

Research report for a stay abroad at University at Buffalo from February to May 2014

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Abstract

The excitation properties of small sodium clusters are investigated in the spherical jellium model. For sufficiently long wavelength and not too small clusters the excitations are governed by collective modes to a significant extent. In an intensive cooperation with Prof. Dr. Eric Suraud (Toulouse), who was at a research stay at the University at Buffalo, the importance of different finite size effects for the collective modes was investigated. Especially the fragmentation of the collective modes can be assigned to three different effects: the contribution of unbound states, the lack of a well-defined wavenumber for the excitations, and interactions with unperturbed particle hole states. The first effect is not present for highly charged clusters, the last two can be separated by a bosonic approximation to the RPA equation, which has no more particle hole states. This approximation ignores the Fermi statistics, but it turns out to describe the main excitation properties at long wavelength quite well.

1 Preface

Most of the results of my investigations are published in chapter 5 of my PhD thesis[4]. Some parts of this report are included there, and a more complete collection of results can be found there as well.

2 Introduction

Systems consisting of a collection of a small number of atoms very often exhibit properties that are very different from the properties of single atoms and differ at the same time significantly from properties of the bulk material.

Bulk properties appear normally only for large numbers of particles, but special features like “magic numbers” appear in systems consisting of a small number of atoms and are caused by the finite size of the system. These properties offer new possibilities in the field of designing new materials. For this purpose detailed understanding of the properties of such systems is of course necessary.

Density Functional Theory (DFT) is a very popular method for describing such collections of atoms in their ground state. The main advantage of DFT is that it is relatively simple, both conceptually and numerically. For these reasons DFT can also be applied to systems of moderate size, where more advanced methods (like FHNC for example) are too complicated, or require too much computer resources. Only ground-state properties are accessible directly via DFT, but one can obtain information on excitation properties from linear response theory building onto the ground-state results. There is also a modified approach to DFT called Time Dependent Density Functional Theory (TDDFT), which is capable of addressing excitations more directly. While it is possible to calculate the ground-state properties of fully symmetry broken sodium clusters in reasonable time, the excitation properties are more complicated. For this reason the spherical jellium model was used for the sodium clusters. Due to the strong electron delocalization in sodium clusters, the jellium approximation is not too crude. The approximation for the clusters to be spherical is only fulfilled for certain “magic” numbers of electrons, therefore only these special sizes were considered for that purpose.

The original intention to introduce effective potentials from FHNC calculations to describe many-particle effects for the excitations could not be executed, because it turned out on short notice, that these potentials are not available. Instead of this, some investigations regarding the behavior and importance of collective modes were performed. The important collective modes of jellium clusters, the surface (Mie) and the plasmon resonance, are only weakly dependent on the Fermi statistics at long wavelength. Neglecting Fermi statistics yields a type of Bogoljubov equation, that can be solved much easier.

3 RPA in Jellium cluster

Linear response theory is used to describe the response of a system in a stationary state (usually the ground-state) when a small external perturbation is applied. Thus in principle one is interested in the solution of the

time-dependent Schroedinger equation:

$$(\hat{H} + \delta v(\vec{r}, t))|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle, \quad (1)$$

where it is assumed, that the perturbation δv is the only time-dependent term. It has to be time-dependent because it has to be turned on at some finite time, and it should also be able to describe for example a laser pulse.

3.1 Time-Dependent-Hartree-Fock

Let us assume, that the unperturbed Hartree-Fock solution is known. That means we have orbitals ψ_i fulfilling the Hartree-Fock equation:

$$\hat{H}^{HF} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (2)$$

and the Slater determinant $|\psi_0\rangle$ of the N lowest eigenstates of this equation solves (1) with $\delta v = 0$. For small perturbation one can make the ansatz:

$$|\psi\rangle = \exp\left(\sum_{ph} c_{ph}(t) a_p^\dagger a_h\right) |\psi_0\rangle. \quad (3)$$

Here and in the following it is assumed that the index p (p', \dots) always runs over all unoccupied Hartree-Fock states, and h (h', \dots) over all occupied ones ($\sum_p = \sum_{p=N+1}^\infty$ and $\sum_h = \sum_{h=1}^N$). This ansatz actually means, that the solution of the disturbed problem (1) can be written as a Slater determinant of states, that are themselves linear combinations of the Hartree-Fock eigenstates. The assumption for the solution to be a Slater determinant is an approximation, for the disturbed as well as the undisturbed system, but the second condition is always fulfilled, because the eigenstates of equation (2) form an orthogonal basis to the entire Hilbert space. The fact that only products of an unoccupied (called particle) and an occupied (called hole) state appear in ansatz (3) is justified, because a combination within the occupied states only does not change the many particle ground-state, since it drops out in the Slater determinant (see for example [5]). We will need the density change for this ansatz later on:

$$\begin{aligned} \rho(\vec{r}, t) &= \langle \psi | \hat{\rho} | \psi \rangle = \langle \psi_0 | \hat{\rho} | \psi \rangle + \langle \psi | \hat{\rho} | \psi_0 \rangle + O(c^2) \\ \hat{\rho} &= \sum_{ij} \psi_i(\vec{r}) \psi_j^*(\vec{r}) a_j^\dagger a_i \\ \delta \rho(\vec{r}, t) &= \sum_{ihph} \psi_i(\vec{r}) \psi_j^*(\vec{r}) \underbrace{\langle \psi_0 | a_j^\dagger a_i a_p^\dagger a_h | \psi_0 \rangle}_{=\delta_{ip}\delta_{jh}} + c.c. + O(c^2) \\ &= \sum_{ph} c_{ph} \psi_p(\vec{r}) \psi_h^*(\vec{r}) + c.c. + O(c^2) \end{aligned} \quad (4)$$

The lagrangian density which leads to (1) is:

$$L = \langle \psi | i\hbar \frac{\partial}{\partial t} - \hat{H} | \psi \rangle \quad (5)$$

Inserting the ansatz (3) into the lagrangian density and expanding it up to second order in the amplitudes $c_{ph}(t)$ yields:

$$\begin{aligned} L(\{c_{ph}\}, \{c_{ph}^*\}) &= \sum_{ph} |c_{ph}(t)|^2 (\epsilon_p - \epsilon_h) + \sum_{ph} (c_{ph}^*(t) \langle p | \delta v | h \rangle + c.c.) \\ &- i \frac{\hbar}{2} \sum_{ph} \dot{c}_{ph}(t) c_{ph}^*(t) - c_{ph}(t) \dot{c}_{ph}^*(t) \\ &+ \frac{1}{2} \sum_{php'h'} (c_{ph}(t) c_{p'h'}(t) \langle pp' | V | h'h \rangle + c_{ph}(t) c_{p'h'}^*(t) \langle ph' | V | p'h \rangle \\ &+ c_{ph}^*(t) c_{p'h'}(t) \langle hp' | V | h'h \rangle + c_{ph}^*(t) c_{p'h'}^*(t) \langle hh' | V | p'h \rangle) \end{aligned}$$

Now one can formulate the Euler-Lagrange equations, of which only one is needed, the other is the complex conjugate:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{c}_{ph}} - \frac{\partial L}{\partial c_{ph}} = 0. \quad (6)$$

The zeroth order term of the resulting equations is just the Hartree-Fock equation (thus it contributes nothing), and the first order terms give the well known TDHF (Time-Dependent-Hartree-Fock) equations, which are most conveniently fourier-transformed into frequency domain and written in a block-matrix form:

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} c_{ph}(\omega) \\ c_{ph}^*(-\omega) \end{pmatrix} = \begin{pmatrix} \delta v_{ph}(\omega) \\ -\delta v_{ph}(-\omega) \end{pmatrix} \quad (7)$$

where the matrices are defined as:

$$\begin{aligned} A_{ph,p'h'} &= (\epsilon_p - \epsilon_h) \delta_{ph,p'h'} + \langle ph | V | p'h' \rangle_a \\ B_{ph,p'h'} &= \langle pp' | V | hh' \rangle_a \end{aligned} \quad (8)$$

At this point it is about time to return to the actual situation of this work. Up to now the derivation assumed, that the solutions to the Hartree-Fock equation were known. However this work does not use the Hartree-Fock, but the DFT method. One can also use these equations for eigenstates and energies obtained from DFT calculations, but one has to replace the explicit exchange terms (denoted by $|hh'\rangle_a$ in equation (8)) by the exchange correlation potential used in DFT. It is actually necessary to do the same thing

already in the zeroth-order terms, because the orbitals do fulfill the Kohn-Sham equation, not the Hartree-Fock equation. This makes the equation simpler, because using the additional assumption that all orbitals are real (they can be chosen this way in DFT) the off-diagonal parts of the matrices A and B become equal now and one can simplify the equations. By taking the sum and the difference of these equations, the difference equation becomes diagonal, and inserting its solution into the other one gives a system of equations with only half the size:

$$(D + 2M - D^{-1}\hbar^2\omega^2)\delta\rho = -2\delta v \quad (9)$$

where:

$$D_{ph,p'h'} = A - B = (\epsilon_p - \epsilon_h)\delta_{ph,p'h'} \quad (10)$$

$$M_{ph,p'h'} = \langle ph|V_C + f_{xc}|p'h'\rangle \quad (11)$$

$$\delta\rho_{ph} = c_{ph}(\omega) + c_{ph}^*(-\omega) \quad (12)$$

$$\delta v_{ph} = \langle p|\delta v|h\rangle \quad (13)$$

and the density change is given by $\delta\rho(\vec{r}, \omega) = \sum_{ph} \delta\rho_{ph}(\omega)\psi_p(\vec{r})\psi_h(\vec{r})$ (fourier transform equation (4)). The same equation can also be derived completely within the framework of DFT, which avoids the need to replace exchange terms intuitively, see for example [3]. It is possible to solve equation (9) directly as a matrix equation with a finite cutoff for the p range, or one can reformulate it into coordinate space to obtain the well-known RPA equation. For this purpose multiply the equations (9) by $\frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2}\psi_p(\vec{r})\psi_h(\vec{r})$ and take the sum over all ph pairs.

$$\begin{aligned} 0 &= \sum_{ph} \frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \psi_p(\vec{r})\psi_h(\vec{r}) \left(\epsilon_p - \epsilon_h - \frac{\hbar^2\omega^2}{\epsilon_p - \epsilon_h} \right) \delta\rho_{ph} \\ &+ 2 \sum_{ph} \frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \psi_p(\vec{r})\psi_h(\vec{r}) \sum_{p'h'} \langle ph|V|p'h'\rangle \delta\rho_{p'h'} \\ &+ 2 \sum_{ph} \frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \psi_p(\vec{r})\psi_h(\vec{r}) \langle p|\delta v|h\rangle \\ &= \sum_{ph} \underbrace{\frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \left(\epsilon_p - \epsilon_h - \frac{\hbar^2\omega^2}{\epsilon_p - \epsilon_h} \right)}_{=1} \underbrace{\delta\rho_{ph}\psi_p(\vec{r})\psi_h(\vec{r})}_{\rightarrow\delta\rho(\vec{r},\omega)} \\ &+ \int 2 \sum_{ph} \underbrace{ph \frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \psi_p(\vec{r})\psi_h(\vec{r})\psi_p(\vec{r}')\psi_h(\vec{r}') V(\vec{r}', \vec{r}')}_{=-\chi_0(\vec{r}, \vec{r}', \omega)} \underbrace{\sum_{p'h'} \psi_{p'}(\vec{r}')\psi_{h'}(\vec{r}') \delta\rho_{p'h'}}_{=\delta\rho(\vec{r}', \omega)} d\vec{r}' d\vec{r}'' \end{aligned}$$

$$\begin{aligned}
& + \int 2 \sum_{ph} \underbrace{\frac{\epsilon_p - \epsilon_h}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \psi_p(\vec{r}) \psi_h(\vec{r}) \psi_p(\vec{r}') \psi_h(\vec{r}')}_{=-\chi_0(\vec{r}, \vec{r}', \omega)} \delta v(\vec{r}') d\vec{r}' \\
& = \delta\rho - \chi_0 V \delta\rho - \chi_0 \delta v
\end{aligned}$$

This is just a different notation for the usual formula

$$\chi = \frac{\chi_0}{1 - V\chi_0}. \quad (14)$$

If one does not want to calculate χ directly, but only searches for its resonance modes, that is energies ω_i and functions $f_i(\vec{r})$ such that $\chi(\omega_i)f_i = +\infty$, it is sufficient to search zeros of the denominator:

$$\chi_0 V f = f \quad (15)$$

This gives the correct resonance energies, for the resonance modes one has to be careful how to normalize them, since (15) corresponds to finding an eigenvalue equal to 1 for a non-symmetric matrix in dependence of the parameter ω .

3.2 Structure factor

The static structure factor is defined via the fourier-transform of the pair density as:

$$S(\vec{k}) = 1 + \frac{1}{N} \int (\rho_2(\vec{r}, \vec{r}') - \rho(\vec{r})\rho(\vec{r}')) e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} d\vec{r}_1 d\vec{r}_2 \quad (16)$$

Alternatively it can be obtained by integrating the dynamic structure factor over all positive energies, where the latter is defined by:

$$S(\vec{k}, \omega) = \frac{-1}{N\pi} \int \text{Im}(\chi(\vec{r}, \vec{r}', \omega)) e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} d\vec{r}_1 d\vec{r}_2 \quad (17)$$

It is also possible to express it directly from the resonance modes and energies, but one has to take care for the proper normalization. The result is:

$$S(\vec{k}, \omega) = \frac{1}{N} \sum_i \left| \int f_i(\vec{r}) e^{i\vec{k}\vec{r}} d\vec{r} \right|^2 \delta(\omega - \omega_i) \quad (18)$$

The dynamic structure factor is found to fulfill several non-trivial conditions, called (energy weighted) sumrules, which are expressed by moments of the distribution (with respect to ω):

$$S(i) = \int_0^\infty \omega^i S(\vec{k}, \omega) d\omega. \quad (19)$$

The most important ones are probably the case $i = 1$ and $i = 0$. In the case $i = 1$ the left side of the condition can be calculated analytically and yields just k^2 , the case $i = 0$ can be understood as being the connection between equation (16) and (17). The ω^0 sumrule is fulfilled for the Kohn-Sham states (that is χ_0), for RPA it is the definition of $S(k)$ because there is no new pair density defined. It can be used as a measure for the quality of the RPA approximation, if $S(k)$ is known for the interacting system from experiments, or better ground-state methods (like Monte Carlo), where realistic pair distributions can be obtained. The ω^1 sumrule can easily be proved, by considering the expectation value of a double commutator in the many-particle ground-state:

$$\langle 0|[Q, [H, Q^\dagger]]|0\rangle = \langle 0|QHQ^\dagger - HQ^\dagger Q - QQ^\dagger H + Q^\dagger HQ|0\rangle \quad (20)$$

$$= \sum_i \left(\langle 0|Q|i\rangle \langle i|HQ^\dagger|0\rangle - \langle 0|HQ^\dagger|i\rangle \langle i|Q|0\rangle \right) \quad (21)$$

$$- \langle 0|Q|i\rangle \langle i|Q^\dagger H\rangle + \langle 0|Q^\dagger|i\rangle \langle i|HQ|0\rangle \quad (22)$$

$$= 2 \sum_i (E_i - E_0) |\langle 0|Q|i\rangle|^2, \quad (23)$$

where a complete set of eigenstates of H was inserted in the second step. On the other hand, for local operators Q only the kinetic energy does contribute to the commutator and thus we have:

$$[Q, [\nabla^2, Q^\dagger]] = Q\nabla^2 Q^\dagger - \nabla^2 Q Q^\dagger - Q Q^\dagger \nabla^2 + Q^\dagger \nabla^2 Q \quad (24)$$

$$Q\nabla^2 Q^\dagger = \underbrace{Q(\nabla^2 Q^\dagger)}_A + \underbrace{Q Q^\dagger \nabla^2}_B + \underbrace{2Q(\nabla Q^\dagger)\nabla}_C \quad (25)$$

$$Q^\dagger \nabla^2 Q = A^\dagger + B + C^\dagger \quad (26)$$

$$-\nabla^2 Q Q^\dagger = \underbrace{-(\nabla^2 Q^\dagger)Q}_{-A} - \underbrace{(\nabla^2 Q)Q^\dagger}_{-A^\dagger} - \underbrace{Q Q^\dagger \nabla^2}_{-B} \quad (27)$$

$$- \underbrace{2(\nabla Q)(\nabla Q^\dagger)}_D - \underbrace{2Q^\dagger(\nabla Q)\nabla}_{-C^\dagger} - \underbrace{2Q(\nabla Q^\dagger)\nabla}_{-C} \quad (28)$$

$$-Q Q^\dagger \nabla^2 = -B \quad (29)$$

$$[Q, [\nabla^2, Q^\dagger]] = -2|\nabla Q|^2 \quad (30)$$

$$(31)$$

Combination of both results yields:

$$\left\langle 0 \left| \frac{\hbar^2}{2m} |\nabla Q|^2 \right| 0 \right\rangle = \sum_i (E_i - E_0) |\langle 0|Q|i\rangle|^2, \quad (32)$$

and if one choses Q as a simple plane wave $Q = e^{i\vec{k}\vec{r}}$, one obtains:

$$\frac{\hbar^2 k^2}{2m} N = \sum_i \omega_i \left| \langle 0 | e^{i\vec{k}\vec{r}} | i \rangle \right|^2 \quad (33)$$

The right side is the dynamic structure factor, but it is defined with $\frac{1}{N}$ in equation (17), and the factor $\frac{\hbar^2}{2m}$ is conveniently used to define the energy unit, leaving k^2 as the result for this sumrule.

3.3 Symmetry and analytical properties

One can obtain some understanding of important features of the response function and the structure factor, by inspecting highly symmetric cases, where analytical results can be obtained. The strongest possible symmetry is the total translation invariance of the homogeneous electron gas. In this case the response function in RPA can be written down analytically. The results for this case are well-known, and are not the interest of this work, but it will be useful to recall some of them. From simple energy and momentum conservation it follows, that the entire weight in the noninteracting dynamic structure factor must lie in an area defined by $\frac{\hbar^2}{2m}(k^2 - 2k \cdot k_F) \leq \hbar\omega \leq \frac{\hbar^2}{2m}(k^2 + 2k \cdot k_F)$. In the interacting case one additional excitation appears, which has a finite energy for $k = 0$. This excitation is called the plasmon, and although resulting from a quantum theory it resembles classical oscillations within a homogeneous plasma at the frequency $\omega_p = \sqrt{\frac{4\pi\rho e^2}{m_e}}$. One possibility to obtain the plasmon is to search for a solution of equation (15) with the property, that $\omega \gg \epsilon_p - \epsilon_h$ for all p and h that contribute to this mode. (In the homogeneous system this condition is easily met in k-space.) We will do this approximation for a general system at first:

$$\begin{aligned} \chi_0(\vec{r}, \vec{r}', \omega) &= \sum_{ph} \frac{2(\epsilon_p - \epsilon_h)}{\omega^2} \varphi_p(\vec{r}) \varphi_h(\vec{r}) \varphi_p(\vec{r}') \varphi_h(\vec{r}') \\ &= \frac{2}{\omega^2} \left(\sum_p \varphi_p(\vec{r}) \epsilon_p \varphi_p(\vec{r}') \sum_h \varphi_h(\vec{r}) \varphi_h(\vec{r}') - \sum_p \varphi_p(\vec{r}) \varphi_p(\vec{r}') \sum_h \varphi_h(\vec{r}) \epsilon_h \varphi_h(\vec{r}') \right) \end{aligned}$$

Now we can use the completeness relation $\sum_i \varphi_i(\vec{r}) \varphi_i(\vec{r}') = \delta(\vec{r} - \vec{r}')$ for the second p sum. The rest term then extends the first p sum to a sum over all states. Furthermore the φ_i are eigenstates of the KS Hamiltonian, whose only nonlocal term is the kinetic energy. The local contributions are cancelled out between the two terms. Then we have:

$$\chi_0(\vec{r}, \vec{r}', \omega) = \frac{2}{\omega^2} \left(\sum_h \varphi_h(\vec{r}) \varphi_h(\vec{r}') \sum_p \varphi_p(\vec{r}') \hat{H} \varphi_p(\vec{r}) - \delta(\vec{r} - \vec{r}') \sum_h \varphi_h(\vec{r}') \hat{H} \varphi_h(\vec{r}) \right)$$

$$\begin{aligned}
&= \frac{-\hbar^2}{m\hbar^2\omega^2} \left(\sum_h \varphi_h(\vec{r})\varphi_h(\vec{r}')\nabla^2\delta(\vec{r}-\vec{r}') - \delta(\vec{r}-\vec{r}') \sum_h \varphi_h(\vec{r}')\nabla^2\varphi_h(\vec{r}) \right) \\
&= \frac{-1}{m\omega^2} \vec{\nabla}\rho\vec{\nabla}
\end{aligned}$$

In the last step χ_0 was transformed from an integral operator into a differential one, the easiest way to verify this is to apply both to some arbitrary function f :

$$\begin{aligned}
\int \chi_0(\vec{r}, \vec{r}', \omega) f(\vec{r}') d\vec{r}' &= \frac{-1}{m\omega^2} \left(\sum_h \varphi_h(\vec{r}) \int \varphi_h(\vec{r}') f(\vec{r}') \nabla'^2 \delta(\vec{r}-\vec{r}') d\vec{r}' \right. \\
&\quad \left. - \sum_h \varphi_h(\vec{r}) f(\vec{r}) \nabla^2 \varphi_h(\vec{r}) \right) \\
&= \sum_h \frac{-1}{m\omega^2} \left(\sum_h \varphi_h(\vec{r}) \nabla^2 (\varphi_h(\vec{r}) f(\vec{r})) - \sum_h (\vec{r}) f(\vec{r}) \nabla^2 \varphi_h(\vec{r}) \right) \\
&= \sum_h \frac{-1}{m\omega^2} \sum_h \varphi_h(\vec{r}) \left(\varphi_h(\vec{r}) \nabla^2 f(\vec{r}) + 2\vec{\nabla}\varphi_h(\vec{r})\vec{\nabla}f(\vec{r}) \right) \\
&= \frac{-1}{m\omega^2} \left(\rho \nabla^2 f(\vec{r}) + \vec{\nabla}\rho(\vec{r})\vec{\nabla}f(\vec{r}) \right) = \frac{-1}{m\omega^2} (\vec{\nabla}\rho\vec{\nabla}) f(\vec{r})
\end{aligned}$$

We insert this approximation of χ_0 into the adjoint equation to (15), which will yield the same resonance energies, but a different normalization for the modes:

$$\frac{-1}{m\omega^2} \int V(\vec{r}, \vec{r}') \vec{\nabla}'\rho(\vec{r}') \vec{\nabla}' f(\vec{r}') d\vec{r}' = f(\vec{r}) \quad (34)$$

To obtain the plasmon in the homogeneous electron gas, we set ρ constant and fourier-transform the equation, using the convolution property and the known fourier-transform of the Coulomb potential. The exchange correlation correction from DFT is constant with respect to k and does not contribute to the limit $k \rightarrow 0$.

$$\omega^2 f(\vec{k}) = \frac{-\rho}{m} \frac{4\pi e^2}{k^2} (-k^2) f(\vec{k}) = \omega_p^2 f(\vec{k}) \quad (35)$$

Equation (34) can also be used to determine collective modes for a spherical system with homogeneous density inside, that is $\rho(\vec{r}) = \rho_0\theta(R - |\vec{r}|)$. For this purpose we need to insert the partial waves expansion of the Coulomb potential $V(|\vec{r}-\vec{r}'|) = \sum_{l=0}^{\infty} V_l(r, r') P_l(\cos(\theta))$, where θ is the angle between the vectors \vec{r} and \vec{r}' and $V_l(r, r') = \frac{\min(r, r')^l}{\max(r, r')^{l+1}}$, and make the ansatz that f is

proportional to a spherical harmonic. Then we get:

$$\begin{aligned} \omega^2 Y_{lm}(\Omega) f(r) &= \int \sum_{l'} \frac{4\pi}{2l'+1} V_{l'}(r, r') Y_{l'm'}(\Omega) Y_{l'm'}^*(\Omega') r'^2 \\ &\times \left(\frac{d\rho}{dr'} \frac{df}{dr'} Y_{lm}(\Omega') + \rho(r') \nabla^2 Y_{lm}(\Omega') f(r') \right) d\Omega' dr' \end{aligned} \quad (36)$$

The laplacian operator applied on the spherical harmonic yields: $\frac{1}{r} \frac{\partial^2}{\partial r^2} (r f(r)) + \frac{l(l+1)}{r^2} f(r)$ and then the Ω' integration disappears by orthonormality of the Y_{lm} . This gives the equation:

$$\omega^2 f(r) = \int \frac{4\pi}{2l+1} V_l(r, r') r'^2 \left(\frac{d\rho}{dr'} \frac{d}{dr'} + \frac{\rho(r')}{r'} \frac{d^2}{dr'^2} r' + \rho(r') \frac{l(l+1)}{r'^2} \right) f(r') dr' \quad (37)$$

In the case of the Coulomb potential and a pure step-function density, this equation has the analytical solution:

$$f(r) = \begin{cases} \frac{r^l}{R^l} & r < R \\ \frac{R^{l+1}}{r^{l+1}} & r > R \end{cases} \quad (38)$$

together with the resonance energy $\omega^2 = \frac{l}{2l+1} \omega_p^2$. In the case $l = 1$ this is called the Mie resonance. The Mie energy ω_{Mie} can also be derived in other ways, either by constructing ratios of sumrules, or classically for dielectric spheres. It is therefore reasonable (and in agreement with lots of experiments) to assume, that this type of mode does appear in real clusters despite the fact, that no real cluster can have a step-function like electron density, because any solution to the Schroedinger equation is always continuous (and continuously differentiable for any potential without $\delta(\vec{r})$ like contributions). Furthermore it seems reasonable, that in a cluster of sufficient size also the plasmon should appear in some form, because the interior is quite homogeneous and the surface becomes less important with size. Equation (35) does only yield the plasmon for arbitrary k value, as long as the particle-hole band energies are negligible. It turns out, that the plasmon has a weak k^2 dispersion, the details can be found for example in [2], the result is:

$$\omega(k) = \omega_p \left(1 + \frac{0.9}{0.66 r_s k_F^2} k^2 + O(k^4) \right) \quad (39)$$

The dispersion behavior is important, because in a finite system it is impossible to have an excitation with a wavelength above the system size, thus $k > \frac{2\pi}{R}$. One could argue that one should use the diameter or maybe the circumference rather than the radius, but this gives a factor 2π at most. Thus

it does not make sense to consider the $k = 0$ case for any excitation (collective or not). If the behavior at small k is of interest, one has to consider $\lim_{k \rightarrow 0} \left(\frac{1}{k^2} S(k) \right)$.

4 First results

In figure 1 the dipole contribution to the dynamic structure factor is shown for a cluster consisting of 92 sodium atoms. The Mie resonance is visible clearly, and there is also some signal from the volume plasmon, but it appears only at higher k and strongly fragmented. The Mie resonance is quite well-defined, but there is a broad range of excitations in between the Mie

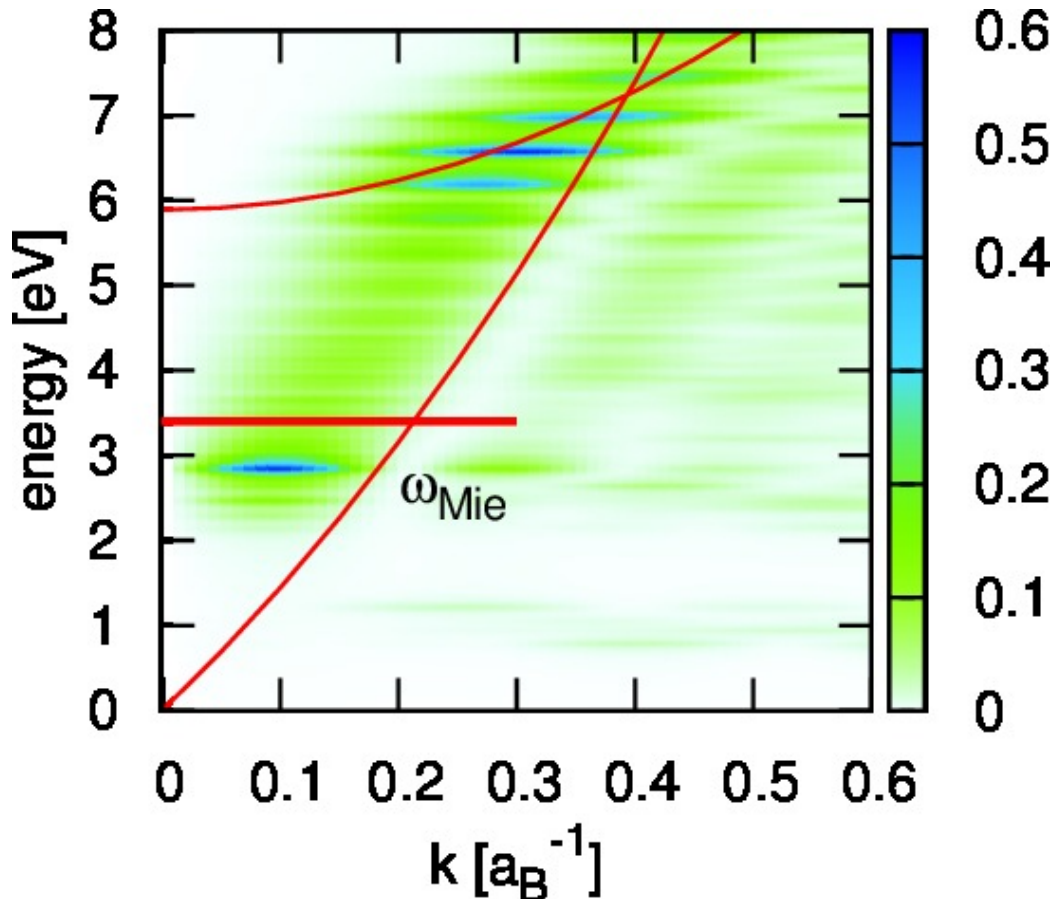


Figure 1: Dynamic structure factor (dipole only) for the cluster Na₉₂. The bulk plasmon, the Mie energy and the particle hole band are shown by red lines.

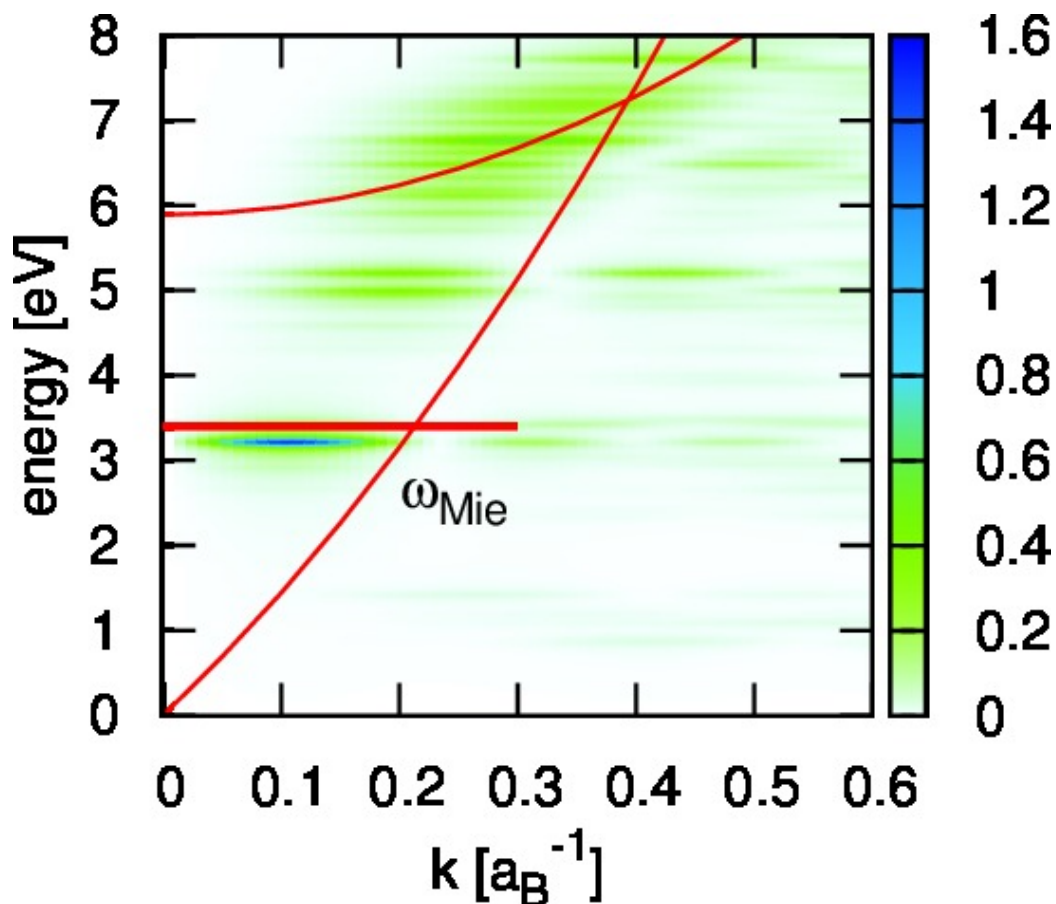


Figure 2: Dynamic structure factor (dipole only) for the cluster Na_{98}^{6+} . The bulk plasmon, the Mie energy and the particle hole band are shown by red lines.

resonance (or surface plasmon) and the volume plasmon. This is a continuum effect, because the ionization potential of these clusters (within DFT, which may not be very accurate) is only 2.4eV. In order to understand the nature of this behavior better, a highly charged version of the same cluster was considered. Due to the charge, the ionization potential is increased, and the collective excitations are bound now. In figure 2 the broad area of excitations between the collective modes is collapsed into a single mode, and the Mie resonance is very sharp, but the plasmon is not. For qualitative statements it is advantageous to consider cuts at fixed k values through the dynamic structure factor. There was also an alternative way to calculate the excitations by Time-Dependent Density Functional Theory (TDDFT), which was provided by Prof. Eric Suraud. The comparison for both methods in

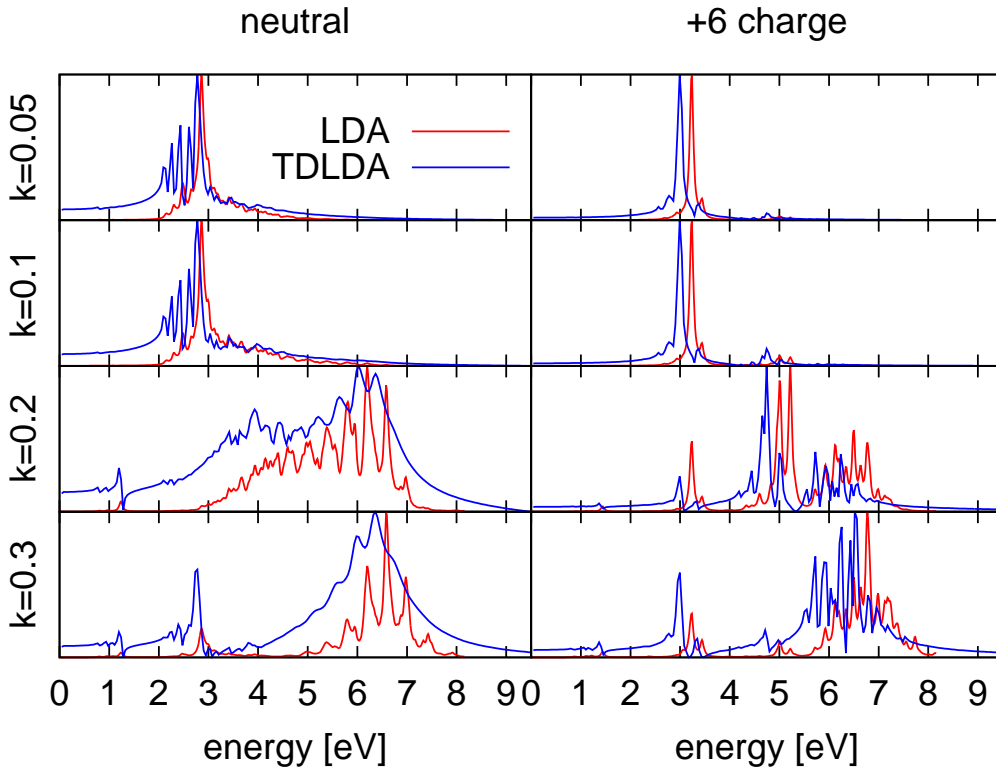


Figure 3: Vertical cuts through the dynamic structure factor for the clusters Na_{92} (left) and Na_{98}^{6+} (right) at different k values. The red line (LDA) shows the same data as in figures 1 and 2, the blue line (TDLDA) is a comparison provided by Prof. Eric Suraud.

figure 3 works quite well, therefore the fragmentation found for the volume plasmon seems to be more than just a method problem.

As a next step the collective approximation (37) was applied to identify the reason for the fragmentation in the plasmon. However for numeric applications this equation is not optimal, because it has a lot of additional (but uninteresting) solutions in the energy range of interest, and it is thus difficult to properly identify the collective modes. Instead of this an approximation by charged bosons was attempted.

5 Boson approximation

The difficulties in solving the RPA equation directly can be accounted to the fermionic nature of electrons. In the case, that effects of Fermi statistics are negligible, this equation can be put into a much simpler form. Of course one

can hardly judge whether the Fermi statistics are important for certain properties of a system, or not, beforehand, but one can use a simple system (like a spherical cluster for example) as a test case and hope, that the importance of Fermi statistics will not increase too much, when geometric symmetry is reduced. Consider the non-interacting response function:

$$\chi_0(\vec{r}, \vec{r}', \omega) = \sum_{ph} \frac{-2(\epsilon_p - \epsilon_h)}{(\epsilon_p - \epsilon_h)^2 - \omega^2} \varphi_p(\vec{r}) \varphi_h(\vec{r}) \varphi_p(\vec{r}') \varphi_h(\vec{r}') \quad (40)$$

and assume, that the system is in a bosonic state, that is only one occupied state exists. Then one can either eliminate the sum over h in favor of a factor N , or just assume that $\epsilon_h = \epsilon_0$ is independent of h . The same argument applied to φ_h , gives for the density $\rho(\vec{r}) = \sum_h |\varphi_h(\vec{r})|^2$ and thus $\varphi_0(\vec{r}) = \sqrt{\rho(\vec{r})}/N$. Then we have for the response function:

$$\chi_0(\vec{r}, \vec{r}', \omega) = -2 \underbrace{\sum_p \frac{(\epsilon_p - \epsilon_0)}{(\epsilon_p - \epsilon_0)^2 - \omega^2} \varphi_p(\vec{r}) \varphi_p(\vec{r}')}_{=\frac{\hat{H} - \epsilon_0}{(\hat{H} - \epsilon_0)^2 - \omega^2}(\vec{r}, \vec{r}')} \underbrace{\sum_h \varphi_h(\vec{r}) \varphi_h(\vec{r}')}_{=\sqrt{\rho(\vec{r})\rho(\vec{r}')}} \quad (41)$$

The first replacement is obtained from the spectral representation of the operator $\hat{H} - \epsilon_0$, because the φ_i are the eigenstates of the Hamiltonian \hat{H} (in the current setting the KS Hamiltonian, but this is not important) and form an orthogonal basis. The contribution of the first (i.e. the only occupied) state is missing in (41), but it is zero anyway. The second replacement is a direct consequence of inserting the density, note that this also absorbs the factor N due to the different normalization of ρ .

For the next step it is convenient to get rid of the potential terms in \hat{H} in favor of the density.

$$\hat{H}\varphi_i = (\hat{T} + V)\varphi_i = \epsilon_i\varphi_i \quad (42)$$

where \hat{T} is the kinetic energy, and V includes both external and Hartree potential (and exchange correlation for DFT). From the equation for the first state ($i = 0$) we have:

$$V = \frac{1}{\varphi_0}(\epsilon_0 - \hat{T})\varphi_0 \quad (43)$$

Inserting this into the operator we need, $\hat{H} - \epsilon_0$, yields a very simple form:

$$\hat{H}' = \hat{H} - \epsilon_0 = \hat{T} - \frac{\hat{T}\sqrt{\rho}}{\sqrt{\rho}} \quad (44)$$

Now consider equation (15) with χ_0 from (41) and \hat{H}' :

$$-2\sqrt{\rho}\frac{\hat{H}'}{\hat{H}'^2 - \omega^2}\sqrt{\rho}Vf = f \quad (45)$$

We need to apply the operator $(\hat{H}'^2 - \omega^2)\frac{1}{\sqrt{\rho}}$ from the left to get rid of the inverse operator, then we insert $f = \sqrt{\rho}g$:

$$\begin{aligned} -2\hat{H}'\sqrt{\rho}Vf &= (\hat{H}'^2 - \omega^2)\frac{1}{\sqrt{\rho}}f \\ -2\hat{H}'\underbrace{\sqrt{\rho}V\sqrt{\rho}}_{=V'}g - \hat{H}'^2g &= -\omega^2g \\ \hat{H}'(\hat{H}' + 2V')g &= \omega^2g \end{aligned}$$

This leads to the equation:

$$\hat{H}'(\hat{H}' + 2V')g = \hbar^2\omega^2g \quad (46)$$

This equation has been used to investigate excitations in bosonic quantum systems, for example in [1]. In the case of fermions it can be considered a weaker approximation, than the collective approximation (37), because one can still get (37) from (46) by neglecting the \hat{H}'^2 -term. Thus it is not surprising, that the Bose equation does yield the same plasmon as the collective one, however the dispersion relation at finite k is different:

$$\omega(k) = \sqrt{\omega_p^2 + k^4}. \quad (47)$$

This can be proved easily by fourier transforming equation (46), whereas the dispersion relation of a homogeneous (electron) system is indeed dependent on the Fermi statistics[2] and more complicated to find.

6 Boson Results

The solution of the bosonic approximation tho the RPA equation offers two possible benefits. First it gives some insight into the origin of the fragmentation seen in the plasmon excitation. Second the results suggest, that the bosonic approximation gives a reasonable description of the main features of the dynamic structure factor at long wavelength. However (46) is numerically much simpler than (14), and could also be applied to clusters beyond the jellium model in the future.

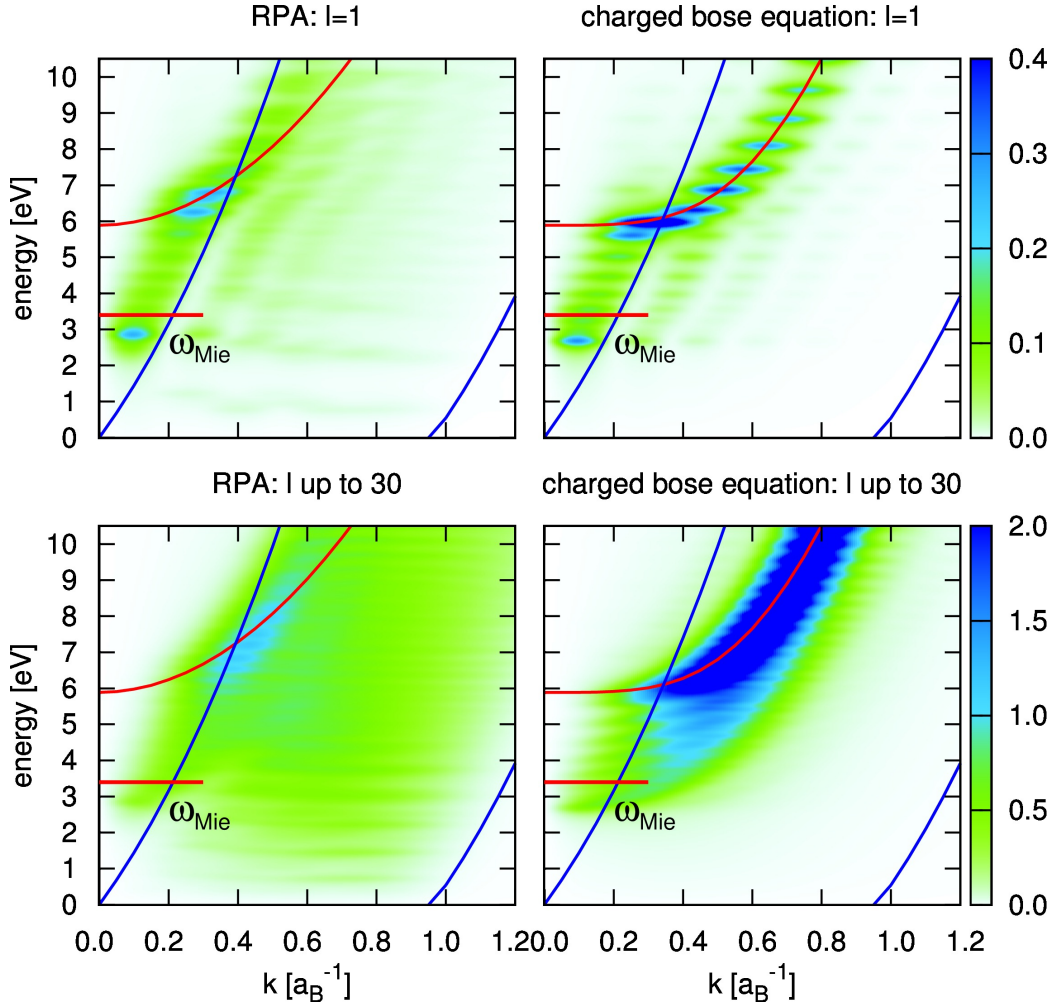


Figure 4: Dynamic structure factor for the cluster Na_{92} . Both the dipole channel (top) and the angular momentum sum (bottom) are displayed for the RPA equation (left) and the bosonic approximation (right). The blue lines show the particle hole band boundaries, the red ones the collective excitations.

The results for the bosonic approximation and the RPA equation are shown in figures 4 and 5 for the same cluster as before, but now the sum over all angular momenta is also included. The long wavelength limit is described well by the dipole channel alone, but for finite wavelength more angular momenta are needed. Figure 6 shows again some vertical cuts for the dynamic structure factor at different k values, now making a comparison between the Bose approximation and the RPA. The same data for a broader range of sizes can be found in my PhD thesis[4].

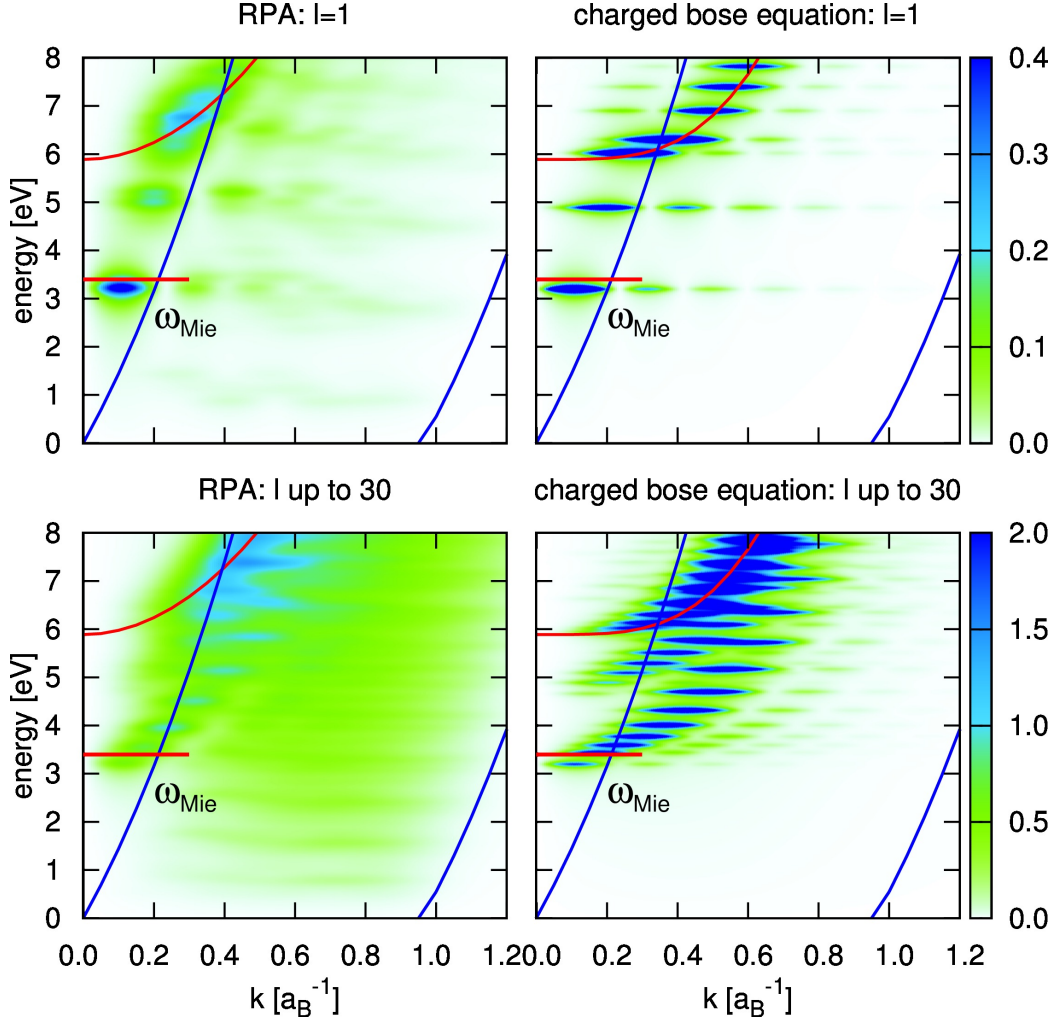


Figure 5: Dynamic structure factor for the cluster Na_{98}^{6+} . Both the dipole channel (top) and the angular momentum sum (bottom) are displayed for the RPA equation (left) and the bosonic approximation (right). The blue lines show the particle hole band boundaries, the red ones the collective excitations.

The Bose approximation reveals, that at least a certain part of the fragmentation seen in the collective modes is a discrete dispersion effect. Due to the finite size of the cluster, all resonance modes have a certain width in the k direction, and then modes with their maximum at different k do overlap. This causes the impression of a mode splitting, when they have different energies. The detailed effects and their size dependence can again be found in [4]. The RPA does have a stronger dispersion, which makes the splitting

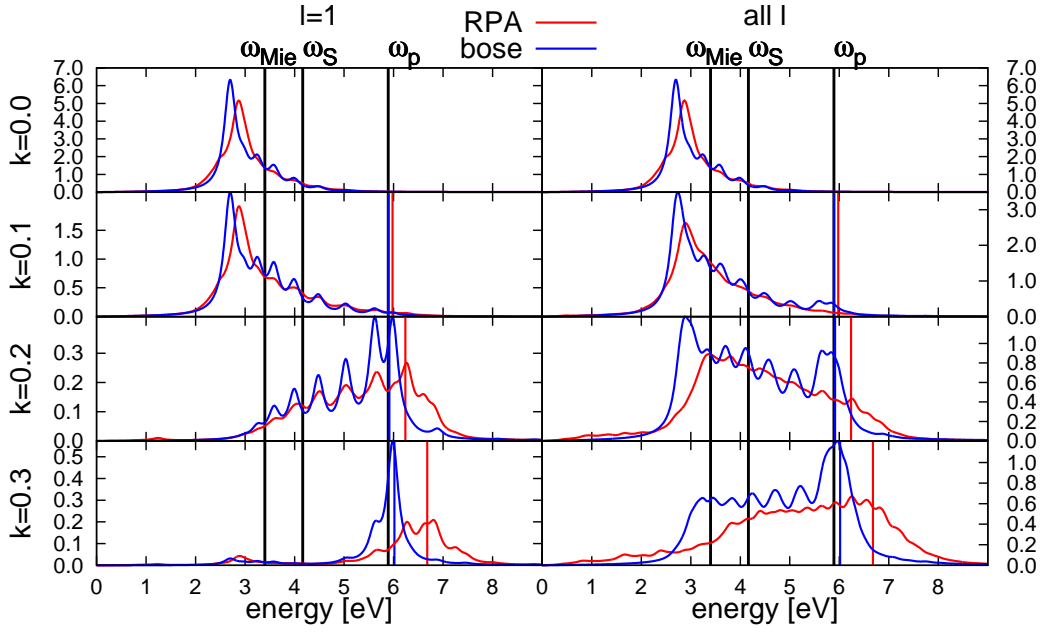
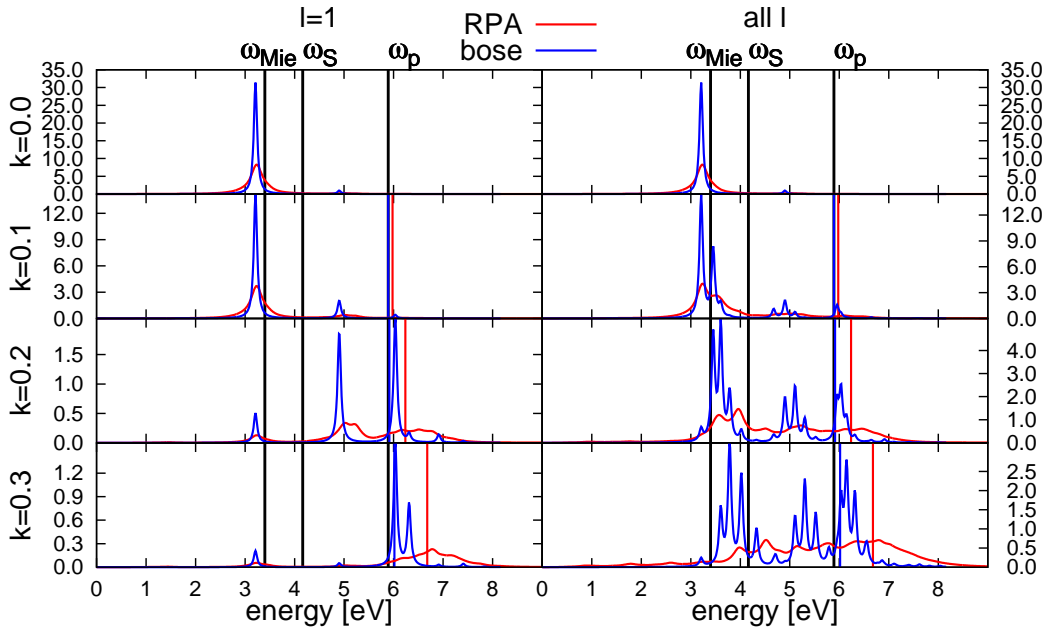


Figure 6: Cuts through dynamic structure factor for the neutral cluster Na_{92} (above) and the charged version Na_{98}^{6+} (below). Theoretical values for collective excitations are shown by vertical lines.



more prominent. Furthermore the plasmon is disturbed upon entering the particle hole band, which is no surprise, since it happens in the homogeneous

system as well, but contributes to the fragmentation as well.

7 Conclusion

In principle the classical collective excitations of a homogeneous sphere can be found in sodium clusters (within the jellium model). The volume excitation is not present for very small clusters and subject to strong fragmentation, which has several sources. The plasmon energy is much higher than the ionization potential, thus there are a lot of unbound states contributing to the plasmon. Furthermore the finite size of the clusters leads to a broad shape of all modes in k space, which causes some broadening in combination with the dispersion behavior. And at last the plasmon as well as the Mie resonance appear quite close to the particle hole band, which introduces some splitting due to the unperturbed ph states. To separate the last two effects a bosonic approximation to the RPA equation was used, which has no particle hole band, but a dispersion relation. This approximation turns out to describe the long wavelength excitations of these clusters quite accurate (up to about $k = 0.3a_B^{-1}$), except for a small energy shift, which seems to be exactly the difference in the plasmon dispersion behavior and can be compensated easily. For this reason it may be interesting to apply this Bose equation to fully symmetry broken cluster models in the future.

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