Chapter 3

Theory.

In this chapter we describe quantitatively the relations between the scattered intensity and the properties of the field on a given plane. We will derive the transfer function of various techniques based on the light scattering. We will show that, under suitable conditions, the field is gaussian. In this case, we will derive the relation between the power spectra of the NFS images and the scattered intensity.

3.1 Scattered intensity and field power spectrum.

From Maxwell equations, we can derive the wave equation for a transverse component of the electric field in the vacuum [14]:

$$\frac{\partial^2}{\partial t^2} E\left(\vec{x}, z, t\right) = c^2 \left[\frac{\partial^2}{\partial z^2} E\left(\vec{x}, z, t\right) + \nabla^2_{\vec{x}} E\left(\vec{x}, z, t\right)\right] \tag{3.1}$$

where $\nabla^2_{\vec{x}}$ is the Laplacian oeprator, with respect to the horizontal coordinate $\vec{x}$. Since we are working with a laser, and we consider only elastic scattering, the only temporal frequency involved is kc:

$$E\left(\vec{x}, z, t\right) = E\left(\vec{x}, z\right) e^{-ikct} \tag{3.2}$$

where k is the wave vector. Eq. (3.1) becomes:

$$\frac{\partial^2}{\partial z^2} E\left(\vec{x}, z\right) + \nabla^2_{\vec{x}} E\left(\vec{x}, z\right) + k^2 E\left(\vec{x}, z\right) = 0 \tag{3.3}$$

We define $E_z\left(\vec{q}\right)$ as the Fourier transform of $E\left(\vec{x}, z\right)$ with respect to $\vec{x}$:

$$\frac{\partial^2}{\partial z^2} E_z\left(\vec{q}\right) = -\left(k^2 - q^2\right) E_z\left(\vec{q}\right) \tag{3.4}$$

The solution is:

$$E_z\left(\vec{q}\right) = E_0\left(\vec{q}\right) e^{i\sqrt{k^2 - q^2} z} \tag{3.5}$$

In order that this solution exists, a condition must be fulfilled:

$$q^2 < k^2, \tag{3.6}$$

This condition is alwais met if we consider only propagating waves.

The quantity $E_z(\vec{q})$ is closely related to the intensity of the light crossing the plane $z = \text{cost}$. Each two-dimensional Fourier mode of amplitude $E_z(\vec{q})$, on a given z, and wavevector $\vec{q}$ is generated by a three-dimensional plane wave of wavevector $[q_x, q_y, k_z]$, where the only value of k_z is obtained by imposing that the wavevector of any plane wave has length k:

$$k_z(q) = \sqrt{k^2 - q^2} \tag{3.7}$$

Given the values of the two-dimensional Fourier modes $E_z(\vec{q})$ on a given $z = 0$, we can evaluate $E(\vec{x}, z)$ for each $\vec{x}$ and z, by using Eq. (3.5) and (3.7). Expressing it by its three-dimensional Fourier transform:

$$E(\vec{q}, k_z) = 2\pi E_0(\vec{q})\,\delta\left[k_z - k_z(q)\right] \tag{3.8}$$

Each three-dimensional component with amplitude $E(\vec{q}, k_z)$ of the electric field represents a plane wave travelling in a different direction. We define $S_E(\vec{q}, q_z)$, the two-dimensional power spectrum of $E(\vec{x}, z)$:

$$\langle E_z(\vec{q})\,E_z^*(\vec{q}\,')\rangle = \delta(\vec{q} - \vec{q}\,')\,S_E(\vec{q}) \tag{3.9}$$

Light intensity, for each scattering direction, can be defined on the basis of $E(\vec{q}, k_z)$:

$$\langle E(\vec{q}, k_z)\,E^*(\vec{q}\,', k_z')\rangle = 4\pi^2\delta(\vec{q} - \vec{q}\,')\,\delta(k_z - k_z')\,\delta\left[k_z - k_z(q)\right] I(\vec{q}, q_z) \tag{3.10}$$

where $I(\vec{q}, q_z)$ has been expressed in terms of the transferred wavevector $[q_x, q_y, q_z] = [k_x, k_y, k_z] - [0, 0, k]$. From Eq. (3.7):

$$q_z(\vec{q}) = \sqrt{k^2 - q^2} - k \tag{3.11}$$

Substituting $E(\vec{q}, k_z)$ of Eq. (3.8) in Eq. (3.10), and comparing the result with Eq. (3.9), we can relate the scattered intensity $I(\vec{q}, q_z)$ to the power spectrum of the field $S_E(\vec{q})$:

$$I(\vec{q}, q_z) = S_E(\vec{q}) \tag{3.12}$$

From Eq. (3.12) we notice that $I(q)$ can be measured by evaluating $E_z(\vec{q})$ on any z.

If the sample is isotropic, $I(\vec{q}, q_z)$ depends only on $Q = |q_x, q_y, q_z|$:

$$Q(q) = \sqrt{2}k\sqrt{1 - \sqrt{1 - \left(\frac{q}{k}\right)^2}} \tag{3.13}$$

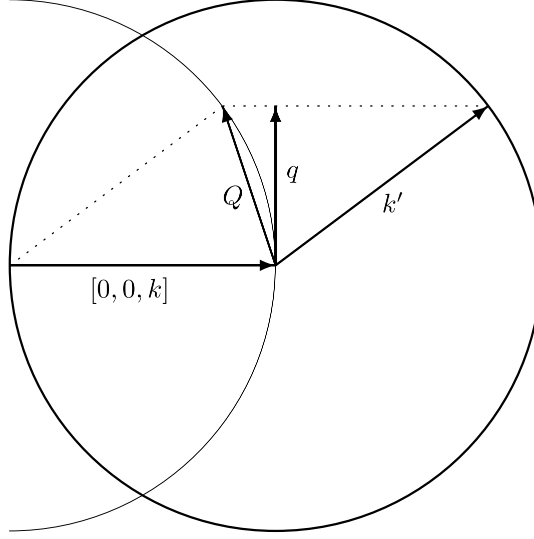

Figure 3.1: Relation between q and Q. Geometrical interpretation of Eq. (3.13)

In this case, Eq. (3.12) can be written in terms on q and Q:

$$I\left[Q\left(q\right)\right] = S_E\left(q\right) \tag{3.14}$$

The geometrical meaning of Eq. (3.13) is explained in Fig. 3.1. For $q \ll k$, Eq. (3.13) can be approximated by $Q\left(q\right) = q$. Moreover, if Rayleigh Gans approximation holds, $I\left(q\right)$ represents the power spectrum of the refraction index of the sample. From these two considerations, we obtain the result that, for scattering on small angles and under Rayleigh Gans condition, the two dimensional correlation function of the electric field is proportional to the correlation function of the light path through the sample.

When performing a far field, small angle scattering measurement, the scattered beams are focused on a screen. In suitable units, each point of the screen has a coordinate q. For small values of the wave vector, q approximates Q', the transferred wavevector. The exact relation is:

$$Q'\left(q\right) = \sqrt{2}k\sqrt{1 - \frac{1}{\sqrt{1 + \left(\frac{q}{k}\right)^2}}} \tag{3.15}$$

Equation (3.13) can be used to correct the results of a Near Field Speckles measurement. Figures 3.1 and 3.2 show the geometrical meaning of equations (3.13) and (3.15). For small values of q, that is $q/k \ll 1$, the two equations can be approximated with $Q = Q' = q$; the error due to this approximation is shown in Fig. 3.3: it's quite small, and it can often be neglected.

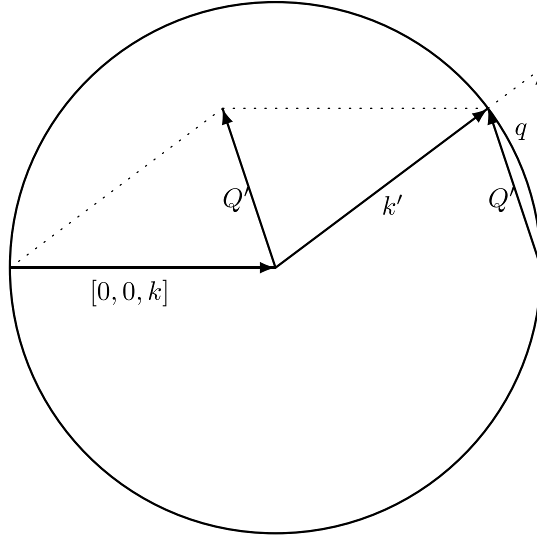

Figure 3.2: Relation between the coordinate q on a screen, in a far field experiment, and the transferred wave vector Q'. Geometrical interpretation of Eq. (3.15)

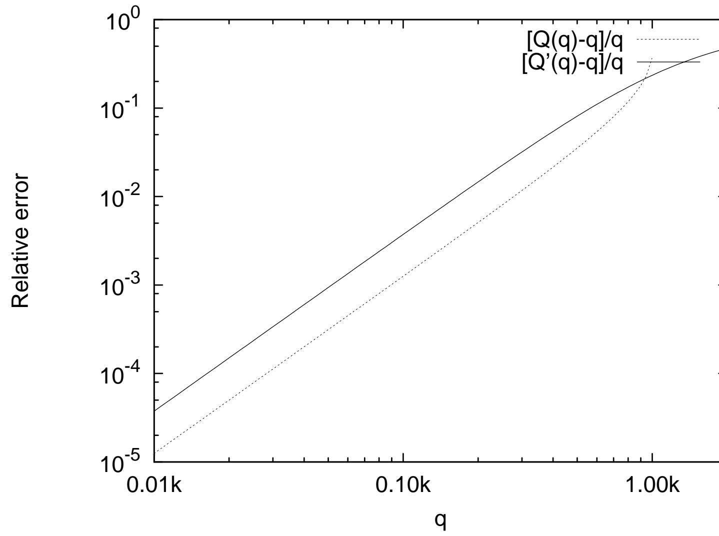

Figure 3.3: Relative error obtained neglecting the non linearity of the ralation between the sample wave vector and the near field wave vector. The graph is obtained from Eqs. (3.13) and (3.15).

3.2 Scattering from a thin sample.

Let us consider a thin sample, with a non homogeneous refraction index, and a light plane wave, moving in the direction of the z axis. For $z = 0$, at the surface of the sample, the field will be:

$$E\left(\vec{x}, z = 0\right) = E_0 e^{i\delta l\left(\vec{x}\right) k} \tag{3.16}$$

where $\delta l\left(\vec{x}\right)$ is the difference between the light path, the integral of the refraction index along z, for a given point $\vec{x}$, and its mean value over the whole sample. If δl is small compared to the light wavelength, we can consider a first order developement:

$$E\left(\vec{x}, z = 0\right) = E_0 \left[1 + i\delta l\left(\vec{x}\right) k\right] \tag{3.17}$$

Neglecting the higher order terms means that we are neglecting higher order diffracted beams than the first.

Using Eq. (3.5) we can find the field for every value of z:

$$E_z\left(\vec{x}\right) = E_0\left(z\right) + \delta E_z\left(\vec{x}\right) \tag{3.18}$$

where

$$\delta E_z\left(\vec{q}\right) = ikE_0\left(z\right)\delta l\left(\vec{q}\right) e^{i\left(\sqrt{k^2 - q^2} - k\right) z} \tag{3.19}$$

is the scattered field, and

$$E_0\left(z\right) = E_0 e^{ikz} \tag{3.20}$$

3.3 Image forming techniques

Microscopy, in its basic form, consists in forming an image of a plane on a device which measures light intensity, such as a photographic film or a CCD sensor. Generally it is used to obtain informations about the intensity of the transmitted light, for example, in the case of an organic tissue, treated by some dye.

If a microscope objective forms the image of a plane on the CCD, the image is given by the interference of the transmitted and the scattered beams. For such an image, the signal can be defined as the difference of the measured intensity $I\left(\vec{x}\right)$ and the transmitted beam intensity I_0, divided by I_0. We will call this signal $i_{shadowgraph}$, for reasons that will be clear later. We consider the case in which the scattered beams are much less intense than the transmitted one. At the first order in δE, the signal is:

$$i_{shadowgraph}\left(\vec{x}\right) = \frac{I\left(\vec{x}\right) - I_0}{I_0} = \frac{2}{I_0}\Re\left[E_0 \delta E^*\left(\vec{x}\right)\right] \tag{3.21}$$

and the Fourier transform is:

$$i_{shadowgraph}\left(\vec{q}\right) = \frac{1}{I_0}\left[E_0 \delta E^*\left(-\vec{q}\right) + E_0^* \delta E\left(\vec{q}\right)\right] \tag{3.22}$$

If the sample is transparent, and we send a plane wave through it, Eq. (3.19) tells us the value of the scattered field:

$$i_{shadowgraph}\left(\vec{q},z\right) = 2k\delta l\left(\vec{q}\right)\sin\left[\left(k-\sqrt{k^2-q^2}\right)z\right] \tag{3.23}$$

In order to obtain the previous result, $\delta l\left(\vec{x}\right)$ has been considered real, so that $\delta l^*\left(-\vec{q}\right) = \delta l\left(\vec{q}\right)$.

For $z=0$, that is, if the thin sample is in the focal plane, $i_{shadowgraph}\left(\vec{q},z\right) = 0$. The intensity is completely uniform, and bears no informations on the sample.

Many techniques has been developed in order to make phase modulations evident: among them, holography and interferometry. A well known way to make phase modulations evident is the phase contrast microscopy. Basically, this technique consists in changing the phase of the transmitted beam by $\pi/2$. At the first order in δE:

$$i_{phase\,contrast}\left(\vec{x}\right) = \frac{I\left(\vec{x}\right)-I_0}{I_0} = \frac{2}{I_0}\Im\left[E_0^*\delta E\left(\vec{x}\right)\right] \tag{3.24}$$

and the Fourier transform is:

$$i_{phase\,contrast}\left(\vec{q}\right) = \frac{i}{I_0}\left[-E_0^*\delta E\left(-\vec{q}\right)+E_0\delta E^*\left(\vec{q}\right)\right] \tag{3.25}$$

Using Eq. (3.19) to evaluate the scattered field:

$$i_{phase\,contrast}\left(\vec{q},z\right) = 2k\delta l\left(\vec{q}\right)\cos\left[\left(k-\sqrt{k^2-q^2}\right)z\right] \tag{3.26}$$

For $z=0$, that is, with the sample in the focal plane:

$$i_{phase\,contrast}\left(\vec{q},z=0\right) = 2k\delta l\left(\vec{q}\right) \tag{3.27}$$

Another way to make phase modulations evident is the so called dark field technique. It consists in stopping the transmitted beam. This is accomplished by focusing the transmitted and the scattered beams by a lens, and by removing the transmitted beam by some kind of reflecting or absorbing object. This is an homodyne technique; the signal must be defined as the ratio between the measured intensity $I\left(\vec{x}\right)$ and the intensity of the transmited beam I_0. Since we have only δE:

$$i_{dark\,field}\left(\vec{x}\right) = \frac{I\left(\vec{x}\right)}{I_0} = \frac{\left|\delta E\left(\vec{x}\right)\right|^2}{I_0} \tag{3.28}$$

Equation (3.19), for $z=0$, gives:

$$i_{dark\,field}\left(\vec{x},z=0\right) = k^2\delta l^2\left(\vec{x}\right) \tag{3.29}$$

In Fourier space:

$$i_{dark\,fielf}\left(\vec{q},z=0\right) = \frac{1}{\left(2\pi\right)^2}k^2\int\delta l\left(\vec{q}'\right)\delta l\left(\vec{q}-\vec{q}'\right)\mathrm{d}\vec{q}' \tag{3.30}$$

The Schlieren technique consists in focusing the beams from the sample by a lens; in the focal plane, a blade stops half of the transmitted beam, along with the beams scattered in one half plane. At the first order in δE, the signal is again, like in shadowgraph:

$$i_{Schlieren}\left(\vec{x}\right) = \frac{I\left(\vec{x}\right) - \tilde{I}_0}{\tilde{I}_0} = \frac{2}{\tilde{I}_0}\Re\left[\tilde{E}_0 \delta\tilde{E}^*\left(\vec{x}\right)\right] \tag{3.31}$$

where the field $\delta\tilde{E}$ is the scattered field, without one half plane in Fourier space:

$$\delta\tilde{E}\left(\vec{q}\right) = \begin{cases} \delta E\left(\vec{q}\right) & \vec{q}\cdot\vec{n} < 0 \\ \delta E\left(\vec{q}\right) & \vec{q}\cdot\vec{n} \geq 0 \end{cases}, \tag{3.32}$$

$\vec{n}$ is the vector ortogonal to the direction of the blade, $\tilde{I}_0 = I_0/2$ and $\tilde{E}_0 = E_0/\sqrt{2}$ are the intensity and the field of the trasmitted beam, after the blade. The Fourier transform is:

$$i_{Schlieren}\left(\vec{q}\right) = \frac{\sqrt{2}}{I_0}\left[E_0\delta\tilde{E}^*\left(-\vec{q}\right) + E_0^*\delta\tilde{E}\left(\vec{q}\right)\right] \tag{3.33}$$

Using Eq. (3.32):

$$i_{Schlieren}\left(\vec{q}\right) = \begin{cases} \frac{\sqrt{2}}{I_0}E_0\delta E^*\left(-\vec{q}\right) & \vec{q}\cdot\vec{n} < 0 \\ \frac{\sqrt{2}}{I_0}E_0^*\delta E\left(\vec{q}\right) & \vec{q}\cdot\vec{n} \geq 0 \end{cases} \tag{3.34}$$

Using Eq. (3.19):

$$i_{Schlieren}\left(\vec{q}, z\right) = \begin{cases} \sqrt{2}ik\delta l\left(\vec{q}\right)e^{-i\left(\sqrt{k^2-q^2}-k\right)z} & \vec{q}\cdot\vec{n} < 0 \\ \sqrt{2}ik\delta l\left(\vec{q}\right)e^{i\left(\sqrt{k^2-q^2}-k\right)z} & \vec{q}\cdot\vec{n} \geq 0 \end{cases} \tag{3.35}$$

In order to obtain the previous result, $\delta l\left(\vec{x}\right)$ has been considered real, so that $\delta l^*\left(-\vec{q}\right) = \delta l\left(\vec{q}\right)$. For $z = 0$, that is, if the thin sample is in the focal plane:

$$i_{Schlieren}\left(\vec{q}, z = 0\right) = \sqrt{2}ik\delta l\left(\vec{q}\right) \tag{3.36}$$

The factor i means that all the Fourier components of $\delta l\left(\vec{q}\right)$ undergo a rotation of $\pi/2$: a sine-like light path modulation gives a cosine-like intensity modulation.

3.4 Misfocused microscopy and shadowgraph.

Equations (3.23), (3.26) and (3.35) allow to evaluate the evolution of the signals as z, the misfocusing, is increased, for a simple microscope objective, for phase contrast and dark field. It should be noted that we are dealing with images formed by laser light: as z increases, it is possible to recover the original shape of the observed objects; this is completely different from a white light microscope, in which the misfocusing simply smears the images.

Equation (3.30) has not been extended for $z \neq 0$; in all the above mentioned techniques, however, the variation of z strongly influences the relation between the light path $\delta l\left(\vec{q}\right)$ and the signal $i\left(\vec{q}\right)$. This is generally a defect: thick objects, or even thin objects dispersed in a thick volume, are difficult to be analysed. In general, all the above mentioned techniques are applied to samples that are thin, and in the focal plane. No improvement is obtained by misfocusing.

A well known exception is shadograph. Shadowgraph technique consists in sending a plane wave onto a sample, and observing the intensity modulations generated by the sample on a plane placed at a distance z from the sample. Using Eq. (3.23), we can derive the transfer function $T_{shadowgraph}\left(\vec{q}, z\right)$ of the shadowgraph technique [15, 16, 17]:

$$T_{shadowgraph}\left(\vec{q}, z\right) = 2k \sin\left[\left(k - \sqrt{k^2 - q^2}\right) z\right] \approx 2k \sin\left(\frac{q^2 z}{2k}\right) \tag{3.37}$$

The approximation holds for $q \ll k$. The transfer function is defined as the ratio between the signal and the light path modulation amplitude:

$$i\left(\vec{q}, z\right) = T\left(\vec{q}, z\right) \delta l\left(\vec{q}\right) \tag{3.38}$$

For $z = 0$, the transfer function vanishes; misfocusing is needed, and is a simple way to make phase modulations evident.

Looking at Eq. (3.26) we can notice that phase contrast transfer function, as a function of z, has a cosinusoidal behaviour:

$$T_{phase\,contrast}\left(\vec{q}, z\right) = 2k \cos\left[\left(k - \sqrt{k^2 - q^2}\right) z\right] \approx 2k \cos\left(\frac{q^2 z}{2k}\right) \tag{3.39}$$

When considering opaque objects, with no phase modulations, the transfer functions are exchanged: cosinusoidal for shadowgraph, sinusoidal for phase contrast.

The shadowgraph image is created by the interference between every scattered beam and the transmitted beam; it's always possible, in principle, to find the value of δl, in every point, simply by a deconvolution. Shadowgraph allows the measurement of one component of the field, which, in turns, is the convolution of the light path with a particular function. The absolute intensity modulation of the shadowgraph image is proportional to the mean intensity and to the light path modulation; the constant of proportionality is the the transfer function. The transfer function vanishes for some wave vectors, but has maxima for other ones. At the maxima, the sensibility equals the sensibility of phase contrast and Schlieren techniques.

Now we evaluate the effect of misfocusing on a dark field microscope. We obtain an image of a plane a distance z from the cell. Using Eq. (3.19), we can derive the relation between the light path and the measured intensity, at a given z:

$$i_{dark\,field}\left(\vec{q}, z\right) = \frac{1}{\left(2\pi\right)^2} k^2 \int \delta l\left(\vec{q}', z\right) \delta l\left(\vec{q} - \vec{q}', z\right) e^{-i\left[\sqrt{k^2 - \left(\vec{q} - \vec{q}'\right)^2} - k\right] z} \mathrm{d}\vec{q}' \tag{3.40}$$

This expression reduces to Eq. (3.30) for $z = 0$. At this point, there's no appearent reason to use a misfocused dark field instead of a focused one.

The knowledge of $i_{dark\,field}(\vec{q}, z)$, for every z, can give some informations about the spreading of the scattered light. For the scattering of a single particle, one can measure the intensity on planes with increasing values of z, and calculate how fast the light is diverging. This provides informations both on the position of the particle and on the scattered intensity. For a sample composed by a great number of particles, this cannot be done, and a different, statistical approach must be applied.

For Schlieren technique, from Eq. (3.35):

$$T_{Schlieren}(\vec{q}, z) = \begin{cases} \sqrt{2}ike^{-i\left(\sqrt{k^2-q^2}-k\right)z} & \vec{q}\cdot\vec{n} < 0 \\ \sqrt{2}ike^{i\left(\sqrt{k^2-q^2}-k\right)z} & \vec{q}\cdot\vec{n} \geq 0 \end{cases} \tag{3.41}$$

By evaluating the square modulus of the transfer function, we obtain:

$$\left|T_{Schlieren}(\vec{q}, z)\right|^2 = 2k^2 \tag{3.42}$$

This means that the power spectrum of the electric field is proportional to the power spectrum of the light path, without any dependence on spatial wavelength and misfocusing.

3.5 Scattering measurements by microscopy techniques

By using Eq. (3.12), we can, in principle, evaluate the scattered intensities by measuring the field on a given plane. The above described microscopy techniques allow the determination of some functions of the electric field. Now, we assume that the scattered electric field is generated by a thin sample. From Eq. (3.19), we derive a property of the electric field:

$$\delta E(-\vec{q}) = -\delta E^*(\vec{q})\, e^{2i\left(\sqrt{k^2-q^2}-k\right)z} \tag{3.43}$$

For shadowgraph, we use Eq. (3.22), in order to evaluate the power spectrum S_i of $i(\vec{x})$:

$$S_i(\vec{q}) = \frac{4}{I_0}\sin^2\left[\left(k-\sqrt{k^2-q^2}\right)z\right] S_E(\vec{q}) \tag{3.44}$$

Using Eq. (3.12), we obtain:

$$S_i(q) = \frac{4}{I_0}\sin^2\left[\left(k-\sqrt{k^2-q^2}\right)z\right] I\left[Q(q)\right] \tag{3.45}$$

In order to use shadowgraph to evaluate the scattered intensity, the sample must be out of the focal plane. This technique has some disadvantages: some

wavevectors cannot be seen, since the transfer function vanishes; moreover, if the sample is thick we cannot define a z: the oscillations of the transfer function are smeared, but it could be hard to know quantitatively how much.

For phase contrast, we use Eq. (3.25), in order to evaluate the power spectrum S_i of $i(\vec{x})$:

$$S_i(\vec{q}) = \frac{4}{I_0} \cos^2 \left[\left(k - \sqrt{k^2 - q^2} \right) z \right] S_E(\vec{q}) \tag{3.46}$$

Using Eq. (3.12), we obtain:

$$S_i(q) = \frac{4}{I_0} \cos^2 \left[\left(k - \sqrt{k^2 - q^2} \right) z \right] I(Q(q)) \tag{3.47}$$

The disadvantages of shadowgraph, as a scattering measurement technique, are also found in phase contrast. Phase contrast has a flat transfer function only if $z = 0$: it's an ideal technique for thin samples.

Dark field doesn't allow to recover any information about the phase of the field. It is not suited to make scattered intensity measurements; a statistical approach, described in the following sections, will give interesting results.

We will describe in Section 3.11 the application of Schlieren technique to the measurement of the scattered intensity.

3.6 Gaussian field generated by the sum of many patterns.

Consider a monodisperse colloid, and the near field scattered light. The field can be decomposed into the sum of the waves coming from the different elements of the colloid. Thus at every distance from the colloid, the field will be given by the sum of many patterns, each randomly placed. An example of this is given in Fig. 3.4 and 3.5. Figure 3.4 shows the pattern: the intensity is linearily dependent on the field $f(\vec{x})$, which we can consider given by the wave scattered by a particle of the colloid. Figure 3.5 shows the sum of the patterns, the function $\rho(\vec{x})$:

$$\rho(\vec{x}) = \sum_{i=1}^{N} f(\vec{x} - \vec{x}_i) \tag{3.48}$$

where the N $\vec{x}_i$ are randomly distributed in a surface of measure S.

Now we will evaluate the P-point correlation functions of the sum of many patterns, $\rho(\vec{x})$. The results will be obteined, first, for fixed particle density $\mathcal{N} = N/S$, and $N \to \infty$; then we will show that, in a suitable limit, the P-point correlation functions, for $P \geq 4$, can be expressed in terms of two-point correlation function, corresponding to the Wick formula. In other words, every connected part of the correlation function developement vanishes: the field becomes gaussian. As a matter of fact, we will prove an extension of the well known central limit theorem.

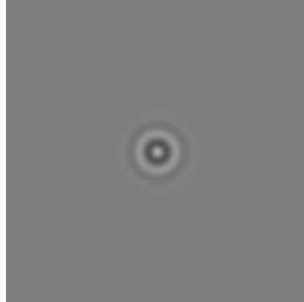

Figure 3.4: Example of the field generated by a particle of the colloid.

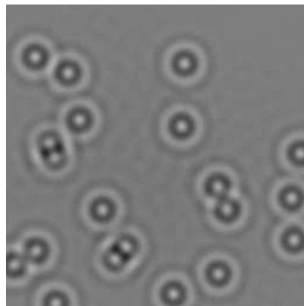

Figure 3.5: Example of the field generated by many particles of the colloid.

In the following, we will consider only functions with a vanishing average value, the other cases being easily obtained from this one. This simplifies the problem, since every odd-P-point correlation function will vanish.

The P-point correlation function of $\rho(\vec{x})$ is:

$$C(\Delta\vec{x}_2,\dots,\Delta\vec{x}_P) = \langle \rho(\vec{x})\,\rho(\vec{x}+\Delta\vec{x}_2)\dots\rho(\vec{x}+\Delta\vec{x}_P)\rangle = \frac{1}{S^{N+1}}$$
$$\sum_{i,j,k,\dots=1}^{N} \int_S f(\vec{x}-\vec{x}_i)\, f(\vec{x}-\vec{x}_j+\Delta\vec{x}_2)\dots f(\vec{x}-\vec{x}_k+\Delta\vec{x}_P)\,\mathrm{d}\vec{x}\mathrm{d}\vec{x}_1\dots\mathrm{d}\vec{x}_N \tag{3.49}$$

The value of the integral does not depend on all the values of the indices $i, j, k, \dots$, but only on which of them are equal; the sum involves NP terms, but many of them are equal. For example, for $P = 4$, the term with $i = 1, j = 2, k = 3, l = 4$ is equal to the one with $i = 2, j = 5, k = 7, l = 9$, but it is different from the one with $i = 1, j = 1, k = 3, l = 4$. The problem is thus to determine in how many ways we can obtain a given configuration.

The calculation can be made more easy using graphs. For evaluating a P-point correlation function, we draw P points on a graph, each one corresponding to one of the points of the correlation function, $0, \Delta\vec{x}_2, \dots, \Delta\vec{x}_P$. Then, we group the points, so that every set contains an even number of points [1]. Each configuration corresponds to many values of the indices $i, j, k, \dots$; the number of them is the multiplicity of the graph. Every set corresponds to an operation of integration on a different $\vec{x}_i$. We call G the number of sets; we will have only G integration variables, being the integrand independent on the other $N+1-G$ variables. The integration on these variables gives a factor S^{N+1-G}. Moreover, every integration corresponds to the evaluation of the correlation function $\tilde{C}$ of the single pattern $f(\vec{x})$:

$$\tilde{C}(\Delta\vec{x}_2,\dots,\Delta\vec{x}_P) = \frac{1}{S}\int f(\vec{x})\, f(\vec{x}+\Delta\vec{x}_2)\dots f(\vec{x}+\Delta\vec{x}_P)\,\mathrm{d}\vec{x} \tag{3.50}$$

The multiplicity of the graph depends on G; its value is $N(N-1)(N-2)\dots(N-G+1)$. For $N \to \infty$, we can consider only the leading term N^G.

We can thus describe the rules for evaluating the correlation functions, as the sum of all the graphs. The value of every graph is the product of the factors given by each set. The factor is the product of $\mathcal{N}$ and the correlation function $\tilde{C}$, which correlates all the points in the set.

For example, we evaluate the two-point correlation function (Tab. 3.1) and the four-point correlation function (Tab. 3.2).

For $\mathcal{N} \to \infty$, the leading term in the developement of the correlation function is the one with the higher power of $\mathcal{N}$: it is the one with the higher number of sets. Since sets with an odd number of elements have a vanishing contribution, the greatest number of sets can be obtained only by making sets of

[1] Sets with odd number of points will give vanishing contributions if $f(\vec{x})$ has a vanishing mean value.

0 $\Delta\vec{x}_1$	$C(\Delta\vec{x}_1) = \mathcal{N}\tilde{C}(\Delta\vec{x}_1)$

Table 3.1: Evaluation of the two-point correlation function.

$$C(\Delta\vec{x}_1, \Delta\vec{x}_2, \Delta\vec{x}_3) =$$

$\Delta\vec{x}_2$ $\Delta\vec{x}_3$ / 0 $\Delta\vec{x}_1$	$\mathcal{N}\tilde{C}(\Delta\vec{x}_1, \Delta\vec{x}_2, \Delta\vec{x}_3) +$
$\Delta\vec{x}_2$ $\Delta\vec{x}_3$ / 0 $\Delta\vec{x}_1$	$\mathcal{N}^2\tilde{C}(\Delta\vec{x}_1)\,\tilde{C}(\Delta\vec{x}_2 - \Delta\vec{x}_3) +$
$\Delta\vec{x}_2$ $\Delta\vec{x}_3$ / 0 $\Delta\vec{x}_1$	$\mathcal{N}^2\tilde{C}(\Delta\vec{x}_2)\,\tilde{C}(\Delta\vec{x}_1 - \Delta\vec{x}_3) +$
$\Delta\vec{x}_2$ $\Delta\vec{x}_3$ / 0 $\Delta\vec{x}_1$	$\mathcal{N}^2\tilde{C}(\Delta\vec{x}_3)\,\tilde{C}(\Delta\vec{x}_1 - \Delta\vec{x}_3)$

Table 3.2: Evaluation of the four-point correlation function.

two points. This means that only two point correlation functions of the single pattern $\tilde{C}(\Delta\vec{x})$ contribute to any correlation function $C(\Delta\vec{x}_1,\dots)$ of the sum.

Since $\mathcal{N}$ is dimensional, it is not possible to state if it is small or great. This means that we cannot define, in general, a value of $\mathcal{N}$ so great that the field becomes gaussian. The following heuristic considerations will show that the field is gaussian if $\mathcal{N}A \gg 1$, where A is the area of one pattern, at least if we can define it in some ways. Consider a pattern $f(\vec{x}) = \alpha\chi_A(\vec{x})$. The P-point correlation function of the pattern $f(\vec{x})$, evaluated in $\Delta\vec{x} = 0$, has the value $\tilde{C}(0,\dots)\alpha^P A$. Every graph will have a factor α^P and a factor A^G, where G is the number of sets in the graph. So the factor $\mathcal{N}$ alwais appears multiplied by A. By imposing $\mathcal{N}A \gg 1$, we obtain that the only contributions to the correlation function of the sum of patterns comes from the two point correlation function of the single pattern: all the Wick formulas are valid. In order that $\mathcal{N}A \gg 1$, the mean number of scattering particles inside each area A must be large: many pattern must overlap, in each point.

3.7 Siegert relation for the near field speckles.

Each scatterer of the sample generates a diffraction pattern which, at least in its far field, becomes larger and larger linearly, as the distance z from the screen and the sample is made longer. So, for z longer than a given distance, many diffraction patterns overlap: the Wick formulas should become valid. Unfortunately, the considerations of the previous section cannot be applied directly, since the area the diffraction pattern has not been already defined in a quantitative way.

Now we will prove the Wick formula for the case of Siegert relation, by using the formalism developed in the previous section.

From the results of the previous section, we can evaluate the intensity correlation function of the sum of the patterns, at a given z:

$$\begin{aligned}\left\langle |E_z(\vec{x})|^2 |E_z(\vec{x}+\Delta\vec{x})|^2 \right\rangle = \\ \mathcal{N}\int \left|\tilde{E}_z(\vec{x})\right|^2 \left|\tilde{E}_z(\vec{x}+\Delta\vec{x})\right|^2 d\vec{x} + \\ \mathcal{N}^2\int \left|\tilde{E}_z(\vec{x})\right|^2 \left|\tilde{E}_z(\vec{y}+\Delta\vec{x})\right|^2 d\vec{x}d\vec{y} + \\ \mathcal{N}^2\int \tilde{E}_z(\vec{x})\tilde{E}_z^*(\vec{x}+\Delta\vec{x})\tilde{E}_z^*(\vec{y})\tilde{E}_z(\vec{y}+\Delta\vec{x})\,d\vec{x}d\vec{y} + \\ \mathcal{N}^2\int \tilde{E}_z(\vec{x})\tilde{E}_z(\vec{x}+\Delta\vec{x})\tilde{E}_z^*(\vec{y})\tilde{E}_z^*(\vec{y}+\Delta\vec{x})\,d\vec{x}d\vec{y}\end{aligned} \tag{3.51}$$

where $\tilde{E}_z(\vec{x})$ is the field from a single scatterer, at a distance z. Assuming that the phases are random, and considering that the correlation function of any field

does not change with z:

$$\langle I_z(\vec{x})\, I_z(\vec{x}+\Delta\vec{x})\rangle = \mathcal{N}\int \tilde{I}_z(\vec{x})\,\tilde{I}_z(\vec{x}+\Delta\vec{x})\,d\vec{x} + \\ \mathcal{N}^2\left[\int \tilde{I}_0(\vec{x})\,d\vec{x}\right]^2 + \mathcal{N}^2\left|\int \tilde{E}_0(\vec{x})\,\tilde{E}_0^*(\vec{x}+\Delta\vec{x})\,d\vec{x}\right|^2 \tag{3.52}$$

The first term on the right hand side depends on z: it is the intensity correlation function of the diffraction pattern. Since the diffraction pattern becomes larger as z increases, while the total intensity keeps its value, the intensity correlation function of the diffraction pattern decreases, and vanishes as $z \to \infty$.

In order that Siegert relation holds, for a finite value of z, we must impose that the term with the four point correlation function is negligible compared to the two point ones:

$$\mathcal{N}\int \tilde{I}_z(\vec{x})\,\tilde{I}_z(\vec{x}+\Delta\vec{x})\,d\vec{x} \ll \mathcal{N}^2\left[\int \tilde{I}_0(\vec{x})\,d\vec{x}\right]^2 \tag{3.53}$$

The first term can be substituted by its higher value, the one with $\Delta\vec{x} = 0$:

$$\mathcal{N}\frac{\left[\int \tilde{I}_z(\vec{x})\,d\vec{x}\right]^2}{\int \tilde{I}_z^2(\vec{x})\,d\vec{x}} \gg 1 \tag{3.54}$$

The fraction represents the area A covered by the diffraction pattern:

$$\mathcal{N}A \gg 1 \tag{3.55}$$

In order that Siegert relation holds, we need that many particles scatter light inside a single diffraction pattern, that is, any point of the screen must be hit by light coming from many particles. This can be obtained without changing $\mathcal{N}$, but simply increasing z, thus increasing A.

It should be noted that the validity of Vick formulas for a given z does not mean that the field is completely gaussian. For example, we have shown that $\tilde{C}_I^z(\Delta\vec{x}) \to 0$ for $z \to \infty$, where $\tilde{C}_I^z(\Delta\vec{x})$ is the intensity correlation function of the diffraction pattern, defined as $\int \tilde{I}_z(\vec{x})\,\tilde{I}_z(\vec{x}+\Delta\vec{x})\,d\vec{x}$. But this does not imply any uniform convergence. Its integral, $\int \tilde{C}_I^z(\Delta\vec{x})\,d\Delta\vec{x}$, for example, is a constant, and does not vanishes as $z \to \infty$. This means that we can build suitable linear operators, acting on the field, yelding quantities which do not have a gaussian distribution. A dramatic example can be obtained considering the scattering from a two dimensional screen, with many holes of a given shape. As $z \to \infty$, the field meets the Vick formulas ever better. But it is alwais possible to analyze an area, bigger than the diffraction pattern of each hole, and to recover the shape of the holes. This can be done by deconvolving the field by a suitable function: it's the operation made by a lens, which creates an image of the holes. The deconvolution gives any information about the sample,

including the fourth order correlations: the deconvolved field is not gaussian. The gaussianity is only local: once we defined an area, corresponding to the aperture of a lens, there's a distance beyond which we are not able to recover the shape of each hole, and so informations on higher order correlation functions than second order ones are lost.

We can conclude that Eq. (3.55) implies only a local gaussianity; gaussianity is valid only when considering points inside an area small compered with the diffraction pattern of each scatterer. On the other hand, the knowledge of the field on a whole plane allows to recover any information on the correlation function of any order.

3.8 Vanishing of the $\langle EE \rangle$ correlations.

In Eq. (3.51) we neglected the terms like $\int \tilde{E}(\vec{x})\,\tilde{E}(\vec{x}+\Delta\vec{x})\,d\vec{x}$. Such terms should give contributions like $\langle E(\vec{x})\,E(\vec{x}+\Delta\vec{x})\rangle$ in the Vick formulas; we neglected them assuming that the phases are random. In this section we will analyze the conditions under which this happens.

In general, $\langle EE \rangle$ correlations are not negligible. For example, we can consider an opaque screen, with a transmission coefficient dependent on the position, with gaussian distribution. We know that Vick formulas hold. Now, we send a beam through it, and measure the outgoing intensity correlation function, immediately after the screen. Since all the points are in phase, we can assume that the field is real. The Vick formula for the intensity correlation function states that $C_I(\Delta\vec{x}) = \langle I \rangle^2 + 2\,|C_E(\Delta\vec{x})|^2$, due to the not negligible contribution of the term $\langle EE \rangle$, which becomes equal to $\langle EE^* \rangle$. Another example can be found in the theory of shadowgraph: the term $\langle EE \rangle$ is responsible for the oscillations of the transfer function defined in Eq. (3.37).

Now we derive the equations giving the evolution of $\langle EE \rangle$ as z increases. We define:

$$F_z(\Delta\vec{x}) = \int \tilde{E}_z(\vec{x})\,\tilde{E}_z(\vec{x}+\Delta\vec{x})\,d\vec{x} \tag{3.56}$$

The Fourier transform of $F(\Delta\vec{x})$ is:

$$F_z(\vec{q}) = \tilde{E}_z(\vec{q})\,\tilde{E}_z(-\vec{q}) \tag{3.57}$$

We can notice that $F(\vec{q})$ is the power spectrum if $\tilde{E}(-\vec{q})$ is the complex conjugate of $\tilde{E}(\vec{q})$, that is if $\tilde{E}(\vec{x})$ is real. By using Eq. (3.5), we obtain the evolution of $F_z(\vec{q})$:

$$F_z(\vec{q}) = e^{2i\sqrt{k^2-q^2}z}\,\tilde{E}_0(\vec{q})\,\tilde{E}_0(-\vec{q}) \tag{3.58}$$

This gives the evolution equation of $F_z(\vec{q})$:

$$F_z(\vec{q}) = e^{2i\sqrt{k^2-q^2}z}\,F_0(\vec{q}) \tag{3.59}$$

Comparing this equation with Eq. (3.5), we see that $F_z(\vec{q})$ evolves like the electric field $E_z(\vec{q})$, but two times faster than it, as z increases.

The root mean square amplitude of $F_z(\vec{q})$ is a conserved quantity; since $F_z(\vec{x})$ gets larger and larger as z increases, its amplitude must decrease like $1/z$. We can thus define a condition which is enough to ensure that the terms $\langle EE \rangle$ are negligible: the diffraction pattern must be much larger than the correlation lenght. This is implied by Eq. (3.55). The gaussianity condition expressed by Eq. (3.55) is met if many diffraction patterns overlap in every point. This implies that the diffraction pattern of each object must be much larger than the object itself, and than its correlation function, at least if the objects themselves do not overlap.

Some difficulties arise when we consider the power spectrum, or the Fourier transform of $\langle EE \rangle$ terms. As we already explained, the root mean square value of $\langle EE \rangle$ does not depend on z. A Fourier transform, made over a whole plane at a given z, could be divergent, for some values of q, as z increases. For example, we consider a Fourier transform made on a given area S, and we evaluate its mode with wavelength 0, that is, the integral of $F_z(\vec{x})$ over S. It is proportional to S/z. We can consider a square area S, of side $2\pi/q_1$, where q_1 is the wavevector of the longest wavelenght Fourier mode of the square S. So $F_z(\vec{q}=0) \propto 1/q_1^2 z$. Once we selected a q_1, the lowest wavevector we will consider, in order that $\langle EE \rangle$ is negligible with respect to a given value, independent on z, we must impose a $z \propto 1/q_1^2$.

A more quantitative result can be obtained by considering the evaluation of the Fourier transform on S as the evaluation of the Fourier transform on the whole plane, followed by the convolution with the Fourier transform of $\chi_S(\vec{x})$. This is equivalent to considering the discretization of the allowed wavelengths, due to a finite area S. Near a given value of q, the exponential term in Eq. (3.59) makes an oscillation in about k/qz. The discretized intervals are spaced by q_1: if $k/qz \ll q_1$ the oscillations are avereged and vanish. In general, the oscillations will be more visible for small values of q. In order that the oscillations are never visible, $k/q_1 z \ll q_1$: once we have selected q_1, that is the side of S, we must provide that:

$$z \gg \frac{k}{q_1^2}. \tag{3.60}$$

In shadowgraph technique, Eq. (3.60) means that the oscillations of the transfer function are so fast that they cannot be resolved by the sensor, and are thus averaged.

Equation (3.60) has a geometrical interpretation. The vanishing of $\langle EE \rangle$ can be expressed in terms of Fourier modes:

$$\langle E(\vec{q})\, E(-\vec{q}) \rangle = 0 \tag{3.61}$$

The beams, scattered by a modulation with wavevector q, hit the sensor at an angle q/k. Every modulation with wavevector q scatters at two simmetric angles; the resulting modulation on the sensor is thus given by light coming from two different regions, of area S, whose distance is about $2qz/k$. If the distance is longer than $2\pi/q_1$, the side of S, the regions do not overlap: see Fig. 3.6. Equation (3.60) states that we must provide that the regions do not

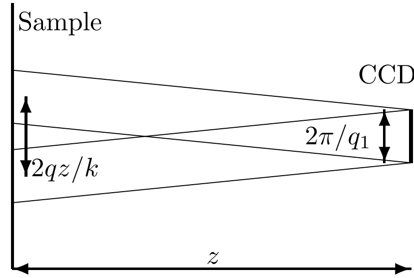

Figure 3.6: Description of the condition of non overlapping of the scattering regions.

overlap. This means that light collected at symmetric angles is not correlated, as required by Eq. (3.61). This condition ensures that the field is gaussian, only if the density of scatterers $\mathcal{N}$ is so that $\mathcal{N}S \gg 1$.

For the scattering from a thin sample, the intensities of the beams scattered at two symmetric angles are equal, and the phases are defined. Since the angles are symmetric, the interference of the scattered beams with the much intense transmitted beam gives two interference patterns, sinusoidal modulations, with the same wavevector, and a given phase. Changing z, the two diffraction patterns change their phase; at some z they sums, and at other values they cancel out. This is the origin of the oscillations in the transfer function of shadowgraph technique, defined in Eq. (3.37). If the condition of Eq. (3.60) is met, the phases of the beams scattered at symmetric directions is random: on average, the transfer function is constant.

The vanishing of the $\langle EE \rangle$ terms can be obtained also by increasing the thickness of the sample. When we pass from the two dimensional, Raman Nath scattering to the three dimensional, Bragg scattering, the correlations between the two beams scattered at the symmetric angles by a given sinusoidal modulation are not preserved. In shadowgraph language, the transfer function oscillations are washed out by superposing many layers, at different z. The thickness of the sample δz must meet the condition $\delta z > k/q_1^2$.

3.9 Homodyne near field speckles.

This technique has been presented very recently [1, 2]. The device for the measurement of the Near Field Speckles is, basically, a misfocused dark field microscope. The transmitted beam is removed, and the image is due only to the light scattered from the sample.

Some of the parameters of the system must be selected: the distance z from the sample to the focal plane of the objective, or from the CCD, if the objective is missing; the diameter D of the sample and of the incident beam; the superficial particle density of the sample. The parameters must be selected on the basis of

the required wavevector range $[q_{min}, q_{max}]$. The ratio q_{max}/q_{min} cannot exceed two decades, due to the finite size and discretization introduced by the CCD sensor. The range $[q_{min}, q_{max}]$ is generally selected in order to cover interesting wavelenghts of the sample: for example, from one tenth to ten diameters of the particles, in the case of the scattering from a monodisperse colloid. Three conditions must be fulfilled.

1. The misfocusing z must be selected in order to meet the condition expressed by Eq. (3.60), with $q_1 = q_{min}$, in order that the correlations $\langle EE \rangle$ vanish:
$$z \gg \frac{k}{q_{min}^2} \tag{3.62}$$
This condition is stronger than $z \gg k/(q_{typ}q_{min})$, where $2\pi/q_{typ}$ is the typical diameter of the particles. Since $2\pi/q_{min}$ is the side L of the images we take, Eq. (3.62) implies that $q_{typ}z/k \gg L$: the diffraction pattern of each particle covers a surface much bigger than the observed one, as required in order that the Fourier transform of the field can be considered gaussian.

2. In order that the field is gaussian, many diffraction patterns must overlap, in each point. Under the condition of Eq. (3.62), in order to fulfill Eq. (3.55), we must only provide that there are many particles in the surface S covered by an image:
$$\mathcal{N}S \gg 1 \tag{3.63}$$
. For particles suspended in a three dimensional volume, we can define the superficial particle density by multipling the volumetric particle density by the thickness of the cell. In order to fulfill condition (3.63), we can increase the volumetric particle density, or increase the thickness of the sample. Care must be teken in order to avoid multiple scattering.

3. The images we take must collect light scattered at any angle by the sample. The highest wavevector we want to measure is q_{max}; in order that the sensor collect light scattered by that wavevector, coming from any area of the sample, its diameter D must satisfy:
$$D \gg \frac{q_{max}}{k} z \tag{3.64}$$
This condition ensures that the sensor cannot see the sample boundaries: the sample can be considered as infinite. If the diameter is much less than the one imposed by Eq. (3.64), the speckles are governed by the classical, Van Cittert and Zernike theorem.

Under Eq. (3.62), (3.63) and (3.64), Siegert relation holds:

$$C_I(\Delta\vec{x}) = \langle I(\vec{x})\, I(\vec{x} + \Delta\vec{x}) \rangle = \langle I \rangle^2 + |C_E(\Delta\vec{x})|^2 \tag{3.65}$$

where the $\langle\cdot\rangle$ is the mean over $\vec{x}$ and $C_E(\Delta\vec{x})$ is the field correlation function. The intensity we measure in a point is not directly connected with any physical part of the sample: each speckle is generate by the superposition of many diffraction patterns.

The measurement of the intensity allows to recover the modulus of the field correlation function through Eq. (3.65). Since $C_E(\Delta\vec{x})$ is the Fourier transform of the power spectrum, which is symmetric and real, $C_E(\Delta\vec{x})$ is also real. Moreover, if we think $C_E(\Delta\vec{x})$ is alwais positive, we can calculate it by extracting a square root. Then, we Fourier transform $C_E(\Delta\vec{x})$, thus obtaining $S_E(\vec{q})$:

$$S_E(q) = \mathcal{F}\left[\sqrt{C_I(\vec{x}) - \langle I\rangle^2}\right](q) \tag{3.66}$$

Using Eq. (3.19), we obtain, for a thin sample:

$$k^2 S_{\delta l}(q) = \frac{1}{\langle I\rangle}\mathcal{F}\left[\sqrt{C_I(\vec{x}) - \langle I\rangle^2}\right](q) \tag{3.67}$$

Using Eq. (3.14), we obtain the scattered intensity:

$$I[Q(q)] = \mathcal{F}\left[\sqrt{C_I(\vec{x}) - \langle I\rangle^2}\right](q) \tag{3.68}$$

The results do not depend on z. The misfocusing z must be enough, in order that the field is gaussian, but its value does not affect the results.

The extraction of the square root of the difference between two experimental data is a dangerous operation, since the difference could be negative. In general, as any other inversion of experimental data, it involves an increase and a distorsion of noise. Chapter 7 provides a detailed description of this problem. This kind of problems are avoided by using ENFS or SNFS, described in Sects. 3.10 and 3.11.

We must notice that Eqs. (3.62) and (3.64) give $D \gg q_{max}/q_{min}^2$. We can think q_{max}/q_{min} as the wavevector dynamic range we want to measure; hopefully it can be about one hundred for spatial measurements. On the other hand, $2\pi/q_{min}$ is of the order of some length of the particles, for example ten times. For example, if we consider 10μm colloids, each image must cover about 100μm. In order to cover two decades in wavelength, we need a D about one hundred times wider: about 1cm. This is not a huge length; moreover, from the industrial point of view, there's no problem in making many acquisitions, with different magnifications and z, for every wavevector range, since each acquisition needs no accurate positioning.

On the other hand, in some cases, for scientific purposes, D should be too wide. This is the case of measurements of non-equilibrium fluctuations, described in Chapt. 9. In this case, we want to evaluate power spectra on two decades in spatial frequencies. The dimension of the largest fluctuations is about one tenth of millimeter: a good statistical sample is about a millimeter large, and the whole sample must be two decades bigger: about 10cm. The building of a Soret cell, or a free diffusion cell, with such an big diameter can be avoided by using SNFS, which will be described in Section 3.11

3.10 Heterodyne near field speckles.

We developed this technique very recently; the device has been patented [3, 4]. The setup for hEterodyne Near Field Speckles measurement is identical to ONFS one, but the beam stop is missing. The transmitted beam is not removed, and the image is due to the interference of the light scattered from the sample with the transmitted beam.

Two parameters of the system must be selected: the distance z from the sample to the focal plane of the objective, or from the CCD, if the objective is missing and the diameter D of the sample and of the incident beam. In ENFS, the superficial particle density of the sample plays no role. The parameters must be selected on the basis of the required wavevector range $[q_{min}, q_{max}]$. The ratio q_{max}/q_{min} cannot exceed two decades, due to the finite size and discretization introduced by the CCD sensor. The range $[q_{min}, q_{max}]$ is generally selected in order to cover interesting wavelenghts of the sample: for example, from one tenth to ten diameters of the particles, in the case of a monodisperse colloid. Two conditions must be fulfilled.

1. The misfocusing z must be selected to meet Eq. (3.62), in order that the correlations $\langle EE \rangle$ vanish. This condition is stronger than $z \gg k/(q_{typ}q_{min})$, where $2\pi/q_{typ}$ is the typical diameter of the particles. Since $2\pi/q_{min}$ is the side L of the images we take, Eq. (3.62) implies that $q_{typ}z/k \gg L$: the diffraction pattern of each particle covers a surface much bigger than the observed one, as required in order that the Fourier transform of the field can be considered gaussian.

2. The images we take must collect light scattered at any angle by the sample. The highest wavevector we want to measure is q_{max}; in order that the sensor collect light scattered by that wavevector, coming from any area of the sample, its diameter D must satisfy Eq. (3.64). This condition ensures that the sensor cannot see the sample boundaries: the cample can be considered as infinite. If the diameter is much less than the one imposed by Eq. (3.64), the speckles are governed by the classical, Van Cittert and Zernike theorem.

We can notice that the conditions expressed by Eq. (3.62) and (3.64) must hold for both ONFS and ENFS. On the contrary, in ENFS no condition is imposed on the particle density, in analogy with (3.63), since the field does not need to be gaussian.

In general, Eq. (3.63) is fulfilled by the sample; in that case, the field is gaussian, and the ENFS image represents the interference of a gaussian field with a plane wave. The particle density can be so small that the field is not gaussian; this does not mean that the speckles we see represent real objects in the sample. Each speckle is due to the interference between light scattered by many different particles.

Care must be taken in order to avoid multiple scattering. Since we want avoid multiple scattering, the scattered intensity is small compared to the transmitted

beam intensity: the second order effects in $\delta E/E_0$ can be neglected, and Eq. 3.21 holds.

$$C_i(\Delta\vec{x}) = +\frac{2}{I_0}\Re C_{\delta E}(\Delta\vec{x}) + \frac{2}{I_0^2}\Re\left[E_0^{*2}\langle\delta E(\vec{x})\,\delta E(\vec{x}+\Delta\vec{x})\rangle\right] \tag{3.69}$$

Under Eq. (3.62), the $\langle EE\rangle$ correlations vanish:

$$C_i(\Delta\vec{x}) = \frac{2}{I_0}\Re C_{\delta E}(\Delta\vec{x}) \tag{3.70}$$

This means that $S_i(q) = \frac{2}{I_0}S_E(q)$. The measurement of the intensity allows to recover the field power spectrum.

Using Eq. (3.19), we obtain, for a thin sample:

$$2k^2 S_{\delta l}(q) = S_i(q) \tag{3.71}$$

Under (3.64), Eq. (3.14) holds. We obtain the scattered intensity:

$$I[Q(q)] = \frac{1}{2}I_0 S_i(q) \tag{3.72}$$

The results do not depend on z. The misfocusing z must be sufficent, in order that the correlations $\langle EE\rangle$ vanish, but its value does not affect the results.

The considerations about the diameter D of the sample hold also for ENFS: Eq. (3.62) and (3.64) give $D \gg q_{max}/q_{min}^2$. This problem has been discussed in Section 3.9. The result is that, in some cases, the sample and the laser beam have to be extremely large. In that cases, SNFS can be used instead of ENFS: that technique will be described in Section 3.11.

Equation (3.72) must be compared with Eq. (3.45), that holds for values of z much less than those imposed by Eq. (3.62). The oscillations in the sensibility of shadowgraph technique come from the non vanishing of $\langle EE\rangle$ correlations, essentially due to the phase relation of the beams scattered at symmetric angles by a thin sample. For example, the zeroes of the transfer function are due to the distructive interference of the symmetrically scattered beams. In ENFS, the phase relation is destroied, because the light that hit the sensor at symmetric angles comes from different regions.

3.11 Schlieren-like near field speckles.

For Schlieren technique, we can use Eq. (3.34), in order to evaluate the power spectrum S_i of the signal $i(\vec{x})$:

$$S_i(\vec{q}) = \begin{cases} \frac{2}{I_0}S_E(-\vec{q}) & \vec{q}\cdot\vec{n} < 0 \\ \frac{2}{I_0}S_E(\vec{q}) & \vec{q}\cdot\vec{n} \geq 0 \end{cases} \tag{3.73}$$

We assume the sample is isotropic, so that $I(\vec{q})$ depends only on $|\vec{q}|$. Using Eq. (3.14):

$$I[Q(\vec{q})] = \frac{1}{2}I_0 S_i(\vec{q}) \tag{3.74}$$

Schlieren technique can alwais be applied to measure the scatterered intensity, no matter how long the misfocusing is. The sample can be thick or thin, in the focal plane or away from it: the result is never affected.

Once the dimension of the image has been selected, in order to observe an interesting range of wavevectors, the diameter of the sample must fulfill the condition expressed by Eq. (3.64), as in ONFS and ENFS, but in this case there's no limitation on z. The diameter will be, in general, sufficient to give a good statistical sample of the particles we are measuring; z will be as small as we can.

In general, for a thick sample, some of the objects will be too small, or too far from the focal plane, to be completely resolved. But their presence will prodece a speckle field, analogous to that of NFS. We will call this technique Schlieren-like Near Fiels Speckles, since it behaves like a true Schlieren technique only for big objects in the focal plane, while for the other cases it allows to measure the statistical properties of a speckle field.

Equation (3.74) must be compared with Eq. (3.45), that holds for values of z much less than those imposed by Eq. (3.62), and without the blade. The oscillations in the sensibility of shadowgraph technique come from the non vanishing of $\langle EE \rangle$ correlations, essentially due to the phase relation of the beams scattered at symmetric angles by a thin sample. In SNFS, the phase relation is destroied, because one of the beams scattered at symmetric angles is stopped.

3.12 Why using NFS instead of classical scattering measurement?

Classical, high angle light scattering works only for scattering angles higher than some degrees. Small angle light scattering (SALS) can measure light scattered by wavelengths of some microns; its main problem is the stray light. The new techniques allow an accurate subtraction of the stray light; in particular, for ENFS and SNFS stray light can be evaluated and subtracted point by point.

All SALS instruments must include some device to stop the transmitted beam, like in ONFS. Moreover, the solid state sensors must be accurately positioned with reference to the focus of transmitted beam. In an industrial instrument, the position of both the beam stop and the sensors must be electronically controlled, in order to correct the deformations due to mechanical stress and temperature dilatations. On the contrary, ENFS has an extremely simple and robust structure, which does not require any adjustment. This makes ENFS suited for industrial applications of light scattering measurement, like particle sizing. In Chapter 8, we will show some particle size measurements performed with ENFS.

In Chapter 9, we will show that SNFS can be used to make a measurement of the power spectrum of the non equilibrium fluctuations in a free diffusion process. Such fluctuations have never been observed by SALS, since they are extremely weak and involve mainly low wavevectors. This shows that NFS

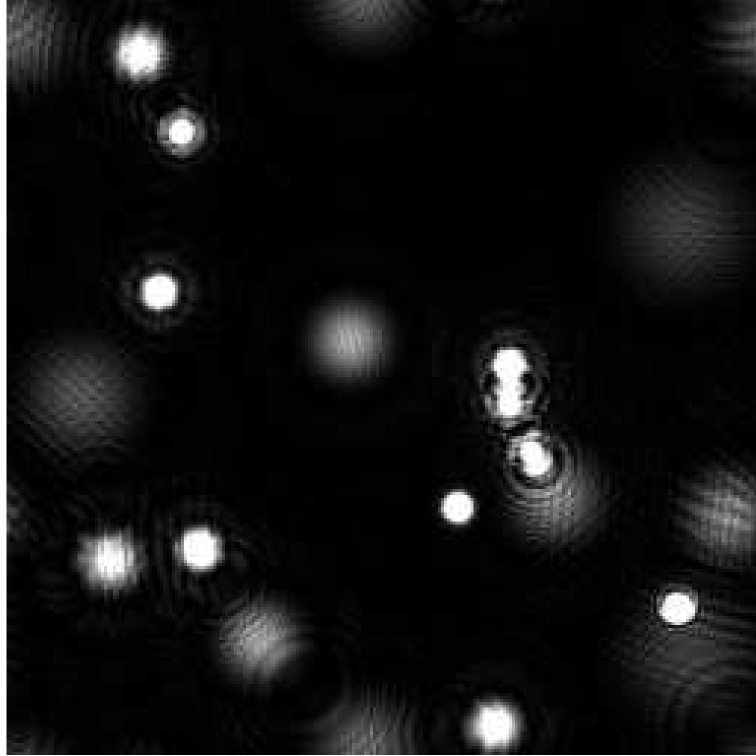

Figure 3.7: Example of dark field image.

techniques can be used to obtain measurements not possible with SALS.

3.13 Why using NFS instead of classical microscopy?

The near scattered field keeps only one feature associated to the observed sample, the correlation function. For example, Figure 3.7 shows a dark field image, and 3.8 shows the corresponding NFS image. The correlation function of the two fields is the same, but looking at the second immage we cannot figure that it comes from a set of discs. With near field scatterig we will never distinguish an amoeba from a paramecium: it is not a microscopy technique. Why using NFS instead of dark field?

The first answer comes from the analysis of Figure 3.7 and 3.8. In Figure 3.7, some of the discs are in the focal plane, other aren't. If we want to analyze a dark field image, we must be able to select the particles which are in the focal plane, and exclude from the analysis all the others. On the contrary, NFS gives informations which are never affected by the misfocusing z: it provides three dimensional informations, and works well for thin samples as well as for thick

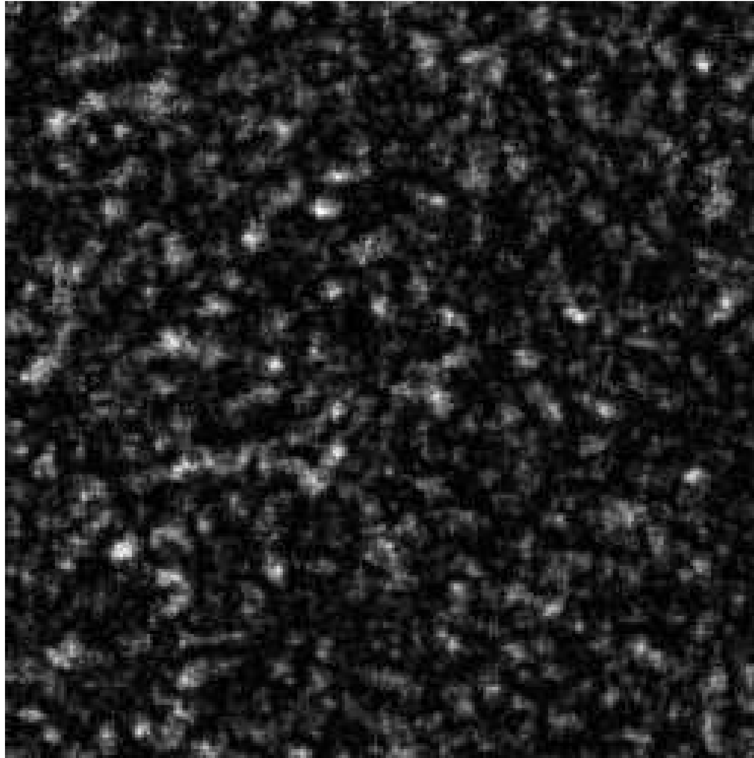

Figure 3.8: Example of Near Field Speckles image.

ones.

If we want to analyze, for example, a colloid by a microscopy technique, we must use a thin sample, in order that the particles can be focused. If the concentration is low, it could be hard to find even one particle. Generally, one microscopic image could show only some particles. On the contrary, NFS can work on thick samples. We can use a given colloid, with any concentration, and put it in a cell so thick that it shows a suitable attenuation.

Another reason leads to use ONFS technique instead of a dark field technique. Dark field image intensity is given by equation 3.29: every calculation based on dark field images will concern the square value of the refraction index fluctuations. In facts, two point correlation functions of the images will represent four point correlation functions of the refraction index fluctuations. We consider a fluid, for which the refraction index fluctuations has a give distribution. We are interested in measuring the two point correlation, but dark field images allow us to work only on four point one. Of course, four point correlation function involves the two point one, but has a non trivial connected contribution. In NFS images, every connected term in correlation functions vanishes: we can measure quantities directly connected with two point correlation functions.

3.14 Meaning of the light path correlation function.

We have shown that NFS allows the measurement of the light scattered in a quite wide range of angles. If Reyleight Gans condition is met, the scattered intensity represents the power spectrum of the sample, evaluated in the transferred wavevector. For the scattering at small angles, the spectrum is evaluated in the direction ortogonal to the incident beam. A measurement of this componet of the spectrum leads, through a Fourier transform, to the correlation function of the light path through the sample:

$$C_{\delta l}\left(\Delta\vec{x}\right) = \int \delta n\left(\vec{x}, z\right) \delta n\left(\vec{x} + \Delta\vec{x}, z'\right) \mathrm{d}z \mathrm{d}z' \mathrm{d}\vec{x}. \tag{3.75}$$

This quantity is directly accessible from NFS measurements. Its Fourier transform is the power spectrum for $q_z = 0$:

$$\int C_{\delta l}\left(\Delta\vec{x}\right) e^{-i\vec{q}\cdot\Delta\vec{x}} \mathrm{d}\Delta\vec{x} = \frac{1}{(2\pi)^6} \int \delta n\left(\vec{q}', q_z'\right) \delta n\left(\vec{q}'', q_z''\right) e^{i\left(\vec{q}'+\vec{q}''\right)\cdot\vec{x} + i\left(\vec{q}''-\vec{q}\right)\cdot\Delta\vec{x} + iq_z z + iq_z' z'} \mathrm{d}\vec{q}' \mathrm{d}\vec{q}'' \mathrm{d}\vec{x} \mathrm{d}\Delta\vec{x}. \mathrm{d}q_z' \mathrm{d}q_z'' \mathrm{d}z \mathrm{d}z' = \left|\delta n\left(\vec{q}, q_z = 0\right)\right|^2 \tag{3.76}$$

Through a measurement of the scattered light we can know the power spectrum in the plane perpendicular to the direction of the incident beam. This

means that the light path correlation function bears less informations than the refraction index correlation function, but the light path correlation function is connected to the refraction index correlation function:

$$C_{\delta l}\left(\Delta\vec{x}\right) = \int \delta n\left(\vec{x}, z\right) \delta n\left(\vec{x} + \Delta\vec{x}, z + \Delta z\right) \mathrm{d}\vec{x}\mathrm{d}z\mathrm{d}\Delta z = \int C_{\delta n}\left(\Delta\vec{x}, \Delta z\right) \mathrm{d}\Delta z. \quad (3.77)$$

If the sample is isotropic, its power spectrum depends only on the modulus of the wave vector. If we know the light path correlation function, we can evaluate its Fourier transform, extend it to the three dimensions, and then, appling again the Fourier transform, we obtain the refraction index correlation function. This operation is generally performed by using the well known Abel transform.