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General methods for determining the droplet size distribution in emulsion systems

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We present a general method that allows us to figure out the size distribution of an isolated collection of droplets of dilute emulsion system using nuclear magnetic resonance pulsed gradient spin echo measurements. We show that the expression to obtain the volume fraction distribution function is equivalent to a Fredholm integral equation of the first kind. We prove, using the Dirac notation, that a solution of this equation can be easily found if its kernel has a complete biorthogonal system of eigenvectors. Two numerical procedures are discussed. The first, termed indirect, is based on the expansion of the unknown distribution function in the eigenfunctions of the kernel. The second one, called direct, uses the properties of shifted Legendre polynomials to integrate numerically the integral equation and evaluates the unknown distribution by means of a constrained least square procedure. The computational limits are analyzed. To extract the distribution's form directly by experimental data we have constructed a generating function using the shifted Jacobi polynomials. The procedures have been tested on simulated and experimental data and appear to be a powerful and flexible method to obtain the size distribution function directly by the experimental data. © *1999 American Institute of Physics.* [S0021-9606(99)51702-9]

I. INTRODUCTION

It is well known that the emulsions are heterogeneous systems of one component liquid dispersed in another in the form of droplets having radii on the order of micrometers.[1] These systems are widely used in important fields of application, such as adhesives, cosmetics, foodstuff, pharmaceuticals, and in emulsion polymerization. It is evident that the emulsions are multiphase systems whose properties depend on the *morphology*, i.e., on the droplet size distribution.

Since the particle size distribution of a dispersion influences many important properties such as: viscosity, turbidity, and sedimentation velocity, it is essential to know the characteristic parameters of the distribution.

In dilute emulsions, where the interactions between the droplets are practically absent and the droplet shape is spherical, the droplet size distribution can be calculated by the pulsed gradient spin echo-nuclear magnetic resonance (PGSE-NMR) technique.[2,3]

Actually, several methods[4–6] have been proposed to obtain the droplet size distribution from NMR data. Recently we re-examined[7] the nature of the restricted diffusion results and found that the hypothesis *a priori* of a lognormal distribution is not essential to compute the size polydispersity.

In that paper we presented an approach which permits us to figure out the size distribution of an isolated collection droplets of a liquid dispersed in another. The echo decay coming from the ensemble of droplets with different radii was related to the droplet size distribution and to the echo attenuation. The distribution function was approximated using a generating function series.

This method gives very good results provided that the generating function does not depart too greatly from the ''true'' distribution. A suitable choice of the generating function, for a given emulsion system, may be based on the knowledge of the behavior of reasonable models under the same experimental conditions. If, for example, the system under investigation is a food emulsion the log-normal distribution appears to be a good model.[8] Therefore for such systems the generating function method can also be used.

Unfortunately there are different cases where the choice of the generating function is not easy. In these cases it is important to have at our disposal a mathematical tool which allows us to evaluate the droplet size distribution and its parameters. For this reason in this paper we develop two more accurate and simple methods. The first is based on the expansion of the solution of a Fredholm integral equation of the first kind in the orthogonal eigenfunctions of the kernel. The second one, on the contrary, solves numerically the integral equation obtaining the distribution function directly by experimental data and its form is studied by means of the Jacobi polynomials.

II. THEORY

A. Basic equation

The PGSE-NMR technique is generally used to study the effects of restricted diffusion phenomenon. In principle the goal of the experiments is quite simple: it measures the mean

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displacement of the spin-bearing molecules during a fixed time interval Δ (the time scale of the experiment). In this lapse of time the diffusion length is $\mathcal{L}=\sqrt{2D\Delta}$. If we assume that there is a single length scale R in the confining geometry (i.e., monodisperse emulsion), deviations from free diffusion are seen for $\mathcal{L}\geqslant R$. This fact is widely utilized to obtain information about the length scale.

For a single sphere of radius R the echo attenuation is given by:[9]

$$E(q,R)=\exp\left(-\frac{2\gamma^2 g^2}{D}\sum_{m=1}^{\infty}\frac{1}{\alpha_m^4(\alpha_m^2R^2-2)}f_m(q,R)\right), \tag{1}$$

with

$$f_m(q,R)=2\delta-\frac{2+e^{-\alpha_m^2D(\Delta-\delta)}-2e^{-\alpha_m^2D\delta}-2e^{-\alpha_m^2D\Delta}+e^{-\alpha_m^2D(\Delta+\delta)}}{\alpha_m^2D}, \tag{2}$$

where α_m is the mth root of the equation $J_{3/2}(\alpha R)-\alpha R J_{5/2}(\alpha R)=0$, D is the self-diffusion coefficient, γ is the magnetogyric ratio, g is the strength of gradient pulses, δ is the length of the gradient pulse, and Δ is the time distance between the gradient pulses. In Eq. (1) it has been assumed the relaxation time T_2 is independent of R.

In polydisperse systems, where on the NMR time scale the exchange between droplets is slow, the droplets of each size will obey Eq. (1). Consequently, the measured echo intensity is a sum of the echo contributions from the various droplets weighted by the volume fraction of each droplet size.

As we showed in a previous paper[7] the echo intensity may be written as

$$I(\delta)=\int_0^{\infty}E(\delta,R)\Phi(R)dR, \tag{3}$$

where the volume fraction distribution function is defined by

$$\Phi(R)dR=\frac{R^3P(R)dR}{\int_0^{\infty}R^3P(R)dR}, \tag{4}$$

and $P(R)$ is the particle size distribution function. The function $\Phi(R)$ is normalized, that is,

$$\int_0^{\infty}\Phi(R)dR=1. \tag{5}$$

Obviously the echo intensity is a function of the experimental parameters, like δ, Δ, and g. However, in a PGSE experiment Δ and g are generally kept constant, therefore the echo intensity is a function of δ only. As we pointed out in Ref. 7 to obtain an acceptable result from the PGSE experiment, it is necessary to use an R interval sufficiently large in comparison with the distribution width. Since such an R interval is experimentally fixed by $\mathcal{L}$, we can replace ∞ by $\mathcal{L}$ in Eqs. (3)–(5). Then the echo intensity becomes

$$I(\delta)=\int_0^{\mathcal{L}}E(\delta,R)\Phi(R)dR. \tag{6}$$

This equation is simplified by introducing the dimensionless variable

$$z=R/\mathcal{L} \tag{7}$$

and the scaled distribution

$$\Phi(R)dR=\Psi(z)dz. \tag{8}$$

The function $\Psi(z)$ must satisfy certain geometrical properties of frequency distributions,[10] namely

$$\Psi(z)\to 0, \quad d\Psi(z)/dz\to 0 \quad \text{at } z=0 \text{ and } z=1. \tag{9}$$

The echo intensity now reads

$$I(\delta)=\int_0^1 E(\delta,z)\Psi(z)dz. \tag{10}$$

This is a Fredholm integral equation[11] of the first kind. $E(\delta,z)$, is the kernel of the equation and defines the effect of the instrument on the *natural* input in producing the measured data. $[0,1]$ and $[0,\delta_{\max}]$ are the domains of support of the variable z explored and the variable δ measured, respectively.

The analysis of such equations has given rise to a well developed theory of *resolution* associated with the names[12] of Hilbert, Smidth, Carleman, Banach, Schur and others. The starting point of our investigation is the following remark: Eq. (9) implies that the function $\Psi(z)$ has a maximum in interval $[0,1]$, then

$$0\leqslant\Psi(z)\leqslant\Psi_{\max} \quad \text{for } z\in[0,1], \tag{11}$$

but on the other hand, the Cauchy–Bunyakovsky–Schwartz inequality[13] gives

$$1=\left|\int_0^1\Psi(z)dz\right|^2\leqslant\int_0^1|\Psi(z)|^2dz\leqslant\Psi_{\max}^2, \tag{12}$$

and therefore we may conclude that the distribution $\Psi(z)$ is a square summable function. Generally the class of all square summable functions supported into $[a,b]$ is indicated with $\mathcal{L}_2(a,b)$. Then, the integral in Eq. (10) transforms any function $\Psi(z)$ of the class $\mathcal{L}_2(0,1)$ into a continuous function $I(\delta)$, supported in $[0,\delta_{\max}]$. The latter can be considered an element of $\mathcal{L}_2(0,\delta_{\max})$. In other words Eq. (10) defines a mapping $\Psi\to I$, which is most easily studied if the domains of the supports are equal. This is done introducing a new dimensionless variable x defined through

$$\delta=x\delta_{\max} \quad \text{with } x\in[0,1]. \tag{13}$$

Finally Eq. (10) is transformed in

$$I(x)=\int_0^1 E(x,z)\Psi(z)dz. \tag{14}$$

Now, Eq. (14) associates every function of $\mathcal{L}_2(0,1)$ with another function of $\mathcal{L}_2(0,1)$. Algebraically, this means that the mapping $\Psi\rightarrow I$ defines an *operator*.

The remarkable structure of this equation is most suggestively revealed introducing an abstract functional space whose elements are termed vectors. This space is analogous to the Euclidean space of all three-dimensional vectors. For the algebra of vectors of this space we will use the Dirac notation.[14]

III. RESULTS AND DISCUSSION

A. Vector analysis

It is possible to proof that the mapping $\Psi\rightarrow I$ defines a compact, injective, and linear operator of $\mathcal{L}_2(0,1)$ into itself. Furthermore if we consider the restriction to class of square summable functions supported in $[0,1]$ the result $I(\delta)$ is an entire analytic function. Such an operator is defined by

$$|\mathbf{E}\zeta\rangle=\mathbf{E}|\zeta\rangle=\int_0^1 E(x,z)\zeta(z)dz \tag{15}$$

that allows us to rewrite Eq. (14) in concise form

$$\mathbf{E}|\Psi\rangle=|\mathbf{I}\rangle. \tag{16}$$

Before explicitly solving this equation we show in a general way that this solution can easily be found, if the linear operator **E** possesses a complete biorthogonal system of eigenvectors. The eigenvectors $|\eta^{(\sigma)}\rangle$, $\langle\tilde{\eta}^{(\sigma)}|$ and eigenvalues are defined as follows:

$$\mathbf{E}|\eta^{(\sigma)}\rangle=\Lambda_\sigma|\eta^{(\sigma)}\rangle \tag{17a}$$

$$\langle\tilde{\eta}^{(\rho)}|\mathbf{E}=\langle\tilde{\eta}^{(\rho)}|\tilde{\Lambda}_\rho. \tag{17b}$$

Multiplying Eq. (17a) by $\langle\tilde{\eta}^{(\rho)}|$ from the left and Eq. (17b) by $|\eta^{(\sigma)}\rangle$ from the right and subtracting both equations, the relation

$$0=(\Lambda_\sigma-\Lambda_p)\langle\tilde{\eta}^{(\rho)}|\eta^{(\sigma)}\rangle \tag{18}$$

is obtained. From Eq. (18) we conclude that $\langle\tilde{\eta}^{(\rho)}|\eta^{(\sigma)}\rangle=0$ must hold for $\tilde{\Lambda}_\sigma\neq\Lambda_\rho$. Only if the eigenvalues coincide, and this occurs if $\tilde{\Lambda}_\sigma=\Lambda_\rho$, can a nonvanishing scalar product $\langle\tilde{\eta}^{(\rho)}|\eta^{(\sigma)}\rangle\neq 0$ exist. It can be normalized to $\langle\tilde{\eta}^{(\rho)}|\eta^{(\sigma)}\rangle=1$. Therefore $\langle\tilde{\eta}^{(\rho)}|$ and $\langle\eta^{(\sigma)}|$ constitute a biorthonormal system with scalar products

$$\langle\tilde{\eta}^{(\rho)}|\eta^{(\sigma)}\rangle=\delta_{\rho\sigma}. \tag{19}$$

Using Riess–Fisher's theorem and the properties of functions belonging to the set $\mathcal{L}_2(0,1)$ (continuity in the mean)[15] we can prove that this system of eigenvectors is complete for the linear operator **E**. The vectors $|\Psi\rangle$ and $|\mathbf{I}\rangle$ can now be expanded in the complete system of eigenvectors of **E**

$$|\Psi\rangle=\sum_{\sigma=1}^{\infty}\psi_\sigma|\eta^{(\sigma)}\rangle, \tag{20}$$

$$|\mathbf{I}\rangle=\sum_{\sigma=1}^{\infty}I_\sigma|\eta^{(\sigma)}\rangle. \tag{21}$$

Equation (16), now yields

$$\sum_{\sigma=1}^{\infty}\psi_\sigma\Lambda_\sigma|\eta^{(\sigma)}\rangle=\sum_{\sigma=1}^{\infty}I_\sigma|\eta^{(\sigma)}\rangle, \tag{22}$$

where Eqs. (20)–(22) and Eq. (17a) have been used. Taking the scalar product of Eq. (22) and $\langle\tilde{\eta}^{(\rho)}|$ under consideration of Eq. (19), leads to

$$\psi_\sigma\Lambda_\sigma=I_\sigma\quad(\sigma=1,2,\cdots N). \tag{23}$$

This set of *decoupled* linear equations, which is derived after expanding $|\Psi\rangle$ and $|\mathbf{I}\rangle$ in eigenvectors of the operator **E**, is equivalent to the original *coupled* (integral) equations. Equation (23) can easily be solved with respect to ψ_σ and inserting it into Eq. (20) the solution is obtained. Equations (20)–(23) shows that the vector $|\Psi\rangle$ can be represented explicitly, as soon as the eigenvectors $|\eta^{(\sigma)}\rangle$ and eigenvalues Λ_σ of the operator **E** have been determined.

B. Eigenvalue/eigenvectors problem

At first the eigenvectors $|\eta^{(\Lambda)}\rangle$ and $\langle\tilde{\eta}^{(\Lambda)}|$ can be expanded in the known orthogonal and complete system of the eigenvectors $|\eta_i\rangle$ and $\langle\eta_j|$:

$$|\eta^{(\Lambda)}\rangle=\sum_{j=1}^{\infty}|\eta_j\rangle c_j^{(\Lambda)}\quad\text{with}\quad c_j^{(\Lambda)}=\langle\eta_j|\eta^{(\Lambda)}\rangle, \tag{24a}$$

$$\langle\tilde{\eta}^{(\Lambda)}|=\sum_{i=1}^{\infty}\tilde{c}_i^{(\Lambda)}\langle\eta_i|\quad\text{with}\quad\tilde{c}_i^{(\Lambda)}=\langle\tilde{\eta}^{(\Lambda)}|\eta_i\rangle. \tag{24b}$$

The equation for the coefficients $c_j^{(\Lambda)}$ and $\tilde{c}_i^{(\Lambda)}$ defined in Eqs. (24a) and (24b) are now found by multiplying Eq. (17a) by $\langle\eta_i|$ from the left and Eq. (17b) by $|\eta_j\rangle$ from the right, respectively (after having replaced σ and ρ by Λ):

$$\sum_{j=1}^{\infty}E_{ij}c_j^{(\Lambda)}=\Lambda c_i^{(\Lambda)}\quad\text{with}\quad E_{ij}=\langle\eta_i|\mathbf{E}|\eta_j\rangle, \tag{25a}$$

and

$$\sum_{j=1}^{\infty}E_{ji}\tilde{c}_j^{(\Lambda)}=\Lambda\tilde{c}_i^{(\Lambda)}\quad\text{with}\quad E_{ji}=\langle\eta_j|\mathbf{E}|\eta_i\rangle. \tag{25b}$$

Equations (25a) and (25b) are a convenient starting point for the determination of the eigenvalues Λ_σ and the coefficients $c_j^{(\Lambda)},\tilde{c}_i^{(\Lambda)}$. They show that the $c_j^{(\Lambda)},\tilde{c}_i^{(\Lambda)}$ represent the right and left eigenvectors of operator **E**, respectively. However, owing to nonhermiticity of the operator **E**, the eigenvalues and eigenvectors may be complex and the numerical resolution is very difficult. To avoid this difficulty we note that the biorthogonality relationship implies that Eqs. (17a) and (17b) are equivalent to:

$$\mathbf{E}^*|\tilde{\eta}^{(\Lambda)}\rangle=\Lambda|\eta^{(\Lambda)}\rangle, \tag{26a}$$

$$\mathbf{E}|\eta^{(\Lambda)}\rangle=\Lambda|\tilde{\eta}^{(\Lambda)}\rangle, \tag{26b}$$

where $\mathbf{E}^*$ is adjoint of **E**.

We are now ready to solve our problem, applying the operator **E** to Eq. (26a) and **E*** to Eq. (26b), where we get:

$$\mathbf{Q}|\eta^{(\Lambda)}\rangle=\Lambda^2|\eta^{(\Lambda)}\rangle, \tag{27a}$$

$$\mathbf{Q}^*|\tilde{\eta}^{(\Lambda)}\rangle=\Lambda^2|\tilde{\eta}^{(\Lambda)}\rangle, \tag{27b}$$

with

$$\mathbf{Q}=\mathbf{E}\mathbf{E}^* \quad \text{and} \quad \mathbf{Q}^*=\mathbf{E}^*\mathbf{E}. \tag{28}$$

The advantage of operator **Q** is now straightforward. It is real and symmetric and therefore its eigenvalues and eigenvectors are real. Further eigenvalues turn out to be distinct and one may use the Ritz variational method,[11] for example, to determine the eigenvalues Λ. Furthermore, as we will see in a subsequent section, Eqs. (27a) and (27b) are numerically equivalent to solve Eq. (16) by means of a linear least square procedure.

C. Computational limits

Of course, from a practical point of view, i.e., for computer calculations, the situation is often more complicated. Indeed, in the numerical method which immediately follows the choice of the orthonormal basis, we have to substitute the infinite series with finite sums. The truncation error together with the experimental error in the data make possible a threshold value, namely M, so that for $\sigma>M$, Λ_α becomes nearly pure noise disastrously amplifying the ψ_α value.

The terms ψ_σ in Eq. (20) are the Fourier coefficients of the set basis. Therefore, according to the Parseval relation,[13] we conclude that the solution of Eq. (16) exists only if the relation

$$\sum_{\sigma=1}^{\infty} \frac{I_\sigma^2}{\Lambda_\sigma^2}<+\infty \tag{29}$$

is satisfied. Generally this condition is not fulfilled when $|\mathbf{I}\rangle$ is corrupted by noise or experimental errors and the solution of Eq. (16) does not exist. This statement can be justified as follows. Let $|\Psi\rangle$ be the exact solution to Eq. (16) corresponding to exact vector intensity $|\mathbf{I}\rangle$ and let $|\mathbf{I}'\rangle$ be any vector that approximates $|\mathbf{I}\rangle$ in the sense that

$$|\mathbf{I}'\rangle=|\mathbf{I}\rangle+|\Delta\mathbf{I}\rangle=\mathbf{E}|\Psi\rangle+|\Delta\mathbf{I}\rangle, \tag{30}$$

where $|\Delta\mathbf{I}\rangle$ is the experimental error or noise. We assume

$$\overline{|\Delta\mathbf{I}\rangle}=0 \tag{31}$$

$$\overline{|\Delta\mathbf{I}_x\rangle|\Delta\mathbf{I}_{x'}\rangle}=\epsilon_I^2\delta(x-x'), \tag{32}$$

where the apexed bar indicates the average over an ensemble of the x's positions.

The first condition assures us that the average echo intensity obeys precisely the restricted diffusion law, that is, that the fluctuations on the average cancel each other. On the contrary, the second one expresses the idea of irregularity assuming that well separated measurements, in x dimension, are statistically independent. In other words, the correlation between the value of $|\Delta\mathbf{I}_x\rangle$ at two positions xx', is different from zero only for x ranges on the order of instrumental uncertainty.

Furthermore we assume that the unknown distribution $|\Psi\rangle$ comes also from white noise with zero mean and power spectrum ϵ_Ψ^2

$$\overline{|\Psi_z\rangle|\Psi_{z'}\rangle}=\epsilon_\Psi^2\delta(z-z') \tag{33}$$

and that the two stocastic variables are uncorrelated. Since $|\eta^{(\sigma)}\rangle$ is a complete system we can write

$$|\Delta\mathbf{I}\rangle=\sum_{\sigma=1}^{\infty}\Delta_\sigma|\eta^{(\sigma)}\rangle \quad \text{where} \quad \Delta_\sigma=\langle\tilde{\eta}^{(\sigma)}|\Delta\mathbf{I}\rangle \tag{34}$$

and then from Eqs. (31)–(33) we get

$$\overline{\Delta_\sigma\Delta_\rho}=\epsilon_I^2\delta_{\sigma\rho}, \tag{35}$$

$$\overline{\psi_\sigma\psi_\rho}=\epsilon_\Psi^2\delta_{\sigma\rho}, \tag{36}$$

using Eq. (20).

Since the stochastic variables have been assumed uncorrelated, we obtained

$$\overline{|\psi_\sigma\Delta_\rho\rangle}=0. \tag{37}$$

Now the components of the reconstructed solution are given by

$$\psi'_\sigma=\psi_\sigma+\frac{\Delta_\sigma}{\Lambda_\sigma} \tag{38}$$

and finally

$$\overline{\psi_\sigma\psi_\rho}=\left(\epsilon_\Psi^2+\frac{\epsilon_\mathbf{I}^2}{\Lambda_\sigma^2}\right)\delta_{\sigma\rho}. \tag{39}$$

Consequently, in the procedure to solve Eq. (16) we can estimate only those components such that the variance ϵ_Ψ^2 of the *signal* ψ_σ is greater than the variance $\epsilon_1^2/\Lambda_\sigma^2$ of the noise contribution $\Delta_\sigma/\Lambda_\sigma^2$, i.e., those components such that

$$\Lambda_\sigma\geqslant\epsilon_I/\epsilon_\Psi, \tag{40}$$

For a given signal/noise ratio ϵ_Ψ/ϵ_I, the largest $\sigma=(1,2,3\ldots M)$ for which Eq. (37) is satisfied determines the number of eigenvalues and eigenvectors to use in Eq. (20). In other words only within these limits is the problem well conditioned and Eq. (16) can be solved by a linear least square fitting.

D. Indirect method

In this section we show how the analytical solution of Eq. (16) previously found, can be approximated by means of a ''mean-square'' procedure on the experimental data. Let $z_i\,(i=1,\ldots M)$ be M points in the interval [0,1] and let us consider the ''function''

$$\Psi=\sum_{\sigma=1}^{M}\psi_\sigma\delta(z-z_k) \tag{41}$$

and inserting it in Eq. (14), we obtain the corresponding echo intensity

$$\mathbf{I}(x)=\sum_{\rho=1}^{M}E(x,z_\rho)\psi_p \tag{42}$$

the unknown parameters ψ_ρ being determined by solving the least squares problem

$$\sum_{j=1}^{N} w_j |\mathbf{I}_j - \mathbf{\dagger}_j|^2 = \text{minimum}, \tag{43}$$

where $\mathbf{I}_j = \mathbf{I}(x_j)$ is the set of the data and the weigth w_j are introduced in order to take into account the nonuniform distribution of the sampling points. Obviously the success of this procedure depends on the ill conditioning of the problem, Eq. (43). This ill condition manifests itself in the behavior of E^{-1}.

Substituting Eq. (42) into Eq. (43) and differentiating with respect to ψ_σ and equating to zero, one obtain

$${}_w\mathcal{E}^T\mathcal{E}|\psi\rangle = {}_w\mathcal{E}^T|\mathbf{\dagger}\rangle. \tag{44}$$

Here $|\psi\rangle$ is the M-dimensional vector of coefficients ψ_ρ, $|\mathbf{\dagger}\rangle$ is the N-dimensional vector of the data, while $\mathcal{E}$ and ${}_w\mathcal{E}^T$ are matrices whose elements are

$$\mathcal{E}_{j\rho} = E(x_j, z_\rho), \tag{45}$$

$${}_w\mathcal{E}^T_{\rho j} = w_j E(z_\rho, x_j). \tag{46}$$

Equation (44) can be interpreted as the discrete form of operator **Q** defined by Eq. (28). It follows that the square roots of the eigenvalues of the matrix ${}_w\mathcal{E}^T\mathcal{E}$ approximate Λ_σ, while the corresponding eigenvectors approximate $|\eta^{(\sigma)}\rangle$.

We computed numerically the eigenvalues of Eq. (27a) [or Eq. (44)] for various and characteristic values of experimental parameters Δ, g. As a complete orthonormal basis set on the interval [0,1] we used

$$\begin{aligned} &|\eta_1\rangle = 1 \\ &|\eta_i\rangle = \sqrt{2}\,\cos[(i-1)\pi x] \quad i = 2,3,\ldots M. \end{aligned} \tag{47}$$

Calculating directly the eigenvales Λ, small fluctuations may have great weight on the small values of ψ, so that the distribution $\Psi(z)$ can present at the ends oscillations which make it negative and therefore empty. This effect can be minimized avoiding the direct computation of eigenvalues. We approximate the distribution $\Psi(z)$ by

$$\Psi(z) = \sum_{j=1}^{M} a_j |\eta_j\rangle, \tag{48}$$

where $|\eta_j\rangle$ is given by Eqs. (46)–(47) and a_k are adjustable parameters. Substituting Eq. (48) into Eq. (14) and integrating we obtain

$$\sum_{j=1}^{M} a_j g_j(x) = I(x), \tag{49}$$

where

$$g_j(x) = \int_0^1 E(x,z)|\eta_j\rangle dz. \tag{50}$$

When Eq. (50) is integrated the parameters a_k are easily evaluated from Eq. (49) by means of a linear least square procedure (henceforth we will call it the *indirect* method). Although the direct computation of eigenvectors has been avoided, the coefficients a_k are linked to them. This statement is immediately verified, when Eq. (24a) is introduced into Eq. (20) so that

$$a_i = \sum_{\sigma=1}^{M} c_i^{(\sigma)} \psi_\sigma. \tag{51}$$

E. Direct method

The idea guiding our steps in this section is to find a numerical resolution of Eq. (10) replacing an integral by a finite sum. We shall follow a Gaussian procedure:[16]

$$\int_0^1 E(x,z)\Psi(z)dz \cong \sum_{j=1}^{s} w_j E(x,z_j)\Psi_j \tag{52}$$

since the quadrature formulas are over the interval [0,1] it follows that z_js are the zeros of shifted Legendre polynomials of degree, and w_j are the weight factors. Let us make the change of variable

$$y_j = w_j \Psi_j \tag{53}$$

so that Eq. (16) takes the form

$$\sum_{j=1}^{s} E_{ij} y_j = I_i \quad (i = 1,2,\cdots N). \tag{54}$$

Furthermore Eq. (5) becomes

$$\sum_{j=1}^{s} y_j = 1, \tag{55a}$$

while Eq. (9) gives

$$y_j \geqslant 0. \tag{55b}$$

From a numerical point of view, Eqs. (55) can be seen as constrains of Eq. (54). Therefore to solve Eq. (54) we employ a constrained least square procedure as described in Ref. 17. This method also presents some difficulties. The N value is fixed only by the number of the experimental data, but on the contrary the s value is chosen in the beginning. This choice is crucial. In fact if s is large, the matrix E_{ij} is so ill conditioned that is impossible to obtain y_is accurately; if s is small the equations in system Eq. (54) are not sufficiently precise to yield accurate value of y_is. Moreover, if s is moderately small, it might happen that the majority of points y_j to satisfy the constraints [Eqs. (55)] are such that $y_j = 0$. Consequently, it is impossible to reconstruct the distribution. We have bypassed this circumstance by exploiting the properties of shifted Legendre polynomials, $P_s^*(x)^j$s. It is well known that between two zeros of $P_s^*(x)$ there is a zero of $P_{s-1}^*(x)$. Therefore if we carry out the foregoing constrained least square for $s = 7,8,9,10$, we will obtain 33 different values of y_j.

F. The form of distribution

Sometimes, expecially to study the emulsification and demulsification kinetics, it is important to know an analytical expression to describe the form of the distribution. To do this our program analyzes the moments of the experimental distribution and creates a suitable generating function.

Let μ_n be the nth moment of distribution $\Psi(z)$. If $\log(\mu_n)$ is a linear function, or an increasing polynomial of n, the distribution $\Psi(z)$ is well approximated with a Gram–Charlier series.[18] The method used to calculate the series' coefficients is similar to that we described in Ref. 7 with the difference that now the distribution moments have been determined with the indirect and direct procedures and therefore such coefficients can be calculated directly.

If the distribution function is of exponential type or if $\log(\mu_n)$ is a decreasing function of $\log(n)$ a Pearson–Charlier[18] series is used. In this case the function $\Psi(z)$ can be approximated with a set of associated Laguerre polynomials:

$$\Psi(z)=\frac{a}{\Gamma(m+1)}\,(az)^m e^{-ax}\sum_{j=1}^{N} c_j L_j^m(az), \tag{56}$$

where a and m are positive constants which may be taken at pleasure, $\Gamma(m+1)$ is the gamma function, and $L_j^m(az)$ is an associated Laguerre polynomial. In order to optimize the rapidity of convergence of the series [Eq. (56)] we choose a and m in such a way that c_1 and c_2 vanish:

$$a=\frac{\mu_1}{\mu_2-\mu_1^2}=\frac{\mu_1}{\sigma^2}$$

and

$$m=\frac{\mu_1^2}{\sigma^2}-1. \tag{57}$$

Making use of the orthogonal property of $L_j^m(az)$ it possible to also establish in this case a recursion relation between the distribution's moment and the coefficients c_k. Unfortunately these expansions have the disvantage that they are only asymptotically convergent, the basic reason being the natural range of the Hermite or Laguerre polynomial is the entire real axis or positive, while the restricted diffusion is defined only into interval [01]. Therefore the Gram–Smid and Pearson–Charlier methods could be insufficient to describe all the experimental situations. For this reason we also constructed a new method using more convenient equations to fit the restricted diffusion results.

Let $W(z)$ be a weight function defined by

$$W(z)=z^{\alpha}(1-z)^{\beta}/B(\alpha+1,\beta+1), \tag{58}$$

where α and β are arbitrary positive constants and the B is the beta function defined by

$$B(\alpha+1,\beta+1)=\int_0^1 z^{\alpha}(1-z)^{\beta}dz. \tag{59}$$

This function ensures that the boundary conditions [Eq. (9)] are satisfied.

Now, the function $\Psi(z)$ is expanded as

$$\Psi(z)=\sum_{k=1}^{\infty} c_k P_k^{\alpha,\beta}(z)W(z), \tag{60}$$

where $P_k^{\alpha,\beta}(z)$ is a generic polynomial of degree k. By virtue of the orthogonality property, we have

$$\int_0^1 P_k^{\alpha,\beta}(z)P_j^{\alpha,\beta}(z)W(z)dz=0 \quad \text{with} \quad k\neq j, \tag{61}$$

where it is easily seen that the polynomial $P_k^{\alpha,\beta}(z)$ coincides with the shifted Jacobi polynomial,[19] i.e., $P_k^{\alpha,\beta}(z)=J_k^{\alpha,\beta}(1-2z)$, J_k being the Jacobi polynomial of degree k. We note that the parameters α and β are still at our disposal, and in order to optimize the rapidity of convergence of the series [Eq. (60)] we choose α andβ in such a way that c_1 and c_2 vanish. Then we have $c_0=1$ (normalization condition), $c_1=c_2=0$. Now, with the aid of Eqs. (60)–(61) it is easy to show that, once again, the coefficients c_k (with $k\geqslant 3$) depend on the distribution's moment only. As a consequence they can be calculated without using any least square procedure.

We are still faced with the problem of deciding which value of k is the ''best.'' The following procedure was found very effective. Consider two values c_k and c_{k+1} and χ_k^2 and χ_{k+1}^2, where

$$\chi_k^2=\sum_{j=1}^{N} \epsilon_{j,k}^2, \tag{62}$$

$$\epsilon_{j,k}=I(x_j)-\sum_{s=0}^{k} c_s P_s^{\alpha,\beta}(x_j)W(x_j). \tag{63}$$

In the case where $\chi_{k+1}^2>\chi_k^2$, the c_{k+1} value is rejected.

G. Some applications

The above proposed methods were tested using both simulated and experimental data sets analyzed in a previous paper.[7] The methods were successful in all and furthermore two distribution functions differing in nature from the previous ones have been examined here: beta[20] and Rice distributions.[20] The beta distribution is employed in the form

$$\Phi(z)=\frac{z^{\alpha}(1-z)^{\beta}}{B(\alpha+1,\beta+1)}, \tag{64}$$

where $B(a,b)$ is defined in Eq. (59) and normalizes the distribution function to 1. The Rice distribution is more complex and its form is

$$\Phi(z)=\frac{z}{s^2}\exp\left(-\frac{z^2+m^2}{2s^2}\right)I_0\left(\frac{mz}{s^2}\right), \tag{65}$$

where

$$I_n=(-i)^n J_n(iz) \tag{66}$$

is the modified Bessel[21] function of first kind and order n, $i=\sqrt{-1}$, where m and s are suitable parameters. These functions were selected to permit the study of distributions which cannot be analyzed with the traditional method[8] either by means or the generating functions.[7] For the numerical calculations we assumed $\alpha=3$ and $\beta=5.3$ in Eq. (63), while we put $m\mathcal{L}=2\times10^{-6}$ m and $s\mathcal{L}=7\times10^{-6}$ m in Eq. (65). Obviously the $\mathcal{L}$ value is fixed by the experimental parameters only. We chose as a typical value of a water-in-oil emulsion $g=0.1$ T m^{-1}, $\Delta=0.140$ s, and $D=2.3\times10^{-9}$ m^2 s^{-1}. We described the simulation procedure in Ref. 7. The results of a measurement simulated using the beta distribution function and processed by means of direct and indirect methods are

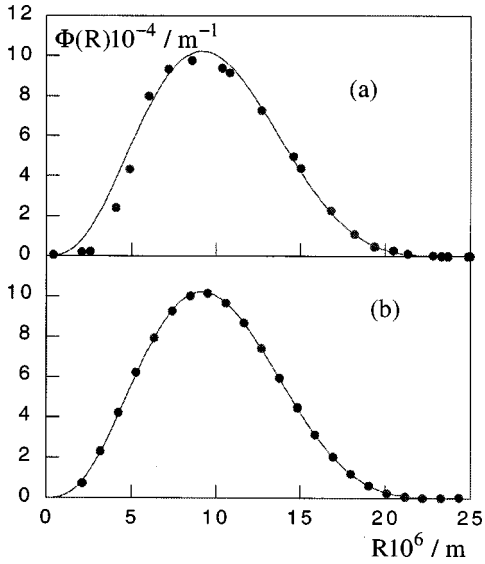

FIG. 1. Volume fraction distribution function calculated with (a) the direct method and (b) the indirect method by a measurement simulated using a beta distribution. The solid line represents the theoretical function, the dots are the calculated points.

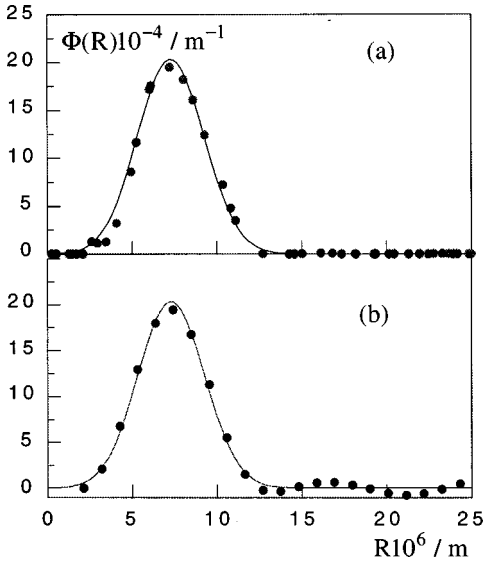

FIG. 2. Volume fraction distribution function calculated with (a) the direct method and (b) the indirect method by a measurement simulated using the Rice distribution. The solid line represents the theoretical function, the dots are the calculated points.

plotted in Fig. 1. Comparing the mean and standard deviation reported in Table I, one can see that the indirect method gives more accurate results. It is important, nevertheless, to note that the accuracy of the indirect method depends crucially on the choice of the M value in Eq. (47). We verified numerically that in most cases $M \leqslant 6$, but if the distribution function is sufficiently narrow it is necessary to increase the M value to minimize the oscillation to its ends. The results of a measurement simulated with a narrow Rice distribution are reported in Fig. 2 and collected in Table I. In this case we are able to damp the fluctuations by only using $M=8$ or $M=9$. Therefore the two methods can be seen as complementary and used together appear to be a powerful and flexible method to directly obtain the size distribution function in the emulsion system by experimental data.

As far as the distribution form is concerned the moments of the function shown in Fig. 2 were calculated and α and β coefficients in Jacobi polynomials were obtained. We found $\alpha=9.35$ and $\beta=24.80$. In Fig. 3 we compare the theoretical distribution function with that obtained using such parameters. It is easily seen that by using only the term c_0 in Eq. (60) the curve reproduces the true distribution with sufficient precision, indicating that it is an efficient method. Hopefully two terms of c: $c_3=0.0187$, $c_4=-0.0034$ are enough to obtain a good result.

TABLE I. Comparison of theoretical mean μ and standard deviation σ with the values calculated with direct and indirect methods. The distribution's parameters used to generate the measurements are reported in the text.

	Theoretical		Direct method		Indirect method	
Type	$\mu 10^6$/m	$\sigma 10^6$/m	$\mu 10^6$/m	$\sigma 10^6$/m	$\mu 10^6$/m	$\sigma 10^6$/m
Asymmetric Eq. (28) of Ref. 7	13.01	4.00	13.18	3.79	13.14	3.72
Bimodal[a] Eq. (29) of Ref. 7	12.51	5.27	12.10	5.96	12.41	5.94
Beta	9.86	3.68	10.25	3.61	9.85	3.65
Rice	7.29	1.95	7.35	2.12	7.27	1.88

[a]The μ and σ values reported concern the whole distribution; therefore the methods avoid the problem reported in Ref. 7 for the bimodal distribution and reproduce both the modes very well.

IV. CONCLUSIONS

In the case of emulsions, the experimental echo attenuation obtained in the PGSE-NMR experiment contains information on the droplet size distribution. When the normalized variables are used to analyze the experimental data, one ob-

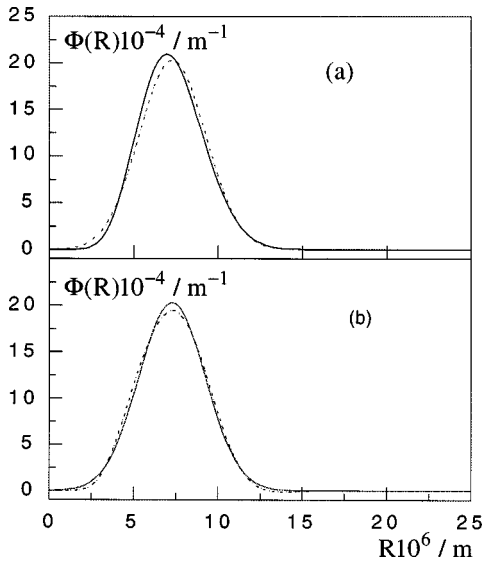

FIG. 3. Comparison between the theoretical distribution's form (Rice distribution) and that calculated using Jacobi polynomials with: (a) zero term c and (b) two terms c.

tains a Fredholm integral equation of the first kind. The procedures discussed in Sec. III are accurate, simple, and direct methods to give detailed information on the droplet collections. We found that a suitable expansion in the series of Jacobi polynomials is able to generate the distribution's form. Consequently, this method appears to be powerful enough to follow the kinetics in a polydisperse emulsion system. Finally we note that although we have applied our method to the emulsion system with restricted diffusion it, in principle, may be utilized also in another system and in different physical situations. Obviously we must change only the kernel in the integral equation.

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