-\left(\sqrt{1+6s}\frac{\Omega}{\omega_0}\right)^2\right\}\frac{\omega_0^4\omega_L}{\omega_T^5}\frac{\varepsilon_\infty^{3/2}k_B^4}{\hbar^3c^3}T^4, \tag{3.49}$$

where inside the brackets the dimensionless term depending on the coupling gives us the pressure signal, as we can see in figure 13, where we easily get the interesting coupling transition $\Omega_T/\omega_0 = \frac{1}{1+s+\sqrt{1+6s}}$.

The negative sign in P is because the lower polaritons decrease their energy with increasing coupling, so this negative contribution comes from the derivative with respect to Ω applied to the term corresponding to ω_- in eq.(3.39). If this negative part exceeds the other positive term inside the brackets in eq.(3.39), the pressure of the lower polariton gas is negative. The presence of a negative pressure indicates that unless there is an external source of pressure, the system would tend to collapse into itself. In real physical systems, other interactions may prevent the collapse. In other hand, this effect may be a driving force for possible phase transitions in such materials.

Figure 13 – Pressure as a function of T^4 at low temperatures, taking $\pi/a = \omega_0\sqrt{\varepsilon_\infty}/c$.

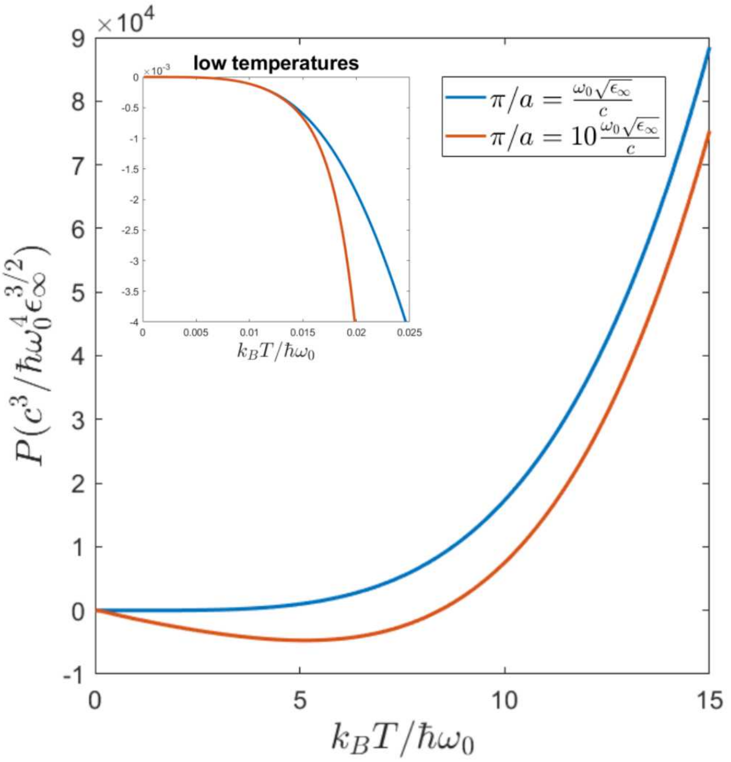


Source: Elaborated by the author (2024).

Figure 14 shows the pressure as we vary the size of the unit cell. Note that for low temperatures, the pressure is nearly independent of the unit-cell size. This is because the pressure consists of the exchange of momentum between the coupled medium and the walls of the cavity, but in the low-temperature regime the dominant wave vectors are small (long wavelengths) and so the size of the unit cell is irrelevant.

It is interesting to comment that for all thermodynamic quantities at regimes of high temperatures, we obtain a result where we have separated the component corresponding to the free system from the components coming from the coupling, making a clearer visualization of the effect of the light-matter interaction. Another important point is to note that the crystalline structure details are irrelevant at such regimes (the coupling effects depend only on Ω, and not s). On the other hand, for low temperatures, we note a dependence on s, denoting an expected structure dependence. Given this, a more detailed structural analysis of the physical properties at

Figure 14 – Pressure ranging the Brillouin zone for the coupling magnitude $\Omega/\omega_0 = 0{,}7$.



Source: Elaborated by the author (2024).

low temperatures may be appropriate.

4 CONCLUSIONS AND FUTURE WORKS

In this work we focus on a general model applicable to cases where the material elementary excitations can be interpreted as charged simple harmonic oscillators, strongly interacting with light. As a starting point, we connect ourselves to a simplified situation by considering only isotropic lattices, aiming to obtain an initial physical vision of such systems. Through a quantum formalism, considering the canonical ensemble, we were able to analyze the statistical features of the quantum system, where, through the thermodynamic connection, we explored the thermodynamic properties of the coupled system.

We can analytically preview the behavior of the considered physical properties in the low and high temperature regimes, commenting on the expected behavior and the physical implications of the light-matter interaction. Our work opens doors for the study of other thermodynamic properties such as entropy, bulk modulus, coefficient of thermal expansion, and even other thermodynamic ensembles of interest.

To obtain the physical properties, we limit ourselves to approximations that simplify the calculations. Such implemented approximations are important to have an overall physical understanding of the coupling effect in materials. With this in mind, we plan to refine our established model by making our assumptions more general, taking into account the details of the lattice, by directly evaluating different crystalline structures.

For future works, we pretend to include ground state terms in our accounts, exploring your hole for the thermodynamic properties. We also plan to take advantage of this work to investigate the possible phase transitions in materials with strong light-matter coupling, taking into account the ground state effects, based on Landau's phenomenological theory for phase transitions. Another future work is to improve the calculation of the ground state relative to the free system, ΔE_{GS}, for physical systems where α has large values, based on the same method used to calculate the Casimir effect.

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APPENDIX A – QUANTUM-CLASSICAL EQUIVALENCE

A.1 One dipole: classical approach

In section 2.2, we did not consider the interactions between different dipoles in the lattice; let us now follow the same path, but taking such interactions into account. The dipoles interact via instantaneous electric field given by

$$\mathbf{E}_{dip}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi\varepsilon_0\varepsilon_\infty}\left[\frac{3\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|^5}(\mathbf{r}'-\mathbf{r}) - \frac{\mathbf{p}}{|\mathbf{r}'-\mathbf{r}|^3}\right]. \tag{A.1}$$

The component $\hat{i}$ of the force that the charge Q of a SHO located in $\mathbf{r}_l$ undergoes due to the dipole in $\mathbf{r}_{l'}$ is

$$F^{\hat{i}}_{dip}(\mathbf{r},\mathbf{r}_{l'}) = \frac{Q}{4\pi\varepsilon_0\varepsilon_\infty}\left(\frac{3\mathbf{p}\cdot\mathbf{r}_{ll'}}{r^5_{ll'}}\mathbf{r}_{ll'} - \frac{\mathbf{p}}{r^3_{ll'}}\right)\cdot\hat{i} = \frac{Q}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}=\hat{x},\hat{y},\hat{z}}\left[\frac{3p^{\hat{j}}_{l'}(\hat{j}\cdot\mathbf{r}_{ll'})(\hat{i}\cdot\mathbf{r}_{ll'})}{r^5_{ll'}} - \frac{p^{\hat{j}}_{l'}(\hat{j}\cdot\hat{i})}{r^3_{ll'}}\right], \tag{A.2}$$

where $\mathbf{r}_{ll'} = \mathbf{r}'_l - \mathbf{r}_l$, $r_{ll'} = |\mathbf{r}'_l - \mathbf{r}_l|$ and $p^{\hat{j}}_{l'}$ is the $\hat{j}$ component of the dipole moment of the SHO in the l'-th unit cell. Substituting $p^{\hat{j}}_{l'} = Qu^{\hat{j}}(\mathbf{r}_{l'})$:

$$F^{\hat{i}}_{dip}(\mathbf{r}_l,\mathbf{r}_{l'}) = \frac{Q^2}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\left(\frac{3r^{\hat{i}}_{ll'}r^{\hat{j}}_{ll'}}{r^5_{ll'}} - \frac{\hat{j}\cdot\hat{i}}{r^3_{ll'}}\right)u^{\hat{j}}(\mathbf{r}_{l'}), \tag{A.3}$$

where $r^{\hat{i}}_{ll'} = \hat{i}\cdot\mathbf{r}_{ll'}$ and $r^{\hat{j}}_{ll'} = \hat{j}\cdot\mathbf{r}_{ll'}$.

The force at direction $\hat{i}$ due to all dipoles of the lattice is

$$F^{\hat{i}}_{dip}(\mathbf{r}_l) = \frac{Q^2}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\sum_{l'}\left(\frac{3r^{\hat{i}}_{ll'}r^{\hat{j}}_{ll'}}{r^5_{ll'}} - \frac{\hat{j}\cdot\hat{i}}{r^3_{ll'}}\right)u^{\hat{j}}(\mathbf{r}_{l'}). \tag{A.4}$$

Where the summation in l' is taken over all "primed" dipoles of the crystal. We could delimit a cutoff for these interactions, but the residue of dipoles that would leave behind is not expendable; the interaction terms are proportional to $1/r^3$ and the residuals must be of the order of $\int_{\rho_c}^{R} d^3\mathbf{r}(1/r^3) \propto \int_{\rho_c}^{R} dr/r = \ln(R/\rho_c)$ where R have the dimensions of the crystal and ρ_c is the cutoff.

Now, the equation of motion for the displacement over the direction $\hat{i}$ and natural frequency ω_0 (assumed to be the same for all directions) will be

$$M\frac{d^2}{dt^2}u^{\hat{i}}(\mathbf{r}_l,t) = -M\omega_0^2u^{\hat{i}}(\mathbf{r}_l,t) + F^{\hat{i}}_{dip}(\mathbf{r}_l,t) + QE^{\hat{i}}_0e^{i(\mathbf{k}\cdot\mathbf{r}_l-\omega t)}, \tag{A.5}$$

where $E^{\hat{i}}_0 = \hat{i}\cdot\mathbf{E}_0$. Let us exchange $u^{\hat{i}}(\mathbf{r}_l,t)$ for its Fourier transform using

$$u^{\hat{i}}(\mathbf{r}_l,t) = \mathscr{N}^{-1/2}\sum_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_l}u^{\hat{i}}(\mathbf{q},t). \tag{A.6}$$

where $\mathscr{N}$ is the total number of unit cells of the lattice. Replacing it on the equation of motion:

$$\begin{aligned}&\mathscr{N}^{-1/2}\left(\frac{d^2}{dt^2}+\omega_0^2\right)\sum_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_l}u^{\hat{i}}(\mathbf{q},t)=\\&\frac{Q^2\mathscr{N}^{-1/2}}{4M\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\sum_{\mathbf{q}}\sum_{l}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i\mathbf{q}\cdot\mathbf{r}_{l'}}u^{\hat{j}}(\mathbf{q},t)+\frac{QE_0^{\hat{i}}}{M}e^{i(\mathbf{k}\cdot\mathbf{r}_l-\omega t)}\end{aligned} \tag{A.7}$$

and applying the Fourier trick − that is, we multiply by $e^{-i\mathbf{k}\cdot\mathbf{r}_l}$ and we sum on $\mathbf{r}_l$ − we have

$$\begin{aligned}&\mathscr{N}^{-1/2}\left(\frac{d^2}{dt^2}+\omega_0^2\right)\sum_{\mathbf{q}}\sum_{l}e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_l}u^{\hat{i}}(\mathbf{q},t)=\\&\frac{Q^2\mathscr{N}^{-1/2}}{4M\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\sum_{\mathbf{q}}\sum_{l,l'}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i(\mathbf{q}\cdot\mathbf{r}_{l'}-\mathbf{k}\cdot r_l)}u^{\hat{j}}(\mathbf{q},t)+\frac{\mathscr{N}QE_0^{\hat{i}}}{M}e^{-i\omega t}.\end{aligned} \tag{A.8}$$

The following sums lead to

$$\sum_l e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_l}=\mathscr{N}\delta_{\mathbf{q},\mathbf{k}} \tag{A.9}$$

and

$$\sum_{l'}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i(\mathbf{q}\cdot\mathbf{r}_{l'}-\mathbf{k}\cdot r_l)}=\sum_{l'}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i\mathbf{k}\cdot\mathbf{r}_{ll'}}\delta_{\mathbf{q},\mathbf{k}}. \tag{A.10}$$

Actually, these summations are also different from zero when the difference vector $\mathbf{q}-\mathbf{k}$ is a reciprocal lattice vector $\mathbf{G}$. Processes involving photons outside of the first BZ are usually referred as Umklapp processes. For now, we will not take these terms into account. Thus, by substituting eq.(A.9) and eq.(A.10) into eq.(A.8) we have

$$\mathscr{N}^{1/2}\left(\frac{d^2}{dt^2}+\omega_0^2\right)u^{\hat{i}}(\mathbf{k},t)=\frac{Q^2\mathscr{N}^{-1/2}}{4M\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\sum_{l,l'}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i\mathbf{k}\cdot\mathbf{r}_{ll'}}u^{\hat{j}}(\mathbf{k},t)+\frac{\mathscr{N}QE_0^{\hat{i}}}{M}e^{-i\omega t}. \tag{A.11}$$

From the translational symmetry of the lattice, we can assume that

$$\sum_{l,l'}\left(\frac{3r_{ll'}^{\hat{i}}r_{ll'}^{\hat{j}}}{r_{ll'}^5}-\frac{\hat{j}\cdot\hat{i}}{r_{ll'}^3}\right)e^{i\mathbf{k}\cdot\mathbf{r}_{ll'}}=\mathscr{N}\sum_{\boldsymbol{\rho}}\left(\frac{3\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^5}-\frac{\hat{j}\cdot\hat{i}}{\rho^3}\right)e^{i\mathbf{k}\cdot\boldsymbol{\rho}}, \tag{A.12}$$

where $\boldsymbol{\rho}$ is the separation vector of the SHO's. The equation of motion will be

$$\begin{aligned}&\left(\frac{d^2}{dt^2}+\omega_0^2\right)u^{\hat{i}}(\mathbf{k},t)=\frac{Q^2}{4M\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\sum_{\boldsymbol{\rho}}\left(\frac{3\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^5}-\frac{\hat{j}\cdot\hat{i}}{\rho^3}\right)e^{i\mathbf{k}\cdot\boldsymbol{\rho}}u^{\hat{j}}(\mathbf{k},t)+\frac{\mathscr{N}^{1/2}QE_0^{\hat{i}}}{M}e^{-i\omega t}\\&=\frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}D^{\hat{i},\hat{j}}(\mathbf{k})u^{\hat{j}}(\mathbf{k},t)+\frac{\mathscr{N}^{1/2}QE_0^{\hat{i}}}{M}e^{-i\omega t},\end{aligned} \tag{A.13}$$

where

$$D^{\hat{i},\hat{j}}(\mathbf{k})=\frac{1}{N\pi}\sum_{\boldsymbol{\rho}}\left(\frac{3\rho^{\hat{i}}\rho^{\hat{j}}}{\rho^2}-\hat{j}\cdot\hat{i}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3} \tag{A.14}$$

is the dimensionless sum term of the array, which is discussed in more detail in Ref. (COHEN; KEFFER, 1955).

Now, as we did in the section 2.2, let us propose $u^{\hat{i}}(\mathbf{r}_l,t) = u_0^{\hat{i}} e^{i(\mathbf{k}'\cdot\mathbf{r}_l - \omega t)}$. The Fourier transform of this function is:

$$u^{\hat{i}}(\mathbf{k},t) = \mathscr{N}^{-1/2} e^{-i\omega t} u_0^{\hat{i}} \sum_l e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_l} = \mathscr{N}^{1/2} e^{-i\omega t} u_0^{\hat{i}} \delta_{\mathbf{k}',\mathbf{k}}. \tag{A.15}$$

Therefore, $u^{\hat{i}}(\mathbf{k},t)$ is only different from zero when the wavevector of the material modes $\mathbf{k}'$ is equal to the light wavevector $\mathbf{k}$. Replacing eq.(A.15) into eq.(A.13), we obtain

$$\left(\omega_0^2 - \omega^2\right) u_0^{\hat{i}} - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} \sum_{\hat{j}} D^{\hat{i},\hat{j}}(\mathbf{k}) u_0^{\hat{j}} = \frac{QE_0^{\hat{i}}}{M}. \tag{A.16}$$

For the amplitude of the transverse modes, we take $\hat{i} = \hat{\lambda}_{\mathbf{k}}$. Furthermore, for simplicity, we can orient the directions of the coordinate axis as $\hat{\lambda}_{\mathbf{k}} = \hat{x}$, $\hat{y} = \hat{k} \times \hat{\lambda}_{\mathbf{k}} = \hat{\lambda}'_{\mathbf{k}}$ and $\hat{z} = \hat{k}$. Thus,

$$\left[\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}(\mathbf{k}) - \omega^2\right] u_0^{\hat{\lambda}_{\mathbf{k}}} - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty}\left[D^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}'_{\mathbf{k}}}(\mathbf{k}) u_0^{\hat{\lambda}'_{\mathbf{k}}} + D^{\hat{\lambda}_{\mathbf{k}},\hat{k}}(\mathbf{k}) u_0^{\hat{k}}\right] = \frac{QE_0}{M}. \tag{A.17}$$

By taking the continuum limit, we can see that the structure matrix elements are diagonal; that is, $D^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}'_{\mathbf{k}}}(\mathbf{k}) = D^{\hat{\lambda}_{\mathbf{k}},\hat{k}}(\mathbf{k}) \simeq 0$ (this is also common in some high symmetry directions of cubic structures, and although not completely general, captures the physics of interest). With these considerations, we will have only

$$\left[\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}(\mathbf{k}) - \omega^2\right] u_0^{\hat{\lambda}_{\mathbf{k}}} = \frac{QE_0}{M}. \tag{A.18}$$

Where

$$D^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}(\mathbf{k}) = \frac{1}{N\pi} \sum_{\boldsymbol{\rho}} \left[3(\hat{\lambda}_{\mathbf{k}} \cdot \hat{\rho})^2 - 1\right] \frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}. \tag{A.19}$$

We thus obtain the relation between the amplitudes:

$$u_{0,T} = \frac{Q/M}{\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D_T(\mathbf{k}) - \omega^2} E_0, \tag{A.20}$$

where the index "T" denotes "transverse". Using it to get the polarization, as we did in eq.(2.2), the expression for the displacement vector becomes

$$\mathbf{D} = \varepsilon_0 \left[\varepsilon_\infty + \frac{NQ^2/M\varepsilon_0}{\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D_T(\mathbf{k}) - \omega^2}\right] \mathbf{E} = \varepsilon_0 \varepsilon(\mathbf{k},\omega) \mathbf{E}, \tag{A.21}$$

where do we get the dielectric function

$$\varepsilon(\mathbf{k},\omega) = \varepsilon_\infty \left[1 + \frac{NQ^2/M\varepsilon_0\varepsilon_\infty}{\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D_T(\mathbf{k}) - \omega^2} \right] = \varepsilon_\infty \left[1 + \frac{4\omega_0\Omega}{\omega_0^2 - \omega_0\Omega D_T(\mathbf{k}) - \omega^2} \right]. \quad \text{(A.22)}$$

For transverse electric field ($\mathbf{E}_0 \cdot \mathbf{k} = 0$), from eq.(2.16) we obtain the dispersion relation for interacting dipoles

$$\omega_\pm(\mathbf{k}) = \sqrt{\frac{\omega_0^2 + \omega_{ph,\mathbf{k}}^2 + \omega_0\Omega(4 - D_T(\mathbf{k}))}{2}} \left\{ 1 \pm \sqrt{1 - \frac{4\omega_{ph,\mathbf{k}}^2 \left(\omega_0^2 - \omega_0\Omega D_T(\mathbf{k})\right)}{\left[\omega_0^2 + \omega_{ph,\mathbf{k}}^2 + \omega_0\Omega(4 - D_T(\mathbf{k}))\right]^2}} \right\}^{1/2}. \quad \text{(A.23)}$$

We can easily obtain the frequency for longitudinal modes by taking $\hat{i} = \hat{k}$ in eq.(A.16). Since the electric field is transverse, the corresponding equation becomes

$$\left[\omega_0^2 - \frac{NQ^2}{4M\varepsilon_0\varepsilon_\infty} D^{\hat{k},\hat{k}}(\mathbf{k}) - \omega^2 \right] u_0^{\hat{k}} = 0, \quad \text{(A.24)}$$

and for a nontrivial solution, we conclude that

$$\omega_L(\mathbf{k}) = \sqrt{\omega_0^2 - \omega_0\Omega D_L(\mathbf{k})}, \quad \text{(A.25)}$$

where the lattice sum factor for longitudinal modes is

$$D_L(\mathbf{k}) = \frac{1}{N\pi} \sum_{\boldsymbol{\rho}} \left[3(\hat{k} \cdot \hat{\rho})^2 - 1 \right] \frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}}}{\rho^3}. \quad \text{(A.26)}$$

One can show the relation $2D_T(\mathbf{k}) + D_L(\mathbf{k}) = 0$. At the continuum limit, where $D_T(\mathbf{k}) \to 4/3$ (COHEN; KEFFER, 1955), one can write the longitudinal frequency as

$$\omega_L = \sqrt{\omega_0^2 + (4 - D_T(\mathbf{k}))\,\omega_0\Omega}. \quad \text{(A.27)}$$

We note that the quantum and classical models are equivalent.

A.2 Two dipoles: classical approach

let us now consider a lattice with the same aspects, but taking into account two different dipoles inside each unit cell. We denominate the oscillators by type 1 and 2, where each one has its specific oscillation natural frequency ω_α, charge Q_α and mass M_α, where $\alpha = 1{,}2$. Following the same path of the discussion with one SHO, from the electric field of eq.(A.1), the $\hat{i}$th component of the force that the charge Q_α of a α dipole of the lth unit cell located in $\mathbf{r}_{\alpha,l}$

feels due to a β dipole in the position $\mathbf{r}_{\beta,l'}$ is

$$F^{\hat{i}}_{dip}(\mathbf{r}_{\alpha.l},\mathbf{r}_{\beta,l'}) = \frac{Q_\alpha}{4\pi\varepsilon_0\varepsilon_\infty}\left(\frac{3\mathbf{p}_\beta\cdot\mathbf{r}_{\alpha\beta,ll'}}{r^5_{\alpha\beta,ll'}} - \frac{\mathbf{p}_\beta}{r^3_{\alpha\beta,ll'}}\right)\cdot\hat{i} = \\ \frac{Q_\alpha}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}=\hat{x},\hat{y},\hat{z}}\left[\frac{3p^{\hat{j}}_{\beta,l'}(\hat{j}\cdot\mathbf{r}_{\alpha\beta,ll'})(\hat{i}\cdot\mathbf{r}_{\alpha\beta,ll'})}{r^5_{\alpha\beta,ll'}} - \frac{p^{\hat{j}}_{\beta,l'}(\hat{j}\cdot\hat{i})}{r^3_{\alpha\beta,ll'}}\right], \tag{A.28}$$

where $\mathbf{r}_{\alpha\beta,ll'} = \mathbf{r}_{\beta,l'} - \mathbf{r}_{\alpha,l}$, $r^{\hat{j}}_{\alpha\beta,ll'} = \hat{j}\cdot\mathbf{r}_{\alpha\beta,ll'}$ and $p^{\hat{j}}_{\beta,l'} = \hat{j}\cdot\mathbf{p}_{\beta,l'}$. Substituting $p^{\hat{j}}_{\beta,l'} = Q_\beta u^{\hat{j}}(\mathbf{r}_{\beta,l'})$:

$$F^{\hat{i}}_{dip}(\mathbf{r}_{\alpha,l},\mathbf{r}_{\beta,l'}) = \frac{Q_\alpha Q_\beta}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{j}}\left[\frac{3(\hat{j}\cdot\mathbf{r}_{\alpha\beta,ll'})(\hat{i}\cdot\mathbf{r}_{\alpha\beta,ll'})}{r^5_{\alpha\beta,ll'}} - \frac{\hat{j}\cdot\hat{i}}{r^3_{\alpha\beta,ll'}}\right]u^{\hat{j}}(\mathbf{r}_{\beta,l'}). \tag{A.29}$$

Therefore, the force due to all dipoles of the lattice on the α dipole in $\mathbf{r}_{\alpha,l}$ will be

$$F^{\hat{i}}_{dip}(\mathbf{r}_{\alpha,l}) = \frac{Q_\alpha}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\beta=1}^{2}\sum_{l',\hat{j}}Q_\beta\left[\frac{3(\hat{j}\cdot\mathbf{r}_{\alpha\beta,ll'})(\hat{i}\cdot\mathbf{r}_{\alpha\beta,ll'})}{r^5_{\alpha\beta,ll'}} - \frac{\hat{j}\cdot\hat{i}}{r^3_{\alpha\beta,ll'}}\right]u^{\hat{j}}(\mathbf{r}_{\beta,l'}). \tag{A.30}$$

The equation of motion for an oscillation mode in the direction $\hat{i}$ for an α oscillator is

$$M_\alpha\frac{d^2u^{\hat{i}}(\mathbf{r}_{\alpha,l})}{dt^2} = -M_\alpha\omega^2_\alpha u^{\hat{i}}(\mathbf{r}_{\alpha,l}) + F^{\hat{i}}_{dip}(\mathbf{r}_{\alpha,l},t) + Q_\alpha E^{\hat{i}}_0 e^{i(\mathbf{k}\cdot\mathbf{r}_{\alpha,l}-\omega t)}. \tag{A.31}$$

Exchanging $u^{\hat{i}}(\mathbf{r}_{\alpha,l})$ for its Fourier transform using

$$u^{\hat{i}}(\mathbf{r}_{\alpha,l},t) = \mathscr{N}^{-1/2}\sum_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_{\alpha,l}}u^{\hat{i}}_\alpha(\mathbf{q},t), \tag{A.32}$$

the equation of motion takes the form

$$\mathscr{N}^{-1/2}\left(\frac{d^2}{dt^2}+\omega^2_\alpha\right)\sum_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_{\alpha,l}}u^{\hat{i}}_\alpha(\mathbf{q},t) = \\ \frac{Q_\alpha\mathscr{N}^{-1/2}}{4M_\alpha\pi\varepsilon_0\varepsilon_\infty}\sum_\beta\sum_{\mathbf{q}}\sum_{\hat{j},l'}Q_\beta\left(\frac{3r^{\hat{i}}_{\alpha\beta,ll'}r^{\hat{j}}_{\alpha\beta,ll'}}{r^5_{\alpha\beta,ll'}} - \frac{\hat{j}\cdot\hat{i}}{r^3_{\alpha\beta,ll'}}\right)e^{i\mathbf{q}\cdot\mathbf{r}_{\beta,l'}}u^{\hat{j}}_\beta(\mathbf{q},t) + \frac{Q_\alpha E^{\hat{i}}_0}{M_\alpha}e^{i(\mathbf{k}\cdot\mathbf{r}_{\alpha,l}-\omega t)}. \tag{A.33}$$

Now, by applying the Fourier trick and assuming the translational symmetry of the crystal

$$\mathscr{N}^{1/2}\left(\frac{d^2}{dt^2}+\omega^2_\alpha\right)u^{\hat{i}}_\alpha(\mathbf{k},t) = \frac{NQ_\alpha\mathscr{N}^{1/2}}{4M_\alpha\varepsilon_0\varepsilon_\infty}\sum_\beta\sum_{\hat{j}}Q_\beta D^{\hat{i},\hat{j}}_{\beta\alpha}(\mathbf{k})u^{\hat{j}}_\beta(\mathbf{k},t) + \frac{\mathscr{N}Q_\alpha E^{\hat{i}}_0}{M_\alpha}e^{-i\omega t}, \tag{A.34}$$

where this time the lattice sum factor takes the following form:

$$D^{\hat{i},\hat{j}}_{\beta\alpha}(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}_{\alpha\beta}}\left(\frac{3\rho^{\hat{i}}_{\alpha\beta}\rho^{\hat{j}}_{\alpha\beta}}{\rho^2_{\alpha\beta}} - \hat{j}\cdot\hat{i}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}_{\alpha\beta}}}{\rho^3_{\alpha\beta}}, \tag{A.35}$$

where $\boldsymbol{\rho}_{\alpha\beta}$ is the separation vector between the dipoles α and β. As in the case for one oscillator, we propose that $u_{\alpha}^{\hat{j}}(\mathbf{r}_{\alpha},t) = u_{0,\alpha}^{\hat{j}} e^{i(\mathbf{k}_{\alpha}\cdot\mathbf{r}_{\alpha}-\omega t)}$ and then your reciprocal function of the Fourier space will be $u_{\alpha}^{\hat{i}}(\mathbf{k},t) = \mathscr{N} e^{-i\omega t} u_{0,\alpha}^{\hat{i}} \delta_{\mathbf{k},\mathbf{k}_{\alpha}}$ and then we get the equation that relates the amplitudes of the oscillators

$$\left(\omega_{\alpha}^{2}-\omega^{2}\right) u_{0,\alpha}^{\hat{i}} - \frac{NQ_{\alpha}}{4M_{\alpha}\varepsilon_{0}\varepsilon_{\infty}} \sum_{\beta=1,2} \sum_{\hat{j}=\hat{x},\hat{y},\hat{z}} Q_{\beta} D_{\beta\alpha}^{\hat{i},\hat{j}}(\mathbf{k}) u_{0,\beta}^{\hat{j}} = \frac{Q_{\alpha}E_{0}^{\hat{i}}}{M_{\alpha}}. \tag{A.36}$$

For a transverse electric field with polarization $\hat{\lambda}_{\mathbf{k}}$, choosing $\hat{k}=\hat{z}$ and $\hat{\lambda}_{\mathbf{k}}=\hat{x}$, taking the mode of oscillation over the direction of polarization, eq.(A.36) becomes

$$\left(\omega_{\alpha}^{2}-\omega^{2}\right) u_{0,\alpha}^{\hat{\lambda}_{\mathbf{k}}} - \frac{NQ_{\alpha}}{4M_{\alpha}\varepsilon_{0}\varepsilon_{\infty}} \sum_{\beta=1,2} Q_{\beta} D_{\beta\alpha}^{\hat{\lambda}_{\mathbf{k}},\hat{j}}(\mathbf{k}) u_{0,\beta}^{\hat{j}} = \frac{Q_{\alpha}E_{0}}{M_{\alpha}}. \tag{A.37}$$

Again, because we are dealing with the classical limit, the interactions of the transverse modes with respect to the parallel modes must be small, and so we neglect them, leading to

$$\left(\omega_{\alpha}^{2}-\omega^{2}\right) u_{0,\alpha}^{\hat{\lambda}_{\mathbf{k}}} - \frac{NQ_{\alpha}}{4M_{\alpha}\varepsilon_{0}\varepsilon_{\infty}} \sum_{\beta=1}^{2} Q_{\beta} D_{\alpha\beta}^{\hat{\lambda}_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}(\mathbf{k}) u_{0,\beta}^{\hat{\lambda}_{\mathbf{k}}} = \frac{Q_{\alpha}E_{0}}{M_{\alpha}}. \tag{A.38}$$

Since we are considering only two oscillators, we will have two equations; one for type 1, and the other for type 2:

$$\left[\omega_{1}^{2} - \frac{NQ_{1}Q_{2}}{4M_{1}\varepsilon_{0}\varepsilon_{\infty}} D_{11}(\mathbf{k}) - \omega^{2}\right] u_{0,1} - \frac{NQ_{1}Q_{2}}{4M_{1}\varepsilon_{0}\varepsilon_{\infty}} D_{21}(\mathbf{k}) u_{0,2} = \frac{Q_{1}E_{0}}{M_{1}} \tag{A.39}$$

$$\left[\omega_{2}^{2} - \frac{NQ_{1}Q_{2}}{4M_{2}\varepsilon_{0}\varepsilon_{\infty}} D_{22}(\mathbf{k}) - \omega^{2}\right] u_{0,2} - \frac{NQ_{1}Q_{2}}{4M_{2}\varepsilon_{0}\varepsilon_{\infty}} D_{12}(\mathbf{k}) u_{0,1} = \frac{Q_{2}E_{0}}{M_{2}}. \tag{A.40}$$

Is easy to note that $D_{11}(\mathbf{k}) = D_{22}(\mathbf{k})$ because these sums are taken from the primitive vectors of the lattice and $D_{12}(\mathbf{k}) = D_{21}(\mathbf{k})$ because for each vector $\boldsymbol{\rho}_{12}$ exist an other $\boldsymbol{\rho}_{21} = -\boldsymbol{\rho}_{12}$ and then we can say that $D_{12}(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}_{21}} \left[\frac{3(\rho_{21}^{\hat{\lambda}_{\mathbf{k}}})^{2}}{\rho_{21}^{5}} - \frac{1}{\rho_{21}^{3}}\right] e^{i\mathbf{k}\cdot\boldsymbol{\rho}_{21}} = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}_{12}} \left[\frac{3(\rho_{12}^{\hat{\lambda}_{\mathbf{k}}})^{2}}{\rho_{12}^{5}} - \frac{1}{\rho_{12}^{3}}\right] e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_{21}} = D_{21}^{*}(\mathbf{k})$. Substituting these relations and organizing eq.(A.39) and eq.(A.40) in matrix form:

$$\begin{pmatrix} A^{2}-\omega^{2} & -B^{2} \\ -C^{2} & F^{2}-\omega^{2} \end{pmatrix} \begin{pmatrix} u_{01} \\ u_{02} \end{pmatrix} = \begin{pmatrix} \frac{Q_{1}}{M_{1}}E_{0} \\ \frac{Q_{2}}{M_{2}}E_{0} \end{pmatrix}. \tag{A.41}$$

Where we are calling

$$A^{2} = \omega_{1}^{2} - \frac{NQ_{1}Q_{2}}{4M_{1}\varepsilon_{0}\varepsilon_{\infty}} D_{11}(\mathbf{k}); \tag{A.42}$$

$$B^{2} = \omega_{2}^{2} - \frac{NQ_{1}Q_{2}}{4M_{1}\varepsilon_{0}\varepsilon_{\infty}} D_{21}(\mathbf{k}); \tag{A.43}$$

$$C^2 = \frac{NQ_1Q_2}{4M_2\varepsilon_0\varepsilon_\infty} D^*_{21}(\mathbf{k}); \tag{A.44}$$

$$F^2 = \omega_2^2 - \frac{NQ_1Q_2}{4M_2\varepsilon_0\varepsilon_\infty} D_{11}(\mathbf{k}). \tag{A.45}$$

and we can obtain the amplitudes $u_{0,1}$ and $u_{0,2}$:

$$u_{0,1} = -\left[\frac{\frac{B^2Q_2}{M_2} + \left(F^2-\omega^2\right)\frac{Q_1}{M1}}{(A^2-\omega^2)(F^2-\omega^2)-(BC)^2}\right] E_0; \tag{A.46}$$

$$u_{0,2} = -\left[\frac{\frac{C^2Q_1}{M_1} + \left(A^2-\omega^2\right)\frac{Q_2}{M2}}{(A^2-\omega^2)(F^2-\omega^2)-(BC)^2}\right] E_0. \tag{A.47}$$

We can get the macroscopic polarization for a transverse oscillation mode $\mathbf{k}$ from $\mathbf{P} = \sum_i N_i \mathbf{p}_i + \mathbf{P}_b$, where N_i is the density of an oscillator type i, $\mathbf{p}_i$ the dipole moment, and $\mathbf{P}_b$ the polarization due to the electronic polarizability, related to the field by eq.(2.9). Since the crystal is constituted by two oscillators per unit cell, $N_1 = N_2 = N$. The dipole moments will be $p_1 = Q_1 u_{0,1} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ and $p_2 = Q_2 u_{0,2} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ and, substituting eq.(A.46) and eq.(A.47) we have

$$\begin{aligned}\sum_i N_i \mathbf{p}_i = &\frac{N}{(A^2-\omega^2)(F^2-\omega^2)-(BC)^2}\left\{Q_1Q_2\left(\frac{B^2}{M_2}+\frac{C^2}{M_1}\right)\right.\\ &\left.-\frac{Q_1^2}{M_1}(\omega^2-F^2) - \frac{Q_2^2}{M_2}(\omega^2-A^2)\right\}\mathbf{E}.\end{aligned} \tag{A.48}$$

Replacing A, B, C and F, and writing again in terms of the coupling frequencies $\Omega_1 = \frac{NQ_1^2}{4M_1\varepsilon_0\varepsilon_\infty\omega_1}$ and $\Omega_2 = \frac{NQ_2^2}{4M_2\varepsilon_0\varepsilon_\infty\omega_2}$, the polarization due to the oscillators becomes

$$\sum_i N_i\mathbf{p}_i = 4\varepsilon_0\varepsilon_\infty\left\{\frac{2\omega_1\omega_2\Omega_1\Omega_2\left(\mathrm{Re}[D_{21}(\mathbf{k})]-D_{11}(\mathbf{k})\right)+\omega_1\Omega_1\left(\omega_2^2-\omega^2\right)+\omega_2\Omega_2\left(\omega_1^2-\omega^2\right)}{\left(\omega^2-\omega_1^2+\omega_1\Omega_1D_{11}(\mathbf{k})\right)\left(\omega^2-\omega_2^2+\omega_2\Omega_2D_{11}(\mathbf{k})\right)-\omega_1\omega_2\Omega_1\Omega_2|D_{21}(\mathbf{k})|^2}\right\}\mathbf{E}. \tag{A.49}$$

The macroscopic equation of the displacement vector $\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0\varepsilon_\infty\mathbf{E} + \sum_i N_i\mathbf{p}_i = \varepsilon_0\varepsilon(\mathbf{k},\omega)\mathbf{E}$ leads to the dielectric function

$$\varepsilon(\mathbf{k},\omega) = \varepsilon_\infty\left(1+4\left\{\frac{2\omega_1\omega_2\Omega_1\Omega_2\left(\mathrm{Re}[D_{21}(\mathbf{k})]-D_{11}(\mathbf{k})\right)+\omega_1\Omega_1\left(\omega_2^2-\omega^2\right)+\omega_2\Omega_2\left(\omega_1^2-\omega^2\right)}{\left(\omega^2-\omega_1^2+\omega_1\Omega_1D_{11}(\mathbf{k})\right)\left(\omega^2-\omega_2^2+\omega_2\Omega_2D_{11}(\mathbf{k})\right)-\omega_1\omega_2\Omega_1\Omega_2|D_{21}(\mathbf{k})|^2}\right\}\right). \tag{A.50}$$

From this equation, we obtain the dispersion relation, by substituting $\varepsilon(\mathbf{k},\omega)$ into eq.(2.16). Note that in the limiting case $\Omega_2 \to 0$, the dielectric function tends to the result that we get for one oscillator:

$$\varepsilon(\mathbf{k},\omega) = \varepsilon_\infty\left[1+\frac{NQ_1^2/M_1\varepsilon_0\varepsilon_\infty}{\omega_1^2 - \frac{NQ_1^2}{4M_1\varepsilon_0\varepsilon_\infty}D_{11}(\mathbf{k})-\omega^2}\right]. \tag{A.51}$$

This is expected, since for $\Omega_2 = 0$ the SHOs of type 2 do not couple to light and do not interact with each other, no oscillation modes are generated, and no polarization is produced. This approach can be easily generalized to more than two oscillator types, where we can obtain the amplitudes (or polarizability) by determinant calculations. Furthermore, we can add the Umklapp processes for a more sophisticated model.

A.3 Two dipoles: quantum approach

Again, let us extend our problem to two SHO on the quantum treatment. For this, we will take all the steps that were taken for one oscillator per unit cell, where our total Hamiltonian will also be $H = H_{dip} + H_{ph} + H_{ph-dip}$.

A.3.1 Dipole Hamiltonian

The energy of both oscillators is trivial, given that we already obtained it in subsection 3.1.1, and therefore

$$H_0 = \sum_{\alpha=1}^{2}\sum_{l}\left[\frac{\mathbf{\Pi}_\alpha^2(\mathbf{r}_l)}{2M_\alpha} + \frac{M_\alpha\omega_\alpha^2}{2}\mathbf{h}^2(\mathbf{r}_l)\right] = \sum_{\alpha=1}^{2}\sum_{l}\sum_{\hat{i}=\hat{x},\hat{y},\hat{z}}\left[\frac{\Pi_\alpha^{\hat{i}\,2}(\mathbf{r}_l)}{2M_\alpha} + \frac{M_\alpha\omega_\alpha^2}{2}h^{\hat{i}2}(\mathbf{r}_l)\right], \quad \text{(A.52)}$$

which in terms of the bosonic operators will be

$$H_0 = \hbar\sum_{\alpha,\hat{i},\mathbf{k}}\omega_\alpha b_{\alpha,\mathbf{k}}^{\hat{i}\,\dagger} b_{\alpha,\mathbf{k}}^{\hat{i}}, \quad \text{(A.53)}$$

where $b_{\alpha,\mathbf{k}}^{\hat{i}}(b_{\alpha,\mathbf{k}}^{\hat{i}\,\dagger})$ annihilates (creates) a boson from the oscillators of type α and wavevector $\mathbf{k}$ with oscillation mode $\hat{i}$.

Now for the part corresponding to the binding energy between dipoles in H_{dip}, using the interaction potential energy, we have

$$\begin{aligned} H_{int} = {} & \frac{1}{8\pi\varepsilon_0\varepsilon_\infty}\sum_{\alpha=1}^{2}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r_{ll',\alpha\alpha}^3} - 3\frac{r_{ll',\alpha\alpha}^{\hat{i}} r_{ll',\alpha\alpha}^{\hat{j}}}{r_{ll',\alpha\alpha}^5}\right) p_{l,\alpha}^{\hat{i}} p_{l',\alpha}^{\hat{j}} \\ & + \frac{1}{4\pi\varepsilon_0\varepsilon_\infty}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r_{ll',12}^3} - 3\frac{r_{ll',12}^{\hat{i}} r_{ll',12}^{\hat{j}}}{r_{ll',\alpha\alpha}^5}\right) p_{l,1}^{\hat{i}} p_{l',2}^{\hat{j}}. \end{aligned} \quad \text{(A.54)}$$

We can note that

$$\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r_{ll',12}^3} - 3\frac{r_{ll',12}^{\hat{i}} r_{ll',12}^{\hat{j}}}{r_{ll',\alpha\alpha}^5}\right) p_{l,1}^{\hat{i}} p_{l',2}^{\hat{j}} = \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r_{ll',\alpha\beta}^3} - 3\frac{r_{ll',\alpha\beta}^{\hat{i}} r_{ll',\alpha\beta}^{\hat{j}}}{r_{ll',\alpha\beta}^5}\right) p_{l,\alpha}^{\hat{i}} p_{l',\beta}^{\hat{j}}, \quad \text{(A.55)}$$

and therefore we can write H_{int} as

$$H_{int} = \frac{1}{8\pi\varepsilon_0\varepsilon_\infty}\sum_{\alpha\beta}\sum_{\hat{i},\hat{j}}\sum_{l,l'}\left(\frac{\delta_{\hat{i},\hat{j}}}{r_{ll',\alpha\beta}^3} - 3\frac{r_{ll',\alpha\beta}^{\hat{i}} r_{ll',\alpha\beta}^{\hat{j}}}{r_{ll',\alpha\beta}^5}\right) p_{l,\alpha}^{\hat{i}} p_{l',\beta}^{\hat{j}}. \quad \text{(A.56)}$$

Substituting $p^{\hat{i}}_{l,\alpha} = Qh^{\hat{i}}(\mathbf{r}_{l,\alpha})$ and writing $h^{\hat{i}}(\mathbf{r}_{l,\alpha})$ in terms of the lifting and lowering operators, $h^{\hat{i}}(\mathbf{r}_{l,\alpha}) = \sqrt{\frac{\hbar}{2M_\alpha\omega_\alpha}}\left(b^{\hat{i}\,\dagger}_{\mathbf{r}_{l,\alpha}} + b^{\hat{i}}_{\mathbf{r}_{l,\alpha}}\right)$, the energy takes the form

$$H_{int} = \frac{\hbar}{16\pi\varepsilon_0\varepsilon_\infty}\sum_{\alpha\beta}\sum_{\hat{i}\hat{j}}\sum_{ll'}\frac{Q_\alpha Q_\beta}{\sqrt{M_\alpha\omega_\alpha M_\beta\omega_\beta}}\left(\frac{\delta_{\hat{i},\hat{j}}}{r^3_{ll',\alpha\beta}} - 3\frac{r^{\hat{i}}_{ll',\alpha\beta}r^{\hat{j}}_{ll',\alpha\beta}}{r^5_{ll',\alpha\beta}}\right)\left(b^{\hat{i}\,\dagger}_{\mathbf{r}_{l,\alpha}}b^{\hat{j}\,\dagger}_{\mathbf{r}_{l',\beta}} + b^{\hat{i}\,\dagger}_{\mathbf{r}_{l,\alpha}}b^{\hat{j}}_{\mathbf{r}_{l',\beta}}\right.$$
$$\left. + b^{\hat{i}}_{\mathbf{r}_{l,\alpha}}b^{\hat{j}\,\dagger}_{\mathbf{r}_{l',\beta}} + b^{\hat{i}}_{\mathbf{r}_{l,\alpha}}b^{\hat{j}}_{\mathbf{r}_{l',\beta}}\right). \tag{A.57}$$

By using the bosonic operators in the reciprocal space, taking $b^{\hat{i}}_{\mathbf{r}_{l,\alpha}} = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{l,\alpha}} b^{\hat{i}}_{\mathbf{k},\alpha}$, without considering the Umklapp processes, we will have

$$H_{int} = \frac{\hbar}{16\pi\varepsilon_0\varepsilon_\infty}\sum_{\alpha\beta}\sum_{\hat{i}\hat{j}}\frac{Q_\alpha Q_\beta}{\sqrt{M_\alpha\omega_\alpha M_\beta\omega_\beta}}\left\{-\left[\sum_{\boldsymbol{\rho}_{\alpha\beta}}\left(3\frac{\rho^{\hat{i}}_{\alpha\beta}\rho^{\hat{j}}_{\alpha\beta}}{\rho^2_{\alpha\beta}} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}_{\alpha\beta}}}{\rho^3_{\alpha\beta}}\right]\right.$$
$$\left.\times\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,-\mathbf{k}} + b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,\mathbf{k}}\right) - \left[\sum_{\boldsymbol{\rho}_{\alpha\beta}}\left(3\frac{\rho^{\hat{i}}_{\alpha\beta}\rho^{\hat{j}}_{\alpha\beta}}{\rho^2_{\alpha\beta}} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{-i\mathbf{k}\cdot\boldsymbol{\rho}_{\alpha\beta}}}{\rho^3_{\alpha\beta}}\right]\left(b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,\mathbf{k}} + b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,-\mathbf{k}}\right)\right\}, \tag{A.58}$$

where $\boldsymbol{\rho}_{\alpha\beta}$ is the separation vector between the oscillators of the type α and β. Introducing the coupling frequencies $\Omega_\alpha = \frac{NQ^2_\alpha}{4M_\alpha\varepsilon_0\varepsilon_\infty\omega_\alpha}$:

$$H_{int} = -\frac{\hbar}{4}\sum_{\alpha\beta}\sum_{\hat{i}\hat{j}}\sum_{\mathbf{k}}\sqrt{\Omega_\alpha\Omega_\beta}\left[D^{\hat{i}\hat{j}}_{\alpha\beta}(\mathbf{k})\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,-\mathbf{k}} + b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,\mathbf{k}}\right)\right.$$
$$\left. + D^{\hat{i}\hat{j}\,*}_{\alpha\beta}(\mathbf{k})\left(b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,\mathbf{k}} + b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,-\mathbf{k}}\right)\right]. \tag{A.59}$$

Where the lattice sum terms are

$$D^{\hat{i}\hat{j}}_{\alpha\beta}(\mathbf{k}) = \frac{1}{N\pi}\sum_{\boldsymbol{\rho}_{\alpha\beta}}\left(3\frac{\rho^{\hat{i}}_{\alpha\beta}\rho^{\hat{j}}_{\alpha\beta}}{\rho^2_{\alpha\beta}} - \delta_{\hat{i},\hat{j}}\right)\frac{e^{i\mathbf{k}\cdot\boldsymbol{\rho}_{\alpha\beta}}}{\rho^3_{\alpha\beta}}. \tag{A.60}$$

Therefore, taking eq.(A.53) and eq.(A.59), the dipole Hamiltonian is

$$H_{dip} = \hbar\sum_{\alpha,\hat{i},\mathbf{k}}\omega_\alpha b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{i}}_{\alpha,\mathbf{k}} - \frac{\hbar}{4}\sum_{\alpha\beta}\sum_{\hat{i}\hat{j}}\sum_{\mathbf{k}}\sqrt{\Omega_\alpha\Omega_\beta}\left[D^{\hat{i}\hat{j}}_{\alpha\beta}(\mathbf{k})\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,-\mathbf{k}} + b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,\mathbf{k}}\right)\right.$$
$$\left. + D^{\hat{i}\hat{j}\,*}_{\alpha\beta}(\mathbf{k})\left(b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}\,\dagger}_{\beta,\mathbf{k}} + b^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{j}}_{\beta,-\mathbf{k}}\right)\right]. \tag{A.61}$$

A.3.2 Coupling to light

As we did in the respective section for one oscillator, the Hamiltonian that describes the light-matter coupling for two oscillators must be

$$H_{dip-ph} = \sum_\alpha\sum_l\left[\frac{Q_\alpha}{M_\alpha}\mathbf{\Pi}_\alpha(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) + \frac{Q^2_\alpha}{2M_\alpha}\mathbf{A}^2(\mathbf{r}_l)\right]. \tag{A.62}$$

By using eq.(2.34) for the potential vector and the canonical moment in eq.(2.25), the first term of the right hand becomes

$$\sum_{\alpha}\sum_{l}\frac{Q_\alpha}{M_\alpha}\mathbf{\Pi}_\alpha(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) = \mathscr{N}^{-1/2}i\hbar\sum_{\alpha}\sum_{\hat{\lambda}_{\mathbf{k}},\hat{i},l,\mathbf{k}}\omega_\alpha\sqrt{\frac{NQ_\alpha^2}{4M_\alpha\varepsilon_0\varepsilon_\infty\omega_\alpha}}\frac{\hat{i}\cdot\hat{\lambda}_{\mathbf{k}}}{\sqrt{\omega_{ph,\mathbf{k}}}}\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{r}_l} - b^{\hat{i}}_{\alpha,\mathbf{r}_l}\right) \times\left(c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}_l} + c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}e^{-i\mathbf{k}\mathbf{r}_l}\right), \tag{A.63}$$

that when we write $b^{\hat{i}}_{\alpha,\mathbf{r}_l} = \mathscr{N}^{1/2}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}_l}b^{\hat{i}}_{\alpha,\mathbf{k}}$, we get

$$\sum_{\alpha}\sum_{l}\frac{Q_\alpha}{M_\alpha}\mathbf{\Pi}_\alpha(\mathbf{r}_l)\cdot\mathbf{A}(\mathbf{r}_l) = i\hbar\sum_{\alpha}\sum_{\hat{\lambda}_{\mathbf{k}},\hat{i},\mathbf{k}}\left(\hat{i}\cdot\hat{\lambda}_{\mathbf{k}}\right)\omega_\alpha\sqrt{\frac{\Omega_\alpha}{\omega_{ph,\mathbf{k}}}}\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}} + b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{-\mathbf{k}} - b^{\hat{i}}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}} - b^{\hat{i}}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{-\mathbf{k}}\right), \tag{A.64}$$

and for the second term of the right hand:

$$\sum_{\alpha}\sum_{l}\frac{Q_\alpha^2}{2M_\alpha}\mathbf{A}^2(\mathbf{r}_l) = \hbar\sum_{\alpha}\sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}}\frac{\omega_\alpha\Omega_\alpha}{\omega_{ph,\mathbf{k}}}\left(c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{-\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{-\mathbf{k}}\right). \tag{A.65}$$

Thus, the coupling Hamiltonian is

$$H_{dip-ph} = \sum_{\alpha=1}^{2}\hbar\omega_\alpha\left\{\sum_{\hat{\lambda}_{\mathbf{k}},\hat{i},\mathbf{k}}\left(\hat{i}\cdot\hat{\lambda}_{\mathbf{k}}\right)i\sqrt{\frac{\Omega_\alpha}{\omega_{ph,\mathbf{k}}}}\left(b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}} + b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{-\mathbf{k}} - b^{\hat{i}}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}} - b^{\hat{i}}_{\alpha,\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{-\mathbf{k}}\right) + \sum_{\hat{\lambda}_{\mathbf{k}},\mathbf{k}}\frac{\Omega_\alpha}{\omega_{ph,\mathbf{k}}}\left(c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{-\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}} + c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{-\mathbf{k}}\right)\right\}. \tag{A.66}$$

A.3.3 Diagonalization

Let us suppose the polariton operator

$$\eta_{\mathbf{k}} = \sum_{\alpha=1}^{2}\sum_{\hat{i}=\hat{x},\hat{y},\hat{z}}\left(u^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{i}}_{\alpha,\mathbf{k}} + v^{\hat{i}}_{\alpha,\mathbf{k}}b^{\hat{i}\,\dagger}_{\alpha,\mathbf{k}}\right) + \sum_{\hat{\lambda}_{\mathbf{k}}}\left(m^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}} + n^{\hat{\lambda}_{\mathbf{k}}}_{\mathbf{k}}c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}\right) \tag{A.67}$$

such that

$$[\eta_{\mathbf{k}}, H] = \hbar\omega_{pol,\mathbf{k}}\eta_{\mathbf{k}}. \tag{A.68}$$

Utilizing the commutation relations

$$\left[b^{\hat{i}}_{\beta,\mathbf{k}'}, b^{\hat{j}\,\dagger}_{\alpha,\mathbf{k}}\right] = \delta_{\beta,\alpha}\delta_{\hat{i},\hat{j}}\delta_{\mathbf{k}',\mathbf{k}} \tag{A.69}$$

and

$$\left[c^{\hat{\lambda}'_{\mathbf{k}'}}_{\mathbf{k}'}, c^{\hat{\lambda}_{\mathbf{k}}\,\dagger}_{\mathbf{k}}\right] = \delta_{\mathbf{k}',\mathbf{k}}\delta_{\hat{\lambda}'_{\mathbf{k}},\hat{\lambda}_{\mathbf{k}}}, \tag{A.70}$$

we will get a set of 16 equations that we organize in a square matrix of dimension 16. Again, taking advantage of the arbitrariness of the coordinate system, we take $\hat{x} = \hat{\lambda}_{1,\mathbf{k}}$, $\hat{y} = \hat{\lambda}_{2,\mathbf{k}}$ and $\hat{z} = \hat{k}$. Furthermore, since we are considering the classical limit, only the diagonal lattice sum terms are different from zero; that is, just $D_{\alpha\beta}^{\hat{\lambda}_{1,\mathbf{k}},\hat{\lambda}_{1,\mathbf{k}}}(\mathbf{k}) \neq 0$, $D_{\alpha\beta}^{\hat{\lambda}_{2,\mathbf{k}},\hat{\lambda}_{2,\mathbf{k}}} \neq 0$ and $D_{\alpha,\beta}^{\hat{k},\hat{k}} \neq 0$. By making such considerations, as in the case of one oscillator, we are left with three independent matrices, one for each direction: $\hat{\lambda}_{1,\mathbf{k}}$, $\hat{\lambda}_{2,\mathbf{k}}$, and $\hat{k}$. The matrix for the transverse modes, with dimensionality 6×6, has the following form:

$$M = \begin{pmatrix} \omega_1-\sigma_{1,\mathbf{k}} & -\sigma_{21,\mathbf{k}} & \sigma_{1,\mathbf{k}} & \sigma_{21,\mathbf{k}} & -i\omega_1\xi_{1,\mathbf{k}} & i\omega_1\xi_{1,\mathbf{k}} \\ -\sigma_{21,\mathbf{k}}^* & \omega_2-\sigma_{2,\mathbf{k}} & \sigma_{21,\mathbf{k}}^* & \sigma_{2,\mathbf{k}} & -i\omega_2\xi_{2,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} \\ -\sigma_{1,\mathbf{k}} & -\sigma_{2,\mathbf{k}} & -\omega_1+\sigma_{1,\mathbf{k}} & \sigma_{21,\mathbf{k}} & i\omega_1\xi_{1,\mathbf{k}} & -i\omega_1\xi_{1,\mathbf{k}} \\ -\sigma_{21,\mathbf{k}}^* & -\sigma_{2,\mathbf{k}} & \sigma_{21,\mathbf{k}}^* & -\omega_2+\sigma_{2,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} & -i\omega_2\xi_{2,\mathbf{k}} \\ i\omega_1\xi_{1,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} & i\omega_1\xi_{1,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} & 2\left(\omega_1\xi_{1,\mathbf{k}}^2+\omega_2\xi_{2,\mathbf{k}}^2\right)+\omega_{ph,\mathbf{k}} & -2\left(\omega_1\xi_{1,\mathbf{k}}^2+\omega_2\xi_{2,\mathbf{k}}^2\right) \\ i\omega_1\xi_{1,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} & i\omega_1\xi_{1,\mathbf{k}} & i\omega_2\xi_{2,\mathbf{k}} & 2\left(\omega_1\xi_{1,\mathbf{k}}^2+\omega_2\xi_{2,\mathbf{k}}^2\right) & -2\left(\omega_1\xi_{1,\mathbf{k}}^2+\omega_2\xi_{2,\mathbf{k}}^2\right)-\omega_{ph,\mathbf{k}} \end{pmatrix}, \tag{A.71}$$

where

$$\sigma_{21,\mathbf{k}} = \frac{1}{2}\sqrt{\Omega_1\Omega_2}D_{21}(\mathbf{k}); \tag{A.72}$$

$$\sigma_{1,\mathbf{k}} = \frac{1}{2}\Omega_1 D_{11}(\mathbf{k}); \tag{A.73}$$

$$\sigma_{2,\mathbf{k}} = \frac{1}{2}\Omega_2 D_{11}(\mathbf{k}); \tag{A.74}$$

$$\xi_{1,\mathbf{k}} = \sqrt{\frac{\Omega_1}{\omega_{ph,\mathbf{k}}}}; \tag{A.75}$$

$$\xi_{2,\mathbf{k}} = \sqrt{\frac{\Omega_2}{\omega_{ph,\mathbf{k}}}}, \tag{A.76}$$

with $D_{21}(\mathbf{k})$ and $D_{11}(\mathbf{k})$ being the lattice sum terms for the transverse modes. Imposing that $\text{Det}(M - \omega_{pol,\mathbf{k}}\mathbb{I}_6) = 0$, and applying some manipulations, we get the

$$-\omega_{ph,\mathbf{k}}^2 + \omega_{pol,\mathbf{k}}^2\left(1+4\left\{\frac{2\omega_1\omega_2\Omega_1\Omega_2\left(\text{Re}[D_{21}(\mathbf{k})]-D_{11}(\mathbf{k})\right)+\omega_1\Omega_1\left(\omega_2^2-\omega_{pol,\mathbf{k}}^2\right)+\omega_2\Omega_2\left(\omega_1^2-\omega_{pol,\mathbf{k}}^2\right)}{\left(\omega_{pol,\mathbf{k}}^2-\omega_1^2+\omega_1\Omega_1 D_{11}(\mathbf{k})\right)\left(\omega_{pol,\mathbf{k}}^2-\omega_2^2+\omega_2\Omega_2 D_{11}(\mathbf{k})\right)-\omega_1\omega_2\Omega_1\Omega_2|D_{21}(\mathbf{k})|^2}\right\}\right) = 0. \tag{A.77}$$

From eq.(2.16), $\omega_{ph,\mathbf{k}}^2 = \frac{\varepsilon(\mathbf{k},\omega_{pol,\mathbf{k}})}{\varepsilon_\infty}\omega_{pol,\mathbf{k}}^2$, and thus

$$\varepsilon(\mathbf{k},\omega_{pol,\mathbf{k}}) = \varepsilon_\infty\left(1+4\left\{\frac{2\omega_1\omega_2\Omega_1\Omega_2\left(\text{Re}[D_{21}(\mathbf{k})]-D_{11}(\mathbf{k})\right)+\omega_1\Omega_1\left(\omega_2^2-\omega_{pol,\mathbf{k}}^2\right)+\omega_2\Omega_2\left(\omega_1^2-\omega_{pol,\mathbf{k}}^2\right)}{\left(\omega_{pol,\mathbf{k}}^2-\omega_1^2+\omega_1\Omega_1 D_{11}(\mathbf{k})\right)\left(\omega_{pol,\mathbf{k}}^2-\omega_2^2+\omega_2\Omega_2 D_{11}(\mathbf{k})\right)-\omega_1\omega_2\Omega_1\Omega_2|D_{21}(\mathbf{k})|^2}\right\}\right), \tag{A.78}$$

which again agrees with the dielectric function obtained in the classical context.

Arriving at such proof is important because it moves us away from the idea that the equivalence is a happy coincidence as we restrict ourselves to a single SHO per unit cell, and closer to the idea that there must be a physical reason for such agreement. Furthermore, we are induced to imagine that this equivalence of formalisms is also valid for general cases with a number of n oscillators. Given this, it is useful to follow the classical path to find functions such as the dielectric function and the relation, given the simplification of a matrix problem of dimensionality $2(n+1)$ (quantum) to one of dimensionality n (classical).