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Communication

# Sample end effects

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ABSTRACT

In high-resolution NMR spectroscopy, the variation of the magnetic field inside the sample has a measurable impact on lineshape. We present a model to calculate the moments of the internal field, as they relate to the current that should be set in the compensation coils to level the magnetic perturbations originating from the sample. We apply this model to common sample geometries, and discuss the practical implications for sample-limited applications.



## 1. Introduction

Modern NMR spectrometers routinely achieve resolutions on the order of parts per billion of the Larmor frequency. Since the magnetic susceptibility of solvents is typically a thousand times higher, the samples own de-magnetizing field can be a non-negligible perturbation. High-resolution measurements commonly use elongated sample tubes, following the idea that the field internal to an infinite cylinder is uniform and amounts to a simple shift in Larmor frequency. In reality, the discontinuity in susceptibility at both ends of the sample causes rapid variations of the internal field, but the inhomogeneity is tolerable as long as the column height is much longer than the window of the probe RF coil.

Spectroscopists or probe designers dealing with limited amounts of sample have an incentive to shorten the sample column with respect to the coil length in order to get the most signal out of their precious material. However, the improved filling factor comes at the expense of the spectral lineshape which is degraded when the sample ends are close to the edges of the detection window, and regions of less homogeneous magnetic field get included in the probe field of view. Even with a shim system capable of preserving the resolution by compensating for low-order field impurities, the broadening caused by un-cancelled high-order gradients results in a loss of peak intensity. For a given sample volume and natural line width, the optimum choice of sample tube size or coil length depends on the residual field distribution.

Most studies of susceptibility effects [1,2] start with numerical field calculations, then simulate their effect on lineshape. By contrast, spectroscopists are interested in the coefficients of the expansion of the field in zonal and tesseral harmonics, which correspond to the currents that have to be adjusted in the compensation coils to level the magnetic perturbations [3]. In this paper, we provide a direct calculation of moments originating from a sample of finite length, in an approach similar to that of Barbara [4]. We study several common sample geometries and discuss the implications of our results on spectral intensity and lineshape.

## 2. Mathematical model

### 2.1. Background

In the absence of electric currents, the magnetic field $\mathbf{H}$ may be obtained by solving for the scalar magnetic potential $\Phi$, which is defined by the relation:

$$\mathbf{H} = -\nabla\Phi \tag{1}$$

The scalar product $\mathbf{M}\cdot\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}$ is the unit vector normal from the boundary and $\mathbf{M}$ is the magnetization, plays the role of a surface charge density. Although NMR samples are almost never magnetically ordered, the polarizing field is in most situations much stronger than the internal field, and the magnetization can therefore be assumed to be uniform to a very good approximation. In this case, by analogy with electrostatics, the expression for the magnetic potential is [5]:

$$\Phi(\mathbf{r}) = \frac{1}{4\pi}\iint_{\text{Surface}} \frac{\mathbf{M}\cdot\hat{\boldsymbol{n}}}{|\mathbf{r}-\mathbf{r}'|}dS \tag{2}$$

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To determine the local Larmor frequency within the sample, we apply the definition of the potential (Eq. (1)) and calculate the component of the magnetic field parallel to the polarizing field. Using the reciprocity between source point and observation point, we obtain:

$$H_z(\mathbf{r}) = \frac{1}{4\pi}\iint_{\text{Surface}} \hat{\boldsymbol{z}}\cdot\nabla_{\mathbf{r}'}\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right](\mathbf{M}\cdot\hat{\boldsymbol{n}})dS \tag{3}$$

where the spherical coordinate system is defined in Fig. 1. Inside the sample, the Green's function $|\mathbf{r}-\mathbf{r}'|^{-1}$ may be expressed as a sum of solid harmonics [6]. The factors that depend only on the observation coordinates $\mathbf{r}$ can be moved out of the integral sign to obtain the Laplace expansion of the magnetic field:

$$H_z(r,\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} C_{lm}P_l^m(\cos\theta)e^{im\varphi} \tag{4}$$

where $P_l^m$ are the associated Legendre functions of degree $l$ and order $m$ (see Appendix A). The coefficients $C_{lm}$ are obtained by integration over the source variable $\mathbf{r}'$:

$$C_{lm} = \frac{1}{4\pi}\iint_{\text{Surface}} \hat{\boldsymbol{z}}\cdot\nabla_{\mathbf{r}'}\left[(-1)^m\frac{e^{-im\varphi'}}{r'^{l+1}}P_l^{-m}(\cos\theta')\right](\mathbf{M}\cdot\hat{\boldsymbol{n}})dS \tag{5}$$

Under our starting assumption, the magnetization is proportional to the polarization field $H_0\hat{\boldsymbol{z}}$ and the volumetric magnetic susceptibility $\chi$. After some algebra involving recursion relations between Legendre functions, expression (5) becomes:

$$C_{lm} = -\frac{\chi H_0}{4\pi}\iint_{\text{Surface}}(-1)^m\frac{e^{-im\varphi'}}{r'^{l+2}}(l+m+1)P_{l+1}^{-m}(\cos\theta')(\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{z}})dS \tag{6}$$

The coefficients $C_{lm}$ have a practical meaning: they represent the current that should be set in each of the compensation (shim) coils to cancel out the magnetic perturbations originating from the sample. In these cumbersome expressions, simplifications arise from sample symmetry: the presence of the scalar product $\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{z}}$ ensures that only the top and bottom extremities contribute to the integral, provided the sample is aligned with the magnetic field. Through the harmonic factor $e^{-im\varphi'}$, additional symmetries in the sample cross section result in the cancellation of many of the coefficients, as will be discussed in specific examples below. The first term of the Laplace expansion is the bulk magnetic susceptibility shift, which is not related to inhomogeneous broadening effects; the associated coefficient $C_{00}$ is called the shape factor [7].

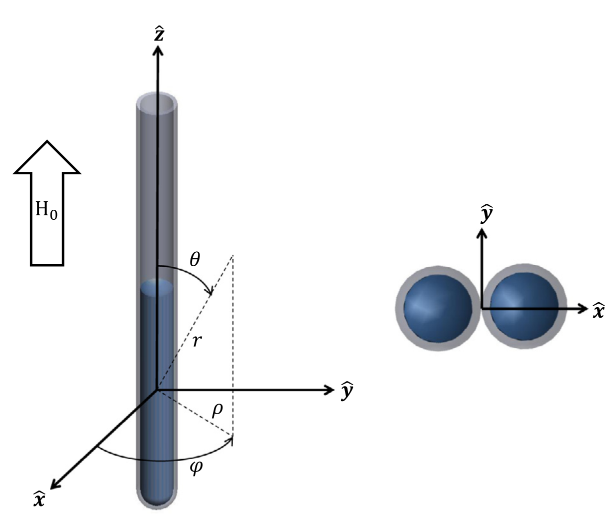


**Fig. 1.** Coordinate system used in the model. The sample tube is aligned with the polarizing field, and centered with respect to the shim coils. In the twin tubes configuration, the samples are offset by ±1.25 mm along $\hat{\boldsymbol{x}}$.

### 2.2. Flat-bottom sample tubes

We first consider a circular tube, where the sample is enclosed between two sections of flat glass. Although not the most common case, it is the simplest geometry to analyze since the sample has the shape of a straight cylinder. We neglect the effect of the glass on the internal field, assuming that the extremities of the container are far from the sample, and the side walls are thin and parallel to the polarizing field. Under these assumptions, the only non-zero coefficients are on-axis terms. Furthermore, the symmetry between the poles eliminates all odd degrees provided the sample is positioned at the center of the shim coils. In this case, expression (6) takes a simpler form:

$$C_{l0} = \frac{\chi H_0}{2z_0^l}\int_{u=\alpha}^{1}(l+1)u^{l-1}P_{l+1}(u)du \quad \text{if } l \text{ is even} \tag{7a}$$

$$C_{l0} = 0 \quad \text{if } l \text{ is odd} \tag{7b}$$

where $z_0$ is the sample half-length, $R$ its radius, and $\alpha = (1+(R/z_0)^2)^{-1/2}$. The integral is a dimensionless term that depends only on the sample form factor and can be evaluated numerically. A simpler expression may be used to evaluate end effects in the limiting case of long samples ($z_0 \gg R$):

$$C_{l0} \approx \frac{\chi H_0 R^2(l+1)}{2z_0^{l+2}} \tag{8}$$

The numerical results are compiled in Table 1 for various sample lengths, in units of ppb/cm$^l$. The evaluations were done with $R = 0.212$ cm and $\chi = -9.05$ ppm for the susceptibility of water [1]. The calculated values indicate that field distortions are noticeable but moderate for samples of common size. However, due to the $\propto 1/z_0^l$ dependence, high-order impurities increase sharply with decreasing length. At a $^1$H Larmor frequency of 600 MHz, these field distortions are predicted to exceed the compensation capacity of Agilent® shim systems for samples shorter than 2 cm. This limit is illustrated in Fig. 2.

In practice, this geometry is found in sample-limited applications where spectroscopists use tubes made of special glass that matches the susceptibility of the solvent. In order to mimic a long cylinder of uniform material, the sample volume is contained between a thick section of glass at the bottom and a plunger at the top. If an actual susceptibility-compensated tube is used, the pre-factor in expressions (7) and (8) is the difference in susceptibility between solvent and glass, and the values in Table 1 have to be scaled accordingly.

### 2.3. Round tubes

Most high-resolution NMR experiments utilize sample tubes with a round bottom. The solvent-to-air interface at the top, called a meniscus, is also non-planar. In this case, the integral in expression (6) has to be evaluated on curved surfaces, but we rely on the following simplification for the differential element:

$$(\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{z}})dS = \pm dxdy = \pm\rho d\rho d\varphi \quad \text{with } \rho = r\sin\theta \tag{9}$$

where the sign is positive for the meniscus, and negative for the round bottom. For the top of the sample, we use the cylindrical coordinate system and parameterize the meniscus profile with a numerically-calculated function $h(\rho)$ (see Appendix B). After normalization of the integration variable by $z_0$ expression (6) becomes: