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Article

Quantum Concepts and Techniques in Classical Domains: Phonons and Plasmons

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Abstract

The turning point which sparked the initiation of quantum theory was the Planck-Einstein postulate that the energy of a monochromatic radiation field is quantized in terms of photons and this was followed by the development of the principles of quantum mechanics by eminent contributors. Quantum mechanics as a well-established discipline continues to be regarded as key for unraveling the mysteries of matter in general. Today the influence of quantum mechanics is evident in its applications, with remarkable technological advances involving diverse aspects of the physical world. What appears to need drawing particular attention to, however, (after hundred years have elapsed since the birth of quantum mechanics) is the impact the concept of the 'quantum' has had beyond traditional quantum mechanics. We describe how the 'quantum' concept has influenced, and continues to influence developments in physical systems which are essentially classical in that they are basically governed, wholly, or in part, by non-quantum laws but in which the physics is distinguished by its own special quantum - the photon analogue. We outline the systematic quantization of plasmons and phonons, both of the polariton (transverse) forms and their longitudinal forms and discuss how these interact with quantum systems such as electrons, atoms and condensed matter. We demonstrate using one case, namely involving longitudinal plasmons, how utilizing quantum concepts and techniques facilitate their interaction with matter, as in electron energy loss spectroscopy (EELS).

Keywords: quanta; phonons; plasmons; elementary excitations

1. Introduction

Condensed matter physics is one of the major areas where the quantum concepts and methodology are used, not just, necessarily, from the point of view of determining the microscopic quantum properties of the condensed matter itself [1,2], but also in order to deal with situations which focus on implementing the useful concept of the collective excitations [3] or the quanta - the photon analogues involved in classical contexts [4,5]. The quantum (or elementary excitation) concept [3], can fortunately be generalized to encompass a large number of situations and has proved to be particularly useful for the study of a number of important features of condensed matter physics. The main aim here is essentially to elucidate this point and to highlight the role that quantum concepts and techniques have played in classical domains.

In most cases, the basic theory relies on assumptions involving the existence of well-defined quantizable fields. Like non-relativistic perturbative quantum electrodynamics and quantum optics [6,7], problems involving condensed-matter quanta are concerned with their exchange via processes of absorption and emission which contribute non-trivially to the macroscopic and quantum properties of condensed matter [1]. They also feature whenever external probes in real experiments involving beams of various species (for example electrons, photons, neutrons and ions) are used to study the elementary excitations of the system [8]. Such problems, and many others are ideally suited for the rigorous application of perturbation techniques in conjunction with quantisation methods of the fields in condensed matter. This framework is known to have exhibited many clear successes, but the fact appears to be unfamiliar to researchers concerned primarily with traditional quantum mechanics.

In the context of condensed matter physics there are numerous examples of elementary excitations [4]. The best known are the phonons, magnons, plasmons, helicons, excitons, polaritons and other hybrid modes of various kinds. We cannot elaborate on the full set and consider it sufficient to focus on plasmons and phonons as illustrative examples to discuss in some detail.

A collective excitation in a condensed matter system can be classified as pure, involving oscillations of one kind, or a hybrid between two or more strongly coupled oscillations [9]. The phonon-polariton quanta [10], for example, are excitations associated with a coupled phonon-photon field described as an electromagnetic wave with lattice vibrations propagating in a medium, forming a well-defined kind of elementary excitation. Another example of hybrid modes are the phonon-plasmon polaritons which involve phonons, plasmons coupled to light [11].

A typical quantizable field is characterized by a field equation, most commonly second order in space and time. The field equation could have arisen directly as in the case of the electromagnetic field in free space, or has emerged as a result of a linearization step for some coupled equations imposed, for example, by the continuum or long-wavelength approximation. A large number of problems fall in this category, but as stated above, we only consider in some detail phonons and plasmons. The field equation normally emerges from an appropriate Lagrangian by application of the well known Euler-Lagrange equation. The corresponding Hamiltonian can then be defined and its quantization can be carried out using standard quantization methods. The appearance of a Hamiltonian of the system is indicative of the presence of an energy-momentum tensor and associated conservation laws involving continuity of energy-momentum flow.

This article is organized as follows. In section II we outline the basic concepts leading to the emergence of the quantum of elementary excitations of a general field, then we consider as an illustration the simplest one-dimensional case (namely the elastic line) which is characterized by a classical scalar field. In section III, we consider fluids as a more complex system in three dimensions where quantum concepts of such classical fields are not normally explored. Section IV deals with plasmons as a real system where mechanical motion of charge carriers in three dimension are governed by Newton's laws when coupled to electromagnetic fields. This system supports elementary excitations in the form of plasmons both transverse and longitudinal and we proceed to discuss their quantization. In section V we discuss the general case of fields in dielectrics with well-defined dielectric functions. This involves the coupling of lattice vibrations to the electromagnetic fields leading to phonons both (transverse) phonon-polaritons and (longitudinal) acoustic phonons and we proceed to quantize the corresponding fields. Section VI deals in general terms with the interactions of the quantized fields with quantum systems and as an application, we outline the theory of the scattering of electrons from quantized bulk plasma modes, leading to a description of electron energy loss spectroscopy of electronically-dense metals. Section VII summarizes the essential points highlighted in this paper with a general discussions about the contexts where the quanta of plasmons and phonons have featured in practical applications involving real materials.

2. Free Continuous Fields

The concept of field is indeed a classical one. Defining a field in a given region of space amounts to associating with every point of the given region a property which can be a scalar (in which case we say we have a scalar field) or a vector (vector field) and, more generally, we may be concerned with a tensor field. The fields we will be concerned with are functions of position $\mathbf{r} \equiv (x, y, z)$ as well as time t . The version of the action principle for this case is obtained in terms of a total Lagrangian L and a Lagrangian density $\mathcal{L}$ such that

$$L = \int d^3r \mathcal{L}(\{\phi_i\}, \{\dot{\phi}_i\}, \{\nabla\phi_i\}, t) \quad (1)$$

We should therefore speak of functionals, i.e. functions of the fields ϕ_i , their spatial derivatives $\nabla\phi_i$ and velocities, i.e. time derivatives $\dot{\phi}_i$. The symbol $\{\phi_i\}$ designates a set of scalar functions either

individually or in components forming, e.g. vector fields. Here, and henceforth, the dot (for example, on $\dot{\phi}_i$) indicates a single time derivative).

The action integral, denoted I , and its variation δI are as follows

$$I = \int_{t_1}^{t_2} L dt; \quad \delta I = 0 \quad (2)$$

but the variational calculus with $\mathcal{L}$ as a functional leads to the Euler-Lagrange equations with $i = x, y, z$

$$\frac{\partial}{\partial t} \left(\frac{\partial \mathcal{L}}{\partial \dot{\phi}_i} \right) + \sum_{j=1}^3 \nabla_j \frac{\partial \mathcal{L}}{\partial (\nabla_j \phi_i)} - \frac{\partial \mathcal{L}}{\partial \phi_i} = 0 \quad (3)$$

A dynamical system characterized by a field ϕ_i minimizes the action integral provided it satisfies the Euler-Lagrange equation (3), and conversely a field system with a given Lagrangian density satisfying the Euler-Lagrange equation automatically conforms with the action principle.

The formalism needed to define a given field ϕ_i would involve a definite Lagrangian density which enables the canonical momentum Π_i conjugate to the field ϕ_i to be derived. We have

$$\Pi_i = \frac{\partial \mathcal{L}}{\partial \dot{\phi}_i} \quad (4)$$

The Hamiltonian density follows by evaluating the expression

$$\mathcal{H} = \sum_i \Pi_i \dot{\phi}_i - \mathcal{L} \quad (5)$$

The final stage in the field quantization procedure involves the imposition of the commutation relation between ϕ_i and its canonically conjugate momentum Π_i at equal times t . The role of ϕ_i in field theory can be seen by analogy with that played by the coordinate q_i in particle dynamics. However here ϕ_i (in view of its continuous dependence on both space and time) pertains to a system that possesses an infinite number of degrees of freedom. We need a commutation relation that is the analogue of $[p_i, q_j] = -i\hbar\delta_{ij}$ and to derive this we begin by dividing space into discrete elements each of volume $(\delta\tau)_n$ and we assume that ϕ_n be the value of ϕ at element n positioned at point $\mathbf{r}$ at time t . Let the corresponding Lagrangian density at the element be $\mathcal{L}_n$. Thus we can write for the corresponding momentum canonically conjugate to ϕ_n

$$p_n = \frac{\partial \mathcal{L}}{\partial \dot{\phi}_n} = (\delta\tau)_n \frac{\partial \mathcal{L}_n}{\partial \dot{\phi}_n} = (\delta\tau)_n \Pi_n(\mathbf{r}) \quad (6)$$

The commutation relations are then

$$[p_{n'}, \phi_n] = -i\hbar\delta_{nn'} \quad (7)$$

and on substituting for $p_{n'}$ in terms of $\Pi_{n'}$ we get

$$[\Pi_{n'}(\mathbf{r}), \phi_n(\mathbf{r}')] = -i\hbar \frac{1}{(\delta\tau)_{n'}} \delta_{nn'} \quad (8)$$

In the limit $(\delta\tau)_n \rightarrow 0$ we have

$$[\Pi(\mathbf{r}), \phi(\mathbf{r}')] = -i\hbar\delta(\mathbf{r} - \mathbf{r}') \quad (9)$$

Therefore we have in general

$$[\Pi_i(\mathbf{r}, t), \phi_j(\mathbf{r}', t)] = -i\hbar\delta_{ij}(\mathbf{r} - \mathbf{r}') \quad (10)$$

We need not of course derive the commutation rules using the method just described. It is sufficient to impose the commutation relations in the continuum form as a requirement of the quantum field theory.

The canonical commutation relations are needed in order to ensure the consistency embodied in the requirement that the field equations follow as Heisenberg equations involving the total Hamiltonian

$$\frac{d\Pi}{dt} = \frac{i}{\hbar}[H, \Pi] \quad (11)$$

We shall see later that at the final stage of second quantization the requirement of satisfying the commutation relations between Π and Φ is equivalent to the imposition of commutation conditions between annihilation and creation operators of the corresponding field quanta. The above canonical procedure is an essential prerequisite for constructing a quantum field theory. However the most useful format of the theory as regards utility for actual applications is that obtained by carrying out the next and final step using the expansion postulate leading to the concept of quanta.

2.1. Quantization of Free Fields

The canonical, procedure when applied to the cases of free fields, leads to the identification of field equations, the construction of a suitable Lagrangian enabling the derivation of the canonical momenta conjugate to the field variables, followed by the imposition of the appropriate commutation relations between them. Finally the Hamiltonian is constructed and expressed in terms of the canonical variables and conjugate momenta.

Quantization, the ultimate stage in the procedure, involves making use of the superposition principle, according to which a physical system can be described entirely in terms of its normal modes. This is quite an old concept that can be traced back to the work of Bernoulli and others [12]. The concept was later extended and adapted to the case of electrodynamics which thus laid the foundations of quantum electrodynamics, regarded to be the gateway to the general subject of quantum field theory. Here we would like to emphasize that this theoretical framework is not a preserve of quantum field theory, but has proved to be useful in many non-quantum contexts.

The stage leading to the appearance of quanta begins with the field equation that should be solved subject to a set of physically motivated boundary conditions. The boundary conditions can, in general, be satisfied by well defined frequencies which determine the spectrum of the excitations that correspond to the given field equation. Each solution is a normal mode with a characteristic energy and the requirement that normal modes form a linearly independent set means that such modes must also be orthogonal.

Once a description in terms of the normal modes is realized, we say that we have, in principle, an exactly solvable problem. The reason is that any state of the system can be described in terms of a function satisfying the given boundary conditions and it must be expressible as a sum in terms of the normal mode functions. Thus the goal is to use the amplitudes of the normal modes as dynamical coordinates to characterize the Lagrangian and Hamiltonian in a specially simple form, namely, the form in which there is no coupling between the coordinates in the equations of motion. The system will then become equivalent to a set of isolated (i.e. non-interacting) harmonic oscillators.

To illustrate the procedure let us consider the simplest one-dimensional case, namely the elastic line which is characterized by a scalar field ϕ that satisfies a given field equation and is subject to a specific set of boundary conditions in the region (x_1, x_2) . Let the set $\{\tilde{\phi}_n(x, t)\}$ be the set of normal modes, defined as the solutions of the field equation conforming with the given boundary conditions. Let ω_n be the corresponding frequency characterizing the normal mode and let $\tilde{\phi}_n$ satisfy the condition

$$\int_{x_1}^{x_2} \tilde{\phi}_n(x) \tilde{\phi}_m(x) dx = \delta_{nm} \quad (12)$$

The superposition principle means that we are allowed to express a general state $\Phi(x, t)$ of the field as a sum,

$$\Phi(x, t) = \sum_n q_n(t) \tilde{\phi}_n(x, t) \quad (13)$$

In practically all of the physically interesting cases, the Lagrangian L can be cast in a simpler form using the orthonormality relation Eq.(12). We have

$$L = \frac{1}{2} \sum_n (\dot{q}_n^2 - \omega_n^2 q_n^2) \quad (14)$$

We may now regard the set of coefficients q_n as the generalized dynamical variables and the Lagrangian in Eq.(14) as the starting point. We then have canonical momenta p_n corresponding to q_n defined by

$$p_n = \frac{\partial L}{\partial \dot{q}_n} = \dot{q}_n \quad (15)$$

The Lagrange equation with L given by Eq.(14) and q_n as a variable gives

$$\ddot{q}_n + \omega_n^2 q_n = 0 \quad (16)$$

The Hamiltonian is obtainable in the usual fashion as follows

$$H = \sum_n (p_n^2 + \omega_n^2 q_n^2) \quad (17)$$

Thus the problem has been simplified enormously. We now have a basis for the standard treatment of dealing with the mechanics of continuous systems. The dynamics of such a system is mathematically equivalent to that of a system of non-interacting harmonic oscillators.

The transition from the description of the normal modes in terms of the variables q_n and p_n to those appropriate for the corresponding harmonic oscillator is now straightforward. We define the lowering and raising operator of the n th mode by

$$a_n = \left(\frac{1}{2\hbar\omega_n} \right)^{\frac{1}{2}} (\omega_n q_n + ip_n); \quad a_n^\dagger = \left(\frac{1}{2\hbar\omega_n} \right)^{\frac{1}{2}} (\omega_n q_n - ip_n) \quad (18)$$

The above relations are formally equivalent to those encountered in the case of the single harmonic oscillator. In particular we can write

$$[a_n, a_m^\dagger] = \delta_{nm}; \quad p_n^2 + \omega_n^2 q_n^2 = \frac{1}{\hbar\omega_n} (a_n a_n^\dagger + a_n^\dagger a_n) \quad (19)$$

Therefore we have

$$H = \frac{1}{2} \sum_n \hbar\omega_n (a_n a_n^\dagger + a_n^\dagger a_n) = \sum_n \hbar\omega_n \left(a_n^\dagger a_n + \frac{1}{2} \right) \quad (20)$$

Also from the definitions of a_n and $a_n^\dagger$ we can write

$$q_n = \left(\frac{\hbar}{2\omega_n} \right)^{\frac{1}{2}} (a_n + a_n^\dagger) \quad (21)$$

The required quantised field $\Phi(x, t)$ emerges at once by substitution in Eq.(13). The result can be written as follows

$$\Phi(x, t) = \sum_n \left(\frac{\hbar}{2\omega_n} \right)^{\frac{1}{2}} \{a_n \tilde{\phi}_n + a_n^\dagger \tilde{\phi}_n^*\} \quad (22)$$

The field Φ given in Eq.(22) is now an operator.

The formal step of the 'quantization' of any given theory begins after the Hamiltonian is derived. It involves, once a commutation relation between the field and its canonically conjugate momentum is written, the immediate recognition of the field as a quantum rather than a classical system. The

continuum case emerges from the above discrete form by converting the summation into an integral. We have

$$\Phi = \int d^3\mathbf{k} C_k \left\{ \tilde{\phi}_k a(\mathbf{k}) + \tilde{\phi}_k^* a^\dagger(\mathbf{k}) \right\} \quad (23)$$

We now apply the procedure described above to the case of a fluid, which is an essentially classical system, but which is unfamiliar in contexts of quantization.

3. Quantized Classical Fluids

By a fluid we mean a physical system consisting of a continuous distribution of a prevalent state of matter in the form of a gas or a liquid. Our interest here is primarily in the macroscopic attributes of fluids [13,14] and we do not consider their microscopic structure, nor their truly quantum properties as in the context of quantum fluids [15]. We expect our fluid system to possess a continuous distribution of mass and that the mass be conserved. It may be electrically neutral or it may possess a continuous distribution of monopole charge as in the case of an electron gas or dipole charge as in the case of an overall neutral, but polarizable medium. For simplicity and in order to highlight the general procedure, we only consider here the simplest case of an incompressible fluid.

We shall restrict the treatment to the case of ideal fluids, defined as those that are non-viscous, since viscosity forces originate in part in friction forces involving microscopic attributes. Our main interest here is their field theoretical description and the quantization of some of the relevant attributes of fluids. We begin, however by a review of some of the basic theory of hydrodynamics, which sets the scene for the more involved aspects of the corresponding canonical theory prior to quantization. First we focus on an electrically neutral fluid.

The dynamics of a neutral fluid is characterized by a mass density which is a scalar field $\rho(\mathbf{r}, t)$, a fluid displacement vector field $\mathbf{u}$ (or, equivalently, a velocity field $\mathbf{v} = \dot{\mathbf{u}}$) and a pressure scalar field p . In a linearized treatment these fields are connected by three basic relations. The first is the equation of continuity which relates the mass density field to the velocity field and is basically a statement of conservation of fluid mass. The second is the equation of motion which is Newton's law, equating the mass acceleration of an element of the fluid to the pressure forces due to the rest of the fluid. The third relates the mass density field to the pressure field.

The mass density of the fluid is defined as usual such that the mass dm contained in a fluid element of volume dV situated at point $\mathbf{r}$ at time t is

$$dm = \rho(\mathbf{r}, t) dV \quad (24)$$

and for a finite volume the amount of mass contained at a specific time t is

$$m = \int_V \rho(\mathbf{r}, t) dV \quad (25)$$

Associated with fluid motion is a fluid displacement field $\mathbf{u}(\mathbf{r}, t)$ and a current density vector $\mathbf{J}(\mathbf{r}, t)$. The current density vector field is defined by

$$\mathbf{J}(\mathbf{r}, t) = \dot{\mathbf{u}}(\mathbf{r}, t) \rho(\mathbf{r}, t) \quad (26)$$

The mass conservation law demands that in a region of fluid of volume V enclosed by a surface S the amount of inward fluid flow crossing the surface per unit time must be balanced by the rate of increase in the mass within the volume

$$\frac{dm}{dt} = - \int_S \mathbf{J} \cdot \hat{\mathbf{n}} dS = \int_V \nabla \cdot \mathbf{J} dV \quad (27)$$

where we have made use of Gauss's theorem. On making use of Equations (24) to (26) we have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \dot{\mathbf{u}}) = 0 \quad (28)$$

which is the equation of continuity relating the mass density of the fluid to its velocity fields.

The equation of motion in the fluid is an equality between the mass acceleration and the gradient of the pressure. The dynamics can be described either in terms of the fluid displacement vector field $\mathbf{u}$, or in terms of the scalar potential field ϕ , such that the velocity field $\mathbf{v} = -\nabla \phi$.

The Lagrangian density $\mathcal{L}$ can thus be expressed either in terms of $\mathbf{u}$, or in terms of ϕ . However, from the point of view of physical interpretation, the most direct form is that in terms of $\mathbf{u}$. The kinetic energy density to leading order is $\mathcal{T} = \frac{1}{2}\rho_0 \dot{\mathbf{u}}^2$, while the potential energy is $\mathcal{V} = \frac{1}{2}\beta^2 (\nabla \cdot \mathbf{u})^2$. We have for the Lagrangian density

$$\mathcal{L} = \mathcal{T} - \mathcal{V} = \frac{1}{2}\rho_0 \left\{ \dot{\mathbf{u}}^2 - \beta^2 (\nabla \cdot \mathbf{u})^2 \right\} \quad (29)$$

where ρ_0 and β are the equilibrium mass density and the oscillations velocity parameter entering the fluid pressure p . The theory is then in terms of a vector field (i.e. three scalar fields) rather than just one if we were to proceed in terms of ϕ . Let us consider the $\mathbf{u}$ form of this field theory first and deal with the ϕ form next in order to compare procedures and physical contents of each. With $\mathcal{L}$ given by Eq.(29) and $\mathbf{u}$ as the field variable, we now define the conjugate momentum $\boldsymbol{\pi}$ by

$$\boldsymbol{\pi} = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{u}}} = \rho_0 \dot{\mathbf{u}} \quad (30)$$

Thus the Euler-Lagrange equations with $\mathcal{L}$ as the Lagrangian density yields

$$\ddot{\mathbf{u}} - \beta^2 \nabla^2 \mathbf{u} = 0 \quad (31)$$

The corresponding Hamiltonian density is

$$\mathcal{H} = \boldsymbol{\pi} \cdot \dot{\mathbf{u}} - \mathcal{L} = \frac{1}{2}\rho_0 \left(\dot{\mathbf{u}}^2 + \beta^2 (\nabla \cdot \mathbf{u})^2 \right) \quad (32)$$

The interpretation is clear : the Hamiltonian is simply the sum of kinetic and potential energies.

Quantization may now proceed as follows, anticipating that $\mathbf{u}$ is an irrotational vector, i.e. $\nabla \times \mathbf{u} = 0$. We expand $\mathbf{u}$ in plane waves in a cubic cavity of volume d^3 subject to periodic boundary conditions. Thus we write

$$\mathbf{u}(\mathbf{r}, t) = \sum_n \hat{\mathbf{k}}_n C_n \left(a_n e^{i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} + a_n^\dagger e^{-i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} \right) \quad (33)$$

where $\hat{\mathbf{k}}_n$ is a unit vector along $\mathbf{k}_n$, C_n is the mode amplitude to be determined, and ω_n is the mode frequency for a plane wave satisfying the wave equation Eq.(31)

$$\omega_n = \beta k_n; \quad k_n = |\mathbf{k}_n| \quad (34)$$

Application of the periodic boundary conditions gives

$$\mathbf{k}_n = \frac{2\pi}{d} (n_1, n_2, n_3) \quad (35)$$

where n_1, n_2 and n_3 are integers ranging from $-\infty$ to ∞ . Thus each mode is specified by three indices. It is convenient however to continue to adopt the single index n to stand for the three.

From Eq.(33) we have

$$\dot{\mathbf{u}}(\mathbf{r}, t) = -i \sum_n \hat{\mathbf{k}}_n \omega_n C_n \left(a_n e^{i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} - a_n^\dagger e^{-i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} \right) \quad (36)$$

and

$$\nabla \cdot \mathbf{u} = i \sum_n \mathbf{k}_n C_n \left(a_n e^{i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} - a_n^\dagger e^{-i(\mathbf{k}_n \cdot \mathbf{r} - \omega_n t)} \right) \quad (37)$$

Substituting in the field Hamiltonian we have

$$H = \frac{1}{2} \rho_0 \int dV \left\{ \dot{\mathbf{u}} \cdot \dot{\mathbf{u}}^\dagger + \beta^2 (\nabla \cdot \mathbf{u}) (\nabla \cdot \mathbf{u})^\dagger \right\} \quad (38)$$

Substituting and making use of the integral

$$\int_V dV e^{i(\mathbf{k}_n - \mathbf{k}_{n'}) \cdot \mathbf{r}} = V \delta_{n,n'} \quad (39)$$

we find that the Hamiltonian reduces to the canonical form

$$H = \frac{1}{2} \sum_n \hbar \omega_n \left(a_n a_n^\dagger + a_n^\dagger a_n \right) \quad (40)$$

provided that the mode coefficient C_n is given by

$$C_n = \sqrt{\frac{\hbar}{2V\rho_0\omega_n}} \quad (41)$$

In the infinite domain we take $d \rightarrow \infty$ and obtain

$$\mathbf{u}(\mathbf{r}, t) = \int d^3\mathbf{k} \left(\frac{\hbar}{2(2\pi)^3\rho_0\omega} \right)^{\frac{1}{2}} \hat{\mathbf{k}} \left[a(\mathbf{k}) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + a^\dagger(\mathbf{k}) e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right] \quad (42)$$

The commutation relation that should accompany the formalism with $\mathbf{u}$ as the field variable is between components of π and $\mathbf{u}$

$$[\pi_i(\mathbf{r}, t), u_j(\mathbf{r}', t)] \quad (43)$$

We obtain by direct substitution of $\pi = \rho_0 \dot{\mathbf{u}}$

$$[\pi_i(\mathbf{r}, t), u_j(\mathbf{r}', t)] = \delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{r}') \quad (44)$$

where $\delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{r}')$ is the longitudinal delta function

$$\delta_{ij}^{\parallel}(\mathbf{r} - \mathbf{r}') = \int d^3\mathbf{k} \hat{k}_i \hat{k}_j e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \quad (45)$$

The emergence of the result of the commutator in this manner is a direct consequence of the fact that $\mathbf{u}$ is irrotational.

4. Plasmons

One of the best examples of a quantisable classical systems that has been and continues to be extensively studied is distinguished by well-define elementary excitations with quanta called plasmons [16]. These excitations arise in the context of a model quasi-continuum material called jellium. The jellium model is exemplified by the case of valence electrons in a metal (where there are typically $\approx 10^{28}$ electrons m^{-3}) or the conduction electrons in a doped semiconductor ($\approx 10^{25} m^{-3}$). The relevant fields are those pertaining to a charged fluid representing the electrons interacting with the electromagnetic fields, which are, themselves, modified by the polarization provided by the charged fluid. Electrons in a metal can thus be viewed as a charged fluid in the presence of an overall neutralizing background charge due to the fixed uniformly distributed nuclei. Since the periodicity of the lattice ions is ignored the situation resembles a jellium whereby the electron fluid oscillates relative

to the positive background provided by the ions. In a linearized approximation the properties of the charged fluid are represented by the polarization amplitude field $\xi(\mathbf{r}, t)$ via which deviations from equilibrium manifest themselves. If n is the equilibrium volume density of electrons (of effective mass m^* and charge e), the deviation Δn of the charge density from equilibrium can be expressed in terms of $\xi(\mathbf{r}, t)$ as follows

$$\Delta n = -n \nabla \cdot \xi \quad (46)$$

ξ may be referred to as the collective amplitude field and is related to the conserved fluid charge density ρ and current density $\mathbf{J}$ by

$$\rho = -ne \nabla \cdot \xi; \quad \mathbf{J} = ne \dot{\xi} \quad (47)$$

The basic equations for this so-called dispersive hydrodynamic model in the absence of any free charges are as follows. First, the fields are coupled to the polarisation charge density and current density via Maxwell's equations

$$\begin{aligned} \nabla \cdot \mathbf{E} &= -\frac{1}{\epsilon_0} ne \nabla \cdot \xi \\ \nabla \times \mathbf{E} &= -\dot{\mathbf{B}} \\ \nabla \times \mathbf{B} &= \mu_0 \epsilon_0 \dot{\mathbf{E}} + \mu_0 ne \dot{\xi} \\ \nabla \cdot \mathbf{B} &= 0 \end{aligned} \quad (48)$$

Second, the fields modify the mechanical motion of the fluid via Newton's law. For an element of the fluid the equation of motion can be written as follows

$$m^* \ddot{\xi}(\mathbf{r}, t) = e \mathbf{E}(\mathbf{r}, t) + m^* \beta_p^2 \nabla (\nabla \cdot \xi) \quad (49)$$

The spatial dispersion is manifest on inclusion of the last term, identified as the pressure term in Eq.(49). The hydrodynamic pressure is

$$\Delta p = -nm^* \beta_p^2 \nabla \cdot \xi \quad (50)$$

In the above β_p is the plasma velocity parameter and m^* is the effective electronic mass in the medium. The force corresponding to the last term in Eq.(49) is equal to $-\nabla(\Delta p)$.

The procedure demands first finding the Lagrangian as the basis for the description of this system. We seek to express fields in terms of electromagnetic potentials. In an arbitrary gauge we write

$$\mathbf{E} = -\dot{\mathbf{A}} - \nabla \Phi; \quad \mathbf{B} = \nabla \times \mathbf{A} \quad (51)$$

The equations of motion are now as follows. The first equation in (48) becomes

$$\nabla \cdot \dot{\mathbf{A}} + \nabla^2 \Phi = \frac{1}{\epsilon_0} ne \nabla \cdot \xi \quad (52)$$

while the third equation in (48) now reads

$$\nabla \times \nabla \times \mathbf{A} = -\mu_0 \epsilon_0 \ddot{\mathbf{A}} - \mu_0 \epsilon_0 \nabla \dot{\Phi} + \mu_0 \epsilon_0 \dot{\xi} \quad (53)$$

Finally Newton's law Eq.(49) becomes

$$m^* \ddot{\xi} = -e(\dot{\mathbf{A}} + \nabla \Phi) + m^* \beta_p^2 \nabla (\nabla \cdot \xi) \quad (54)$$

The Lagrangian must reproduce the above equations and must account for both the electromagnetic and the mechanical contributions together with their coupling interaction. Thus the total Lagrangian density is the sum of three contributions

$$\mathcal{L} = \mathcal{L}_{em} + \mathcal{L}_{\xi} + \mathcal{L}_{int} \quad (55)$$

where $\mathcal{L}_{em}$ pertains to the electromagnetic fields

$$\mathcal{L}_{em} = \frac{1}{2}\epsilon_0 \left([\dot{\mathbf{A}} + \nabla\Phi]^2 - c^2 [\nabla \times \mathbf{A}]^2 \right) \quad (56)$$

$\mathcal{L}_{\xi}$ pertains to the mechanical motion of the electron fluid

$$\mathcal{L}_{\xi} = \frac{1}{2}m^*n \left(\dot{\xi}^2 - \beta_p^2 (\nabla \cdot \xi)^2 \right) \quad (57)$$

Finally $\mathcal{L}_{int}$ represents the coupling between the fields and the fluid's charge and current densities

$$\mathcal{L}_{int} = ne\dot{\xi} \cdot \mathbf{A} + ne(\nabla \cdot \xi)\Phi \quad (58)$$

Consider now the Euler-Lagrange equation with ξ as a variable. We have

$$\frac{\partial \mathcal{L}}{\partial \dot{\xi}} = m^*n\dot{\xi} + ne\mathbf{A} = \mathcal{P} \quad (59)$$

$$\sum_i \partial_i \frac{\partial \mathcal{L}}{\partial (\partial_i \xi)} = ne\nabla\Phi - nm^*\beta_p^2 (\nabla \cdot \xi) \quad (60)$$

$$\frac{\partial \mathcal{L}}{\partial \xi} = 0 \quad (61)$$

On substituting in the Euler-Lagrange equations we recover Eq.(54). Consider next the field equation with $\mathbf{A}$ as a variable. We have

$$\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{A}}} = \epsilon_0(\dot{\mathbf{A}} + \nabla\Phi) = \Pi \quad (62)$$

$$\sum_i \partial_i \frac{\partial \mathcal{L}}{\partial (\partial_i \mathbf{A})} = -\epsilon_0 c^2 \nabla \times \nabla \times \mathbf{A} \quad (63)$$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{A}} = ne\dot{\xi} \quad (64)$$

We can check that the Euler-Lagrange equation with $\mathbf{A}$ as a variable yields Eq(53). Finally consider the case of Φ as a variable. We find

$$\frac{\partial \mathcal{L}}{\partial \Phi} = 0 \quad (65)$$

$$\sum_i \partial_i \frac{\partial \mathcal{L}}{\partial (\partial_i \Phi)} = \epsilon_0 (\nabla \cdot \dot{\mathbf{A}} + \nabla^2 \Phi) \quad (66)$$

$$\frac{\partial \mathcal{L}}{\partial \Phi} = ne\nabla \cdot \xi \quad (67)$$

Once again we can see that the Euler-Lagrange equation with Φ as a variable leads to the first maxwell equation in Eq.(48).

The Hamiltonian density now follows straightforwardly using the familiar prescription

$$\mathcal{H} = \mathcal{P} \cdot \dot{\xi} + \Pi \cdot \dot{\mathbf{A}} - \mathcal{L} \quad (68)$$

Substituting for the canonical momenta from Eqs.(59) and (62) and after cancellations and other simplifications we find

$$\begin{aligned} \mathcal{H} = & \frac{1}{2}m^*n(\dot{\xi}^2 + \beta_p^2[\nabla \cdot \xi]^2) + \frac{1}{2}\epsilon_0(\dot{\mathbf{A}}^2 + c^2[\nabla \times \mathbf{A}]^2) \\ & + \epsilon_0\nabla\Phi \cdot \dot{\mathbf{A}} + \frac{1}{2}\epsilon_0\nabla\Phi \cdot \nabla\Phi - ne(\nabla \cdot \xi)\Phi \end{aligned} \quad (69)$$

This is the desired Hamiltonian for the electromagnetic fields coupled to the jellium and we must emphasise that since no gauge condition has so far been imposed on fields $\mathbf{A}$ and Φ the fields conform with an arbitrary gauge.

We may now make the division of each of the vector fields (represented by $\mathbf{V}$) into its transverse (divergence free) and longitudinal (curl free) components such that

$$\mathbf{V} = \mathbf{V}^T + \mathbf{V}^L; \quad \nabla \cdot \mathbf{V}^T = 0; \quad \nabla \times \mathbf{V}^L = 0; \quad \mathbf{V}^T \cdot \mathbf{V}^L = 0 \quad (70)$$

We therefore end up with two sets of field equations which we may proceed to deal with separately. The transverse set of equations will be referred to as the plasmon polariton set and the longitudinal as the longitudinal plasmon set. The division applies also to the canonical momenta, the Lagrangian and the Hamiltonian.

4.1. Transverse Fields: Plasmon Polaritons

The transverse fields conform with the following set of equations

$$\nabla \cdot \mathbf{E}^T = 0 = \nabla \cdot \xi^T \quad (71)$$

$$\nabla \times \mathbf{E}^T = -\dot{\mathbf{B}} \quad (72)$$

$$\nabla \times \mathbf{B} = \mu_0\epsilon_0\dot{\mathbf{E}}^T + \mu_0ne\dot{\xi}^T \quad (73)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (74)$$

$$m^*\ddot{\xi}^T = e\mathbf{E}^T \quad (75)$$

We now associate the transverse electromagnetic fields with the transverse vector potential $\mathbf{A}^T$ and the longitudinal fields with Φ . The vector potential is required to be transverse everywhere satisfying $\nabla \cdot \mathbf{A}^T = 0$. Then we may drop all terms in the Hamiltonian containing both $\mathbf{A}$ with $\nabla\Phi$ since $\mathbf{A}^T \cdot \nabla\Phi = 0$. Equating the transverse components in Eq.(53), we have

$$\nabla^2\mathbf{A}^T - \mu_0\epsilon_0\ddot{\mathbf{A}}^T = -\mu_0ne\dot{\xi}^T \quad (76)$$

This relation also follows from Eq.(73) with the substitution

$$\mathbf{E}^T = -\dot{\mathbf{A}}^T; \quad \mathbf{B} = \nabla \times \mathbf{A}^T \quad (77)$$

The ξ^T equation now involves $\mathbf{A}^T$ as follows

$$m^*\ddot{\xi}^T = -e\dot{\mathbf{A}}^T \quad (78)$$

The Hamiltonian density can be written at once as the transverse part of the full Hamiltonian density. It is

$$\mathcal{H}^T = \frac{1}{2}m^*n[\dot{\xi}^T]^2 - ne\dot{\xi} \cdot \mathbf{A} + \frac{1}{2}\epsilon_0([\dot{\mathbf{A}}^T]^2 + c^2[\nabla \times \mathbf{A}^T]^2) \quad (79)$$

It can also be checked that the above Hamiltonian density follows from the transverse Lagrangian density with transverse vector potential and transverse canonical momentum.

The Hamiltonian density of the transverse fields, Eq.(79), can be cast in an alternative form, characteristic of polaritons as follows. From Eq.(78) we have $\xi = e\dot{\mathbf{A}}/m^*\omega^2$. The first mechanical energy term and the second (interaction) term in the Hamiltonian can now be written as

$$\frac{1}{2}m^*n[\dot{\xi}^T]^2 - ne\dot{\xi} \cdot \mathbf{A} = -\frac{1}{2}\epsilon_0\frac{\omega_p^2}{\omega^2}\dot{\mathbf{A}}^2 + \epsilon_0\frac{\omega_p^2}{\omega^2}\dot{\mathbf{A}}^2 = \frac{1}{2}\epsilon_0\frac{\omega_p^2}{\omega^2}\dot{\mathbf{A}}^2 \quad (80)$$

where ω_p is the plasma frequency

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m^*} \quad (81)$$

The Hamiltonian density can now be written as

$$\mathcal{H}^T = \frac{1}{2}\epsilon_0 \left(\left\{ 1 + \frac{\omega_p^2}{\omega^2} \right\} [\dot{\mathbf{A}}^T]^2 + c^2 [\nabla \times \mathbf{A}^T]^2 \right) \quad (82)$$

The Hamiltonian density can further be written in a form which is applicable to all transverse polaritons [17]. We can write

$$\mathcal{H}^T = \frac{1}{2} \left(\left\{ \frac{\partial[\omega\epsilon]}{\partial\omega} \right\} [\dot{\mathbf{A}}^T]^2 + \frac{1}{\mu_0} [\nabla \times \mathbf{A}^T]^2 \right) \quad (83)$$

where, in this plasmon polariton case we have introduced the corresponding dielectric function ϵ

$$\epsilon(\omega) = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2} \right) \quad (84)$$

It is easy to see that the wave equation Eq.(76) can now be written as

$$\nabla^2 \mathbf{A}^T + \frac{\omega^2 \epsilon(\omega)}{c^2} \mathbf{A}^T = 0 \quad (85)$$

For plane waves, the plasmon frequency ω versus the wavevector k is then as follows

$$\omega^2 \epsilon(\omega) = c^2 k^2 \quad (86)$$

which yields

$$\omega^2 = \omega_p^2 + k^2 c^2 \quad (87)$$

and $\hbar\omega$ is the quantum energy of the plasmon polariton.

4.2. Quantized Plasmon Polaritons

The quantization of the plasmon polaritons follows the usual procedure so that the total field is written as a superposition of plane wave polariton modes. The transversality of the field indicates the existence of two polarisation states $\hat{e}(\mathbf{k}, j)$, labeled $j = 1, 2$. We thus have

$$\mathbf{A}(\mathbf{r}, t) = \sum_j \int d^3\mathbf{k} C(\mathbf{k}) \left\{ \hat{e}(\mathbf{k}, j) b(\mathbf{k}, j) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + H.c. \right\} \quad (88)$$

where $H.c.$ stands for Hermitian conjugate and the components of the polarization vectors satisfy the rule

$$\sum_{j=1}^2 \hat{e}_\alpha(\mathbf{k}, j) \hat{e}_\beta^*(\mathbf{k}, j) = \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \quad (89)$$

The boson operators $b(\mathbf{k}, j)$ satisfy the commutation rules

$$[b(\mathbf{k}, j), b^\dagger(\mathbf{k}', j')] = \delta_{jj'} \delta(\mathbf{k} - \mathbf{k}') \quad (90)$$

Finally, $C(\mathbf{k})$ is the normalization factor arising from ensuring that the Hamiltonian of the transverse fields reduces to the canonical form

$$H^T = \frac{1}{2} \sum_{j=1}^2 \int d^3\mathbf{k} \hbar \omega(\mathbf{k}, j) \left[b^\dagger(\mathbf{k}, j) b(\mathbf{k}, j) + b(\mathbf{k}, j) b^\dagger(\mathbf{k}, j) \right] \quad (91)$$

4.3. Longitudinal Plasmons

For the longitudinal fields we have the following set of equations

$$\nabla \cdot \mathbf{E}^L = -\frac{1}{\epsilon_0} n e \nabla \cdot \boldsymbol{\zeta}^L \quad (92)$$

$$\dot{\mathbf{E}}^L + \frac{1}{\epsilon_0} n e \dot{\boldsymbol{\zeta}}^L = 0 \quad (93)$$

$$m^* \ddot{\boldsymbol{\zeta}}^L(\mathbf{r}, t) = e \mathbf{E}^L(\mathbf{r}, t) + m^* \beta_p^2 \nabla (\nabla \cdot \boldsymbol{\zeta}^L) \quad (94)$$

The following set of equations follow from those above

$$\boldsymbol{\zeta}^L = -\frac{1}{n e} \epsilon_0 \dot{\mathbf{E}}^L \quad (95)$$

$$-m^* \omega^2 \boldsymbol{\zeta}^L = -\frac{n e^2}{\epsilon_0} \boldsymbol{\zeta}^L + m^* \beta_p^2 \nabla (\nabla \cdot \boldsymbol{\zeta}^L) \quad (96)$$

and since $\nabla (\nabla \cdot \boldsymbol{\zeta}^L) = \nabla^2 \boldsymbol{\zeta}^L + \nabla \times \nabla \times \boldsymbol{\zeta}^L$, but the last term is zero, so this equation can be rearranged to read

$$\left\{ \omega^2 - \omega_p^2 + \beta_p^2 \nabla^2 \right\} \boldsymbol{\zeta}^L = 0 \quad (97)$$

where ω_p is the plasma frequency

$$\omega_p^2 = \frac{n e^2}{m^* \epsilon_0} \quad (98)$$

For plane waves the dispersion relation is

$$\omega^2 = \omega_p^2 + \beta_p^2 k^2 \quad (99)$$

The same equation (97) is satisfied by $\mathbf{E}^L$ and by the corresponding scalar potential. We write

$$\mathbf{E}^L = -\frac{n e}{\epsilon_0} \boldsymbol{\zeta}^L = -\nabla \Phi \quad (100)$$

$$\left\{ \omega^2 - \omega_p^2 + \beta_p^2 \nabla^2 \right\} \Phi = 0 \quad (101)$$

The Hamiltonian density is the longitudinal part of the total density. We have

$$\mathcal{H} = \frac{1}{2} m^* n ([\dot{\boldsymbol{\zeta}}^L]^2 + \beta_p^2 [\nabla \cdot \boldsymbol{\zeta}^L]^2) - \frac{1}{2} \epsilon_0 \nabla \Phi \cdot \nabla \Phi - n e (\nabla \cdot \boldsymbol{\zeta}^L) \Phi \quad (102)$$

Expressing $(\nabla \cdot \boldsymbol{\zeta}^L)$ in terms of Φ in the last term we can write

$$\mathcal{H} = \frac{1}{2} m^* n ([\dot{\boldsymbol{\zeta}}^L]^2 + \beta_p^2 [\nabla \cdot \boldsymbol{\zeta}^L]^2) + \frac{1}{2} \epsilon_0 \nabla \Phi \cdot \nabla \Phi \quad (103)$$

The division is apparent between the mechanical and electrical contributions. Finally we can eliminate the last term in favor of another involving $\boldsymbol{\zeta}^L$ using Eq.(100). We get

$$\mathcal{H} = \frac{1}{2} m^* n \left([\dot{\boldsymbol{\zeta}}^L]^2 + \omega_p^2 [\boldsymbol{\zeta}^L]^2 + \beta_p^2 [\nabla \cdot \boldsymbol{\zeta}^L]^2 \right) \quad (104)$$

Alternatively we may write the Hamiltonian density entirely in terms of Φ . We have

$$\mathcal{H} = \frac{1}{2}\epsilon_0 \left\{ \nabla\Phi \cdot \nabla\Phi + \omega_p^2 \nabla\Phi \cdot \nabla\Phi + \beta_p^2 (\nabla^2\Phi)^2 \right\} \quad (105)$$

4.4. Quantizing the Longitudinal Plasmons

We have seen how the longitudinal plasmons arise from the hydrodynamic jellium model and may be quantized as a Coulomb field in the manner just described. The quantized field Φ in the three dimensional bulk is written as

$$\Phi = \int d^3\mathbf{k} C(\mathbf{k}) \left\{ a(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - a^\dagger(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} \right\} \quad (106)$$

where $C(\mathbf{k})$ is the energy normalization factor such that the Hamiltonian, Eq.(105) reduces to the canonical form

$$H = \int d^3\mathbf{k} \omega(k) \left\{ a^\dagger(\mathbf{k}) a(\mathbf{k}) + \frac{1}{2} \right\} \quad (107)$$

where $\omega^2 = \omega_p^2 + \beta_p^2 k^2$ with ω_p the characteristic plasma frequency and β is the velocity parameter responsible for dispersion. In the literature distinction is made between the low and high-frequency properties of the electron system [18]. These limits give rise to two alternative choices of β_p

$$\beta_p = \sqrt{\frac{1}{3}} v_F; \quad \beta_p = \sqrt{\frac{3}{5}} v_F \quad (108)$$

where v_F is the Fermi velocity. The operators $a(\mathbf{k})$ and $a^\dagger(\mathbf{k})$ are the boson annihilation and creation operators of the bulk plasmon field such that

$$[a(\mathbf{k}), a^\dagger(\mathbf{k}')] = \delta(\mathbf{k} - \mathbf{k}') \quad (109)$$

The most important role played by quantized longitudinal plasmons is in electron energy loss spectroscopy (EELS) which is be discussed below.

5. Phonons

5.1. phonon Polaritons

Another quantizable field is in the context of dielectrics and semiconductors and involves dipole active excitations representing matter waves coupled to the electromagnetic fields. The hybrid modes are transverse elementary excitation called phonon polaritons [10,19,20]. The most direct route to dealing with phonon polaritons is by making use of the known dielectric function of these excitations. We shall not pursue the details of the derivation of the dielectric function and the general formalism in a dielectric [21]. With the dielectric function assumed known we refer to the Hamiltonian density form we derived above for plasmon polaritons, namely Eq.(83). This form applies in general and once the dielectric function is known we can apply the formalism to phonon-polaritons as well. The wave equation for the phonon polaritons has the form given in Eq.(85) given by

$$\nabla^2 \mathbf{A}^T + \frac{\omega^2 \epsilon(\omega)}{c^2} \mathbf{A}^T = 0 \quad (110)$$

where for the phonon-polariton the dielectric function $\epsilon(\omega)$ can be written as [1]

$$\epsilon(\omega) = \epsilon_\infty \frac{(\omega^2 - \omega_L^2 + \beta_L^2 k^2)}{(\omega_T^2 - \omega^2) + \beta_L'^2 k^2} \quad (111)$$

where ω_T is transverse phonon frequency and ω_L is the longitudinal phonon frequency and these are connected by the relation

$$\omega_L = \left(\frac{\epsilon_s}{\epsilon_\infty} \right)^{\frac{1}{2}} \omega_T \quad (112)$$

where ϵ_s and ϵ_∞ are, respectively, the low frequency and the high frequency dielectric functions. Finally the parameter $\beta_L \ll c$ is a velocity characterizing the dispersion of the longitudinal oscillations and $\beta'_L = \beta_L / \epsilon_\infty$.

Since β_L is important only in the context of longitudinal phonons, we may ignore it when focusing on the phonon polaritons. The dielectric function Eq.(111) becomes

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2} \quad (113)$$

The dispersion relation giving ω against k is

$$\omega^2 \epsilon(\omega) = c^2 k^2 \quad (114)$$

Substituting for $\epsilon(\omega)$ from Eq.(113) and solving the resulting equation for ω against k we find there are two branches $\omega_+(k)$ and $\omega_-(k)$ of bulk phonon polaritons. We have

$$\omega_\pm = \frac{1}{2} \left\{ \omega_L^2 + \left(\frac{c^2 k^2}{\epsilon_\infty} \right) \left[\left\{ \omega_L^2 - \frac{c^2 k^2}{\epsilon_\infty} \right\}^2 + \frac{4c^2 k^2 (\omega_L^2 - \omega_T^2)}{\epsilon_\infty} \right]^{\frac{1}{2}} \right\} \quad (115)$$

We therefore write for the Hamiltonian

$$H = \frac{1}{2} \epsilon_0 \sum_i \int d^3 \mathbf{r} \left\{ \frac{\partial [\omega \epsilon(\omega)]}{\partial \omega} \mathbf{E}_i^{T2} + c^2 \mathbf{B}_i^2 \right\} \quad (116)$$

where $\mathbf{E}^T = -\dot{\mathbf{A}}^T$ and $\mathbf{B} = \nabla \times \mathbf{A}^T$.

The quantization of the i^{th} branch now follows by writing for the electric field associated with branch i

$$\mathbf{E}_i(\mathbf{r}) = \int d^3 \mathbf{k} \left(\mathcal{E}_{0i} e^{i\mathbf{k} \cdot \mathbf{r}} b_i(\mathbf{k}) + h.c. \right) \quad (117)$$

where $h.c.$ stands for 'Hermitian conjugate' and b_i and $b_i^\dagger$ are mode annihilation and creation operators satisfying boson commutation relations

$$[b_i(\mathbf{k}), b_{i'}^\dagger(\mathbf{k}')] = \delta_{ii'} \delta(\mathbf{k} - \mathbf{k}') \quad (118)$$

The mode vector amplitudes $\mathcal{E}_{0i}$ are to be determined using the canonical procedure. Since we are dealing with transverse modes there are two unit vectors involved in each phonon polariton branch as was the case for plasmon polaritons. Phonon polaritons interact with electrons in semiconductor structures. For details see [19]).

5.2. Longitudinal Phonons

Assuming that the material has no free charges we have $\nabla \cdot \mathbf{D} = 0$ which for the longitudinal phonons is satisfied by $\mathbf{D} = 0$. This amounts to the condition

$$\epsilon(\omega, k) = 0 \quad (119)$$

Thus from Eq.(111) we have the dispersion relation

$$\omega^2 = \omega_L^2 - \beta_L^2 k^2 \quad (120)$$

For an isotropic medium the parameter β_L is generally recognized as the sound velocity in the medium.

The quantization of the longitudinal phonon modes is very similar to the longitudinal plasmons, except for the sign of the second term in the dispersion relation.

The Lagrangian density can be written in terms of the displacement field $\dot{\mathbf{u}}^L$

$$\mathcal{L} = \frac{1}{2} \left\{ \omega_L^2 \mathbf{u}^{L2} - \dot{\mathbf{u}}^{L2} - \beta_L^2 (\nabla \cdot \mathbf{u}^L)^2 \right\} \quad (121)$$

The inclusion of the spatial dispersion allows the standard quantization program to be carried out in terms of plane waves, as done for longitudinal plasmons, so we shall not provide further details here.

6. Interactions

In the above we have shown how the (transverse) bulk plasmon polaritons and the corresponding longitudinal plasmons can be quantized. We have also discussed the quantization of bulk (transverse) phonon polaritons together with the corresponding longitudinal phonon fields. We are thus in a position to consider interaction processes involving these fields. Typical processes consist of emission and absorption of field quanta, leading to measurable changes in the properties of the systems with which the quantized fields interact. As we pointed out at the outset, the contexts in which the above quantized fields arise include electronically-dense metals and doped semiconductors of the category III-V compounds such as GaAs and GaAlAs. Such semiconductors are typically doped with Si which introduce additional conduction electrons and so leads to the creation of plasmons with which the host electrons interact. This leads to changes to the relaxation rates and so the electric transport properties of the semiconductor itself. The plasmons in electronically-dense metals manifest themselves in processes involving electron energy-loss spectroscopy. Semiconductors also support phonons, both transverse (phonon polaritons) and longitudinal (acoustic) phonons and these influence the electric transport properties in which excited electrons relax their energy by emission of phonons and phonon polaritons.

We could proceed to consider examples where exchanges of quanta with other physical systems occur and lead to real effects which are calculable and results can be compared with experiment. In our case we could consider the exchange of plasmon polaritons, longitudinal plasmons, phonon polaritons and longitudinal phonons. However, due to space limitations we consider as a concrete example of how quantization enables evaluation of physical properties we focus on electron energy loss spectroscopy (EELS) of electronically-dense metals, for example aluminium.

6.1. Electron Energy Loss Spectroscopy

Finally, as mentioned above, we consider only one case which illustrates how quantum techniques have proved to be very powerful and physically transparent. We focus on longitudinal plasmons which have featured prominently in electron energy loss spectroscopy (EELS) [22,23]. In general, EELS is an analytical technique that uses focused beams of electrons to determine a material's properties. As the electrons pass through the sample they lose energy through inelastic scattering. In our case of an electronically dense material the inelastic scattering is dominated by the excitation of longitudinal plasmons. The Hamiltonian of the system is [24]

$$H = \frac{p^2}{2M} + V(\mathbf{r}) + \int d^3\mathbf{k} \omega(k) \left\{ a^\dagger(\mathbf{k}) a(\mathbf{k}) + \frac{1}{2} \right\} \quad (122)$$

The first term represents the Kinetic energy of the electrons in the beam and the last term represents the Hamiltonian of the quantized longitudinal bulk plasmons, while $V(\mathbf{r})$ is the interaction Hamiltonian. It is clearly tempting to write $V(\mathbf{r}) = Q\Phi(\mathbf{r})$ where $\Phi(\mathbf{r})$ is the quantized Coulomb potential of the longitudinal plasmons. However it has been shown that agreement of theory with the experimental

EELS results emerges when a canonical transformation [24] is applied leading to the following form of $V(\mathbf{r})$

$$V(\mathbf{r}) = \frac{Q}{2M\omega} (\mathbf{P} \cdot \nabla \Phi + \nabla \Phi \cdot \mathbf{P}) \quad (123)$$

It is interesting to note that when we write $\mathbf{P}/M = \mathbf{u}$, the velocity, and set $\nabla \Phi = -\mathcal{E}$, the electric field, we can write

$$\frac{Q}{2M} (\mathbf{P} \cdot \nabla \Phi + \nabla \Phi \cdot \mathbf{P}) = -Q\mathbf{u} \cdot \mathcal{E} \quad (124)$$

which is the classical expression of the energy loss rate. Thus the above canonically transformed potential has the advantage of clear classical correspondence.

The standard formalism can now be used to evaluate the cross-section for scattering from an initial state $|i, 0\rangle$ to a final state $|f, \omega\rangle$. The initial state $|i, 0\rangle$ is a plane wave electron state of energy-momentum $(E_i, \mathbf{P}_i)$ and no plasmon excited and the final state $|f, \omega\rangle$ is of energy-momentum $(E_f, \mathbf{P}_f)$ where a plasmon of frequency ω is excited. This process thus involves an energy loss E and momentum transfer q such that

$$E = E_i - E_f; \quad q = |\mathbf{P}_i - \mathbf{P}_f| \quad (125)$$

The evaluation of the cross section $\sigma(E, q)$ follows a standard procedure and it is convenient to set $\hbar = 1$. We have [25]

$$\sigma(E, q) = \left(\frac{\beta_L^2 q^2}{[\omega(q)]^3} \right) \frac{\gamma(q, \omega)}{[\{E - \omega(q)\}^2 + \gamma^2(q, \omega)]} \quad (126)$$

The function γ , calculated using the Golden rule, is found to be

$$\gamma(q, \omega) = \gamma_0 + \left(\frac{Q^2 \omega_p^2}{4M^2 \beta^2} \right) \frac{q^3}{[\omega(q)]^2} \quad (127)$$

where γ_0 is an adjustable parameter representing the residual spectrum when $q = 0$. It is the variation of the cross-section with the energy loss E for a fixed momentum transfer q that is experimentally relevant here. It is seen that for a fixed q the spectrum σ against E given by Eq.(126) is a Lorentzian with a half width at half maximum given by Eq.(127) which changes with q but is constant for a given q . The theoretical predictions outlined above are generally consistent with measurement of EELS of electronically dense metals [26].

7. Summary and Conclusions

The primary aim of this article has been to highlight how the quantum concept has influenced developments in areas of physics that are unfamiliar or seldom visited by researchers whose main concerns are the fundamentals and applications of traditional quantum theory. Our interest has been in the concepts and techniques appropriate for the vast subject of long range processes involving collective excitations. However, our focus was necessarily restricted to a narrow section in condensed matter contexts. We began with the classical ideal fluid as a simple system governed by Newton's laws which serves to illustrate the methodology that leads to the emergence of the classical fluid quanta.

We then tackled the significant topic of plasma oscillations in bulk metals and doped semiconductors. These oscillations are modeled in terms of a charged fluid of electrons with a neutralizing positive background charge and the physics is governed by Newton's laws with coupling to electromagnetic fields. We showed that there are two types of plasma oscillations, namely the transverse (divergence free) also called plasmon polaritons and the longitudinal (curl-free) plasmons. We showed that both types are amenable to quantization and the quanta can be exchanged in processes of emission and absorption by a quantum system with which the plasmons interact. We showed how discrete quanta of longitudinal plasmons are emitted by fast electron beams traversing thin metals. The quantization scheme used to explore the physics in such an electron energy loss spectroscopy (EELS) context illustrates the power of the 'quantum' concept which is clearly confirmed by experiment.

We also considered, as a second significant case, the lattice vibrations in polar semiconductors, which couple to electromagnetic fields, constituting phonon polaritons and longitudinal phonons, for example as in the case of the III-V compounds. Like plasmons these are a mixture of mechanical and electromagnetic oscillations. They too are characterized by a frequency-dependent dielectric function, which incorporates the mechanical as well as the electromagnetic components responsible for both the transverse phonon polaritons and the longitudinal phonons. We could have proceeded to discuss the coupling of the phonon polaritons and longitudinal phonons to electrons in semiconductors. Longitudinal optic phonons, in particular, are important in that they contribute to the energy relaxation of hot electrons [27] and hot phonons [28], which determine the electric transport in semiconductor devices.

Even within this narrow perspective of plasmons and phonons there are further important related issues which, due to need for brevity, we have not covered in this article. These issues are concerned with the presence of surfaces and boundaries between different materials. In our context, the presence of surfaces gives rise to new quanta, namely surface plasmons and surface polar optical phonons. Here too the concept of quantized plasmons and phonons as well as localized plasmons [29] has proved to be extremely useful. For example, the two dimensional quantum well formed of a thin layer of GaAs sandwiched between two thicker layers of AlAs involves the trapping of an electron gas inside the GaAs layer, but the phonons are also modified due to the presence of interfaces between the two materials. Multiple quantum wells such as this can form semiconductor superlattices [30,31], in which the periodicity gives rise to artificially formed matter with special features, such as bands and band-gaps for both the electrons and the plasmons and phonons [32]. The modified excitations are normally probed using Raman scattering [8,33,34].

Finally, we must emphasize that the subject of quantized collective excitations is vast and covers a large number of contexts. It is thus beyond our narrow coverage here, but we shall not consider this matter any further in this article.

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