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Theory of the Dielectric Susceptibility of Polar Liquid Crystals

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Statistical theory of the dielectric susceptibility is derived in the case of polar uniaxial molecules. The orientational and the induced parts of the susceptibility are taken into account. A generalized Claussius–Mossotti approach is used and the reaction field of the dipole moments is neglected (the low density limit). It is explained, in the case of prolate molecules, why the commonly used Maier and Meier formula overestimate the susceptibility component along the phase symmetry axis. Exemplary calculations of the temperature dependence of the order parameters and the susceptibility are presented.

Keywords: dielectric properties; nematic liquid crystal

1. INTRODUCTION

Liquid crystals are systems in which a liquid-like order exists at least in one direction of space, and in which some degree of anisotropy is present [1]. In the case of nematic liquid crystals there is no positional order but molecules tend to be parallel to the selected axes. This leads to the anisotropy of many physical quantities - the dielectric permittivity for example. Generally, it can have three different values ε_λ along the three axes of the phase symmetry. The dielectric theory tries to relate the macroscopic permittivities to the molecular properties. In this paper we would like to consider a theory of the dielectric susceptibility ($\chi = \varepsilon - 1$) for polar nematic phases.

Let us start from the simple derivations in order to introduce the subject and the notation. The potential energy of a dipole $\vec{\mu}$ in the electric field $\vec{E}$ is $U = -\vec{\mu} \cdot \vec{E}$. For a system of N noninteracting dipole moments in the volume V we obtain the polarization P from the

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Boltzmann distribution

$$P = \frac{N}{V}\bar{\mu} = \frac{N\mu}{V}L(\beta\mu E), \tag{1}$$

where $\beta = 1/(k_B T)$, $L(x) = \coth x - 1/x$ is the Langevin function. For small arguments we have the approximation $L(x) \approx x/3$, and thus

$$P = \frac{N\mu^2\beta E}{3V}, \tag{2}$$

The susceptibility is defined as

$$\varepsilon_0\chi = \frac{\partial P}{\partial E} = \frac{N\mu^2}{3Vk_B T}. \tag{3}$$

As a result we find a $1/T$ dependence called the Curie law. It indicates that the dipoles are noninteracting.

Let us consider anisotropic nematic phases (uniaxial or biaxial). The susceptibility becomes a tensor

$$\varepsilon_0\chi_{\lambda\sigma} = \frac{\partial P_\lambda^{tot}}{\partial E_\sigma}, \tag{4}$$

where P^{tot} is the total electric polarization. It can be divided into the part P^{ind} due to the molecular polarizability (the induced polarization) and the part P^{dip} due to the dipole moment (the orientation polarization)

$$P^{tot} = P^{ind} + P^{dip}, \tag{5}$$

$$P_\lambda^{ind} = \frac{N}{V}\langle P_\lambda\rangle, \tag{6}$$

$$P_\lambda^{dip} = \frac{N}{V}\langle \mu_\lambda\rangle, \tag{7}$$

$$\mu_\lambda = \sum_i \mu_i R_{i\lambda}, \tag{8}$$

where $i = 1,2,3$; $\lambda = x,y,z$; μ_i are the components of the permanent molecule dipole moment $\vec{\mu}$. The bar refers to the potential energy of the dipole moment in the electric field and the brackets to the nematic potential. We describe the molecule orientation by means of the three orthonormal vectors $(\vec{l},\vec{m},\vec{n})$. We denote their components as

$$l_\lambda = R_{1\lambda},\ m_\lambda = R_{2\lambda},\ n_\lambda = R_{3\lambda}. \tag{9}$$

The electric field $\vec{E}$ induces the electric moment $\vec{p}$ with the components

$$p_i = \alpha_i \varepsilon_0 E_i,\ i = 1,2,3, \tag{10}$$

$$E_i = \sum_\sigma R_{i\sigma} E_\sigma,\ \sigma = x,y,z. \tag{11}$$

The corresponding component along the λ-axis is

$$p_\lambda = \sum_i p_i R_{i\lambda} = \sum_\sigma \alpha_{\lambda\sigma} \varepsilon_0 E_\sigma, \tag{12}$$

$$\alpha_{\lambda\sigma} \equiv \sum_i \alpha_i R_{i\lambda} R_{i\sigma}. \tag{13}$$

We calculate the orientation polarization using the linear approximation

$$\langle \bar{\mu}_\lambda \rangle = \left\langle \mu_\lambda \left(1 + \beta \sum_\sigma \mu_\sigma E_\sigma \right) \right\rangle = \sum_\sigma \langle \mu_\lambda \mu_\sigma \rangle \beta E_\sigma. \tag{14}$$

The susceptibility is equal to

$$\varepsilon_0 \chi_{\lambda\sigma} = \frac{N}{V} (\varepsilon_0 \langle \alpha_{\lambda\sigma} \rangle + \beta \langle \mu_\lambda \mu_\sigma \rangle). \tag{15}$$

The diagonal values of the susceptibility can be writen as

$$\chi_{\lambda\lambda} = \frac{N}{V} \sum_i \langle R_{i\lambda}^2 \rangle \left(\alpha_i + \beta \mu_i^2 / \varepsilon_0 \right). \tag{16}$$

Note that the formulae (15) was derived under the assumption that the electric field acting on the molecules is equal to the external electric field. In many cases it is not true and that is why more exact models are needed.

The theory of the dielectric properties of isotropic polar liquids was given by Onsager. In his approach a molecule was represented by a polarizable point dipole in a spherical cavity of molecular dimensions and surrounded by a continuum with the macroscopic properties of the dielectric. He took into account the fact that the dipole moment polarizes its surroundings. This leads to the presence of the reaction field. Maier and Meier (MM) [2] extended the Onsager theory to the nematic liquid crystals. We can write their results in the form which can be used for the isotropic, the uniaxial and the biaxial nematic phases

$$\varepsilon_0 \chi_{\lambda\lambda} = \frac{N}{V} h F (\varepsilon_0 \langle \alpha_{\lambda\lambda} \rangle + \beta F \langle \mu_\lambda \mu_\lambda \rangle), \tag{17}$$

where h and F are the factors introduced by Onsager

$$h = \frac{3\tilde{\chi} + 3}{2\tilde{\chi} + 3}, \tag{18}$$

$$F = \frac{1}{1 - \tilde{\alpha}\varepsilon_0 f}, \tag{19}$$

$$\varepsilon_0 f = \frac{2\tilde{\chi}}{2\tilde{\chi} + 3}\left(\frac{3N}{V}\right). \tag{20}$$

In the expressions for h, F, and f the average susceptibility $\tilde{\chi}$ and the average polarizability $\tilde{\alpha}$ were used, i.e. the anisotropy was neglected. Apart from that, the molecule under consideration was contained in a *spheroidal* cavity. It is unrealistic for liquid crystals and that is why we would like to present a different approach which is a generalization of the results on nonpolar liquid crystals [3].

The organization of this paper is as follows: In Section 2 the relation among the susceptibility, the polarizability, and the order parameters is established. Section 3 is devoted to some applications of the presented theory. Section 4 contains the summary while Appendix A provides the definitions of the molecule shape factors.

2. THE DIELECTRIC SUSCEPTIBILITY

The molecule orientational ordering in the nematic phase can be described by the meanfield theories [4,5], the Landau-de Gennes theory [6,7], the lattice cluster theory [8], and the density functional theory [9]. We need only the temperature dependence of the order parameters and that is why we use the Straley model of biaxial nematics [10]. Within his model it is possible to describe the uniaxial and the biaxial molecules and phases. Thus, let us move to the description of the generalized Claussius–Mossotti (GCM) theory for the dielectric susceptibility.

The internal electric field $\vec{E}^{int}$ acting on the molecules differs from the external field $\vec{E}^{ext}$ because of the medium polarization. The internal field component can be expressed as

$$E_i^{int} = \sum_{\sigma} R_{i\sigma}\left(E_\sigma^{ext} + \frac{P_\sigma^{tot}\Omega_i}{\varepsilon_0}\right), \tag{21}$$

where Ω_i are the shape factors calculated in Appendix A for different molecule shapes. The electric field $\vec{E}^{int}$ induces the electric moment $\vec{p}$ with the components

$$p_i = \alpha_i \varepsilon_0 E_i^{\mathrm{int}}. \tag{22}$$

The component along the λ-axis has the following form

$$p_\lambda = \sum_i \alpha_i R_{i\lambda} \varepsilon_0 E_i^{int}. \tag{23}$$

Hence, we find the average value

$$\langle p_\lambda \rangle = \sum_\sigma \langle \alpha_{\lambda\sigma} \rangle \varepsilon_0 E_\sigma^{ext} + \sum_\sigma \left\langle \sum_i \alpha_i \Omega_i R_{i\lambda} R_{i\sigma} \right\rangle P_\sigma^{tot}. \tag{24}$$

The orientation polarization is calculated within the linear approximation

$$\begin{aligned} \langle \bar{\mu}_\lambda \rangle &= \left\langle \mu_\lambda \left(1 + \beta \sum_i \mu_i E_i^{int} \right) \right\rangle \\ &= \sum_\sigma \langle \mu_\lambda \mu_\sigma \rangle \beta E_\sigma + \sum_\sigma \left\langle \mu_\lambda \sum_i \mu_i \Omega_i R_{i\sigma} \right\rangle \beta P_\sigma^{tot} / \varepsilon_0. \end{aligned} \tag{25}$$

Finally, we get from Equations (4)–(8) and (24)–(25) the following result

$$\begin{aligned} \chi_{\lambda\sigma} = &\frac{N}{V} \langle \alpha_{\lambda\sigma} \rangle + \frac{N\beta}{V\varepsilon_0} \langle \mu_\lambda \mu_\sigma \rangle \\ &+ \frac{N}{V} \sum_\rho \left\langle \sum_i \alpha_i \Omega_i R_{i\lambda} R_{i\rho} \right\rangle \chi_{\rho\sigma} + \frac{N\beta}{V\varepsilon_0} \sum_\rho \left\langle \mu_\lambda \sum_i \mu_i \Omega_i R_{i\rho} \right\rangle \chi_{\rho\sigma}. \end{aligned} \tag{26}$$

The diagonal values are

$$\chi_{\lambda\lambda} = \frac{N/V \sum_i \langle R_{i\lambda}^2 \rangle (\alpha_i + \mu_i^2 \beta / \varepsilon_0)}{1 - (N/V) \sum_i \langle R_{i\lambda}^2 \rangle \Omega_i (\alpha_i + \mu_i^2 \beta / \varepsilon_0)}. \tag{27}$$

In the case of the uniaxial molecules and the uniaxial nematic phase, the elements $\langle R_{i\lambda}^2 \rangle$ can be expressed by means of the order parameter $S = \langle (3\cos^2\theta - 1)/2 \rangle$

$$\begin{aligned} &\langle R_{1x}^2 \rangle = \langle R_{1y}^2 \rangle = \langle R_{2x}^2 \rangle = \langle R_{2y}^2 \rangle = (2+S)/6, \\ &\langle R_{1z}^2 \rangle = \langle R_{2z}^2 \rangle = \langle R_{3x}^2 \rangle = \langle R_{3y}^2 \rangle = (1-S)/3, \\ &\langle R_{3z}^2 \rangle = (2S+1)/3. \end{aligned} \tag{28}$$

In the case of the biaxial molecules or phases, more order parameters should be used [11].

3. EXEMPLARY CALCULATIONS

In this section we carry out the detailed calculations for the system of polar uniaxial molecules. We use dimensionless quantities, i.e., the temperature T is given in T_C (the temperature of the isotropic-nematic transition), the polarizability in the molecule volume V_{mol}, the dipole moment in $\sqrt{\varepsilon_0 V_{mol} k_B T_C}$, and the density as the packing fraction NV_{mol}/V.

The numerical values of the selected parameters (T_C, V_{mol}, μ) are similar to the PAA (p-azoxyanisole [12]) but others are chosen in order to test the presented theory (the density, the dipole moment direction). We used the polarizabilities

$$\alpha_1 = \alpha_2 = 0.69,\ \alpha_3 = 1.57, \tag{29}$$

$$\tilde{\alpha} = \frac{(\alpha_1 + \alpha_2 + \alpha_3)}{3}, \tag{30}$$

the density 0.1, and the dipole moment 1.65.

The temperature dependence of the order parameter S is presented in Figure 1. It was calculated from the Straley theory in the case of the

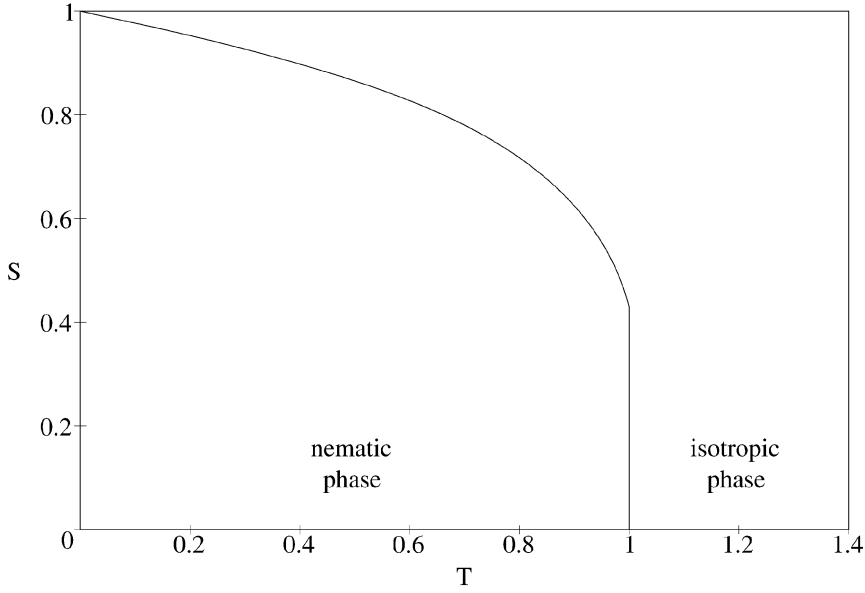

FIGURE 1 Temperature dependence of the order parameter S. There is the first-order transition from the isotropic to the uniaxial nematic phase. T denotes the dimensionless temperature.

uniaxial molecules. There is the first order transition from the isotropic to the uniaxial nematic phase. Figure 2 shows the shape factors for the ellipsoidal (solid lines) and the cylindrical molecules (dashed lines). We can notice the difference between the ellipsoids and the cylinders. For very long molecules $\Omega_3 = 0$ but $\Omega_1 = \pi/4$ (ellipsoids) or $\Omega_1 = 1/2$ (cylinders). For very short (disc-like) molecules $\Omega_1 = 0$ while $\Omega_3 = +\infty$ (ellipsoids) or $\Omega_3 = 1$ (cylinders). From a steric point of view, the PAA molecule is a rigid rod of length 20 Å and width 5 Å. That is why we used the shape factors for the ellipsoids 1:4 and we checked that for the cylinders 1:4 the results are similar.

The temperature dependence of the susceptibilities is presented in Figures 3 and 4 where the results from the GCM theory (solid lines) and, for comparison, from the MM theory (dashed lines) are shown. In Figure 3 the molecule dipole moment is oriented along the long molecule axis and this leads to the relation $\chi_{zz} > \chi_{xx}$. In Figure 4 the molecule dipole moment is oriented along the short molecule axis and we get $\chi_{xx} > \chi_{zz}$. In both cases χ_{zz} from the MM theory is significantly larger than χ_{zz} from the GCM theory, whereas the χ_{xx} values are comparable.

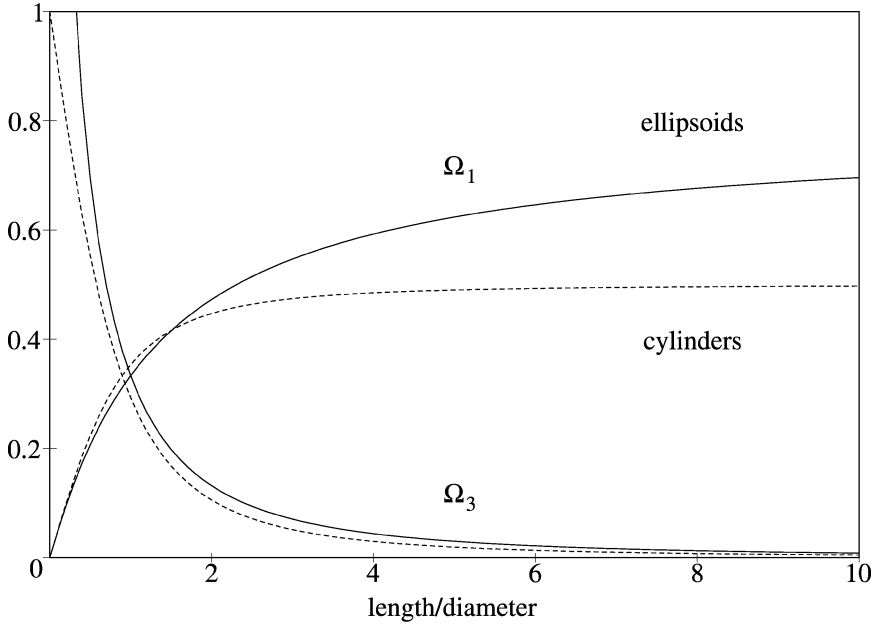

FIGURE 2 Shape factors Ω_1 and Ω_3 for ellipsoids (solid lines) and cylinders (dashed lines).

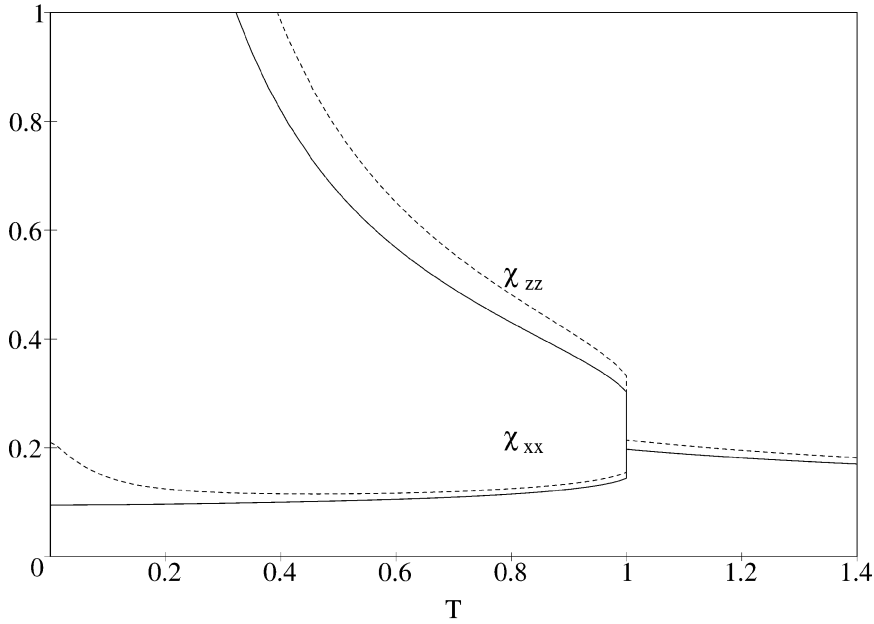

FIGURE 3 Temperature dependence of the susceptibilities according to the GCM theory (solid lines) and the MM theory (dashed lines). The dipole moment is oriented along the long molecule axis. T denotes the dimensionless temperature.

In order to explain this discrepancy, we consider the h factor which is connected with the electric field in a cavity. In the limit of small susceptibilities we can write the following expansion

$$h = \frac{3\chi + 3}{2\chi + 3} \approx 1 + \frac{\chi}{3}, \tag{31}$$

where we recognize the shape factors $\Omega_i = 1/3$ for a spherical cavity. However, for the prolate molecules the prolate cavity is more suitable. For the infinitely long cylindrical cavity we can calculate two different values of the h factor: $h_3 = 1$ along the cavity and

$$h_1 = h_2 = \frac{2 + 2\chi}{2 + \chi} \approx 1 + \frac{\chi}{2}, \tag{32}$$

in the perpendicular directions. The corresponding shape factors for very long cylinders are $\Omega_1 = \Omega_2 = 1/2$ and $\Omega_3 = 0$. The difference in the factor h and the shape factors is the main reason why the GCM theory and the MM theory differ in their results and why the GCM theory is better.

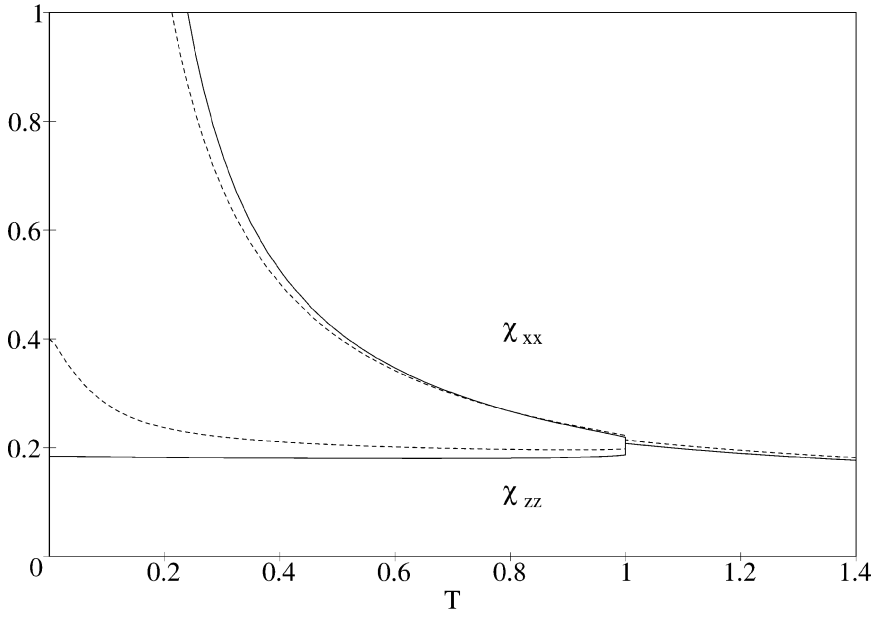

FIGURE 4 Temperature dependence of the susceptibilities according to the GCM theory (solid lines) and the MM theory (dashed lines). The dipole moment is oriented along the short molecule axis. T denotes the dimensionless temperature.

Additionally, Figures 3 and 4 show the increase of χ_{xx} and χ_{zz} below $T = 0.2$ if calculated according to the MM theory. It can be explained by the reacting field increase: the factors h and F become significant. Thus, this is the border of the GCM theory applicability.

4. SUMMARY

In this paper the statistical theory of the dielectric susceptibility for polar liquid crystals was presented. A generalized Claussius–Mossotti approach was used and the reaction field was neglected. It is acceptable in the case of the low density or the small susceptibility. In order to calculate the susceptibility, it is necessary to provide the density, the polarizability, the shape factors, the temperature, the dipole moment, and the phase order parameter. The derived formulas can be used in the case of the uniaxial or the biaxial molecules and phases. As a special case the recent results for nonpolar liquid crystals are obtained [3].

Our exemplary calculations show that the MM formula overestimates the influence of the external electric field in the direction parallel to the long molecule axis. As a result, the susceptibility component along the phase symmetry axis is too high.

On the other hand, for the high density and $\chi > 1$ the reacting field can not be neglected because the factors h and F are significant. In this case the MM formula should be used as a better compact expression is not known. It is difficult to take into account the reacting field in the case of nonspherical molecules. It can also be added that in real molecules the permanent dipole moment do not have to be placed in the molecule center. The total dipole moment can be a sum of the dipole moments that come from the molecule building blocks (for example a cyanide group).

APPENDIX A

The shape factors for the uniaxial molecules with the $D_{\infty h}$ and $C_{\infty v}$ symmetry. The reference point, where we calculate the electric field, is always placed in the molecule mass center.

1. Ellipsoids with the axes $2a \times 2a \times 2c$ (the $D_{\infty h}$ symmetry group).

$$\Omega_1 = \Omega_2 = J(0, 1 - a^2/c^2), \tag{33}$$

$$\Omega_3 = J(1 - c^2/a^2, 1 - c^2/a^2), \tag{34}$$

where the function $J(x,y)$ is defined for $x < 1$ and $y < 1$ as

$$J(x,y) = \int_0^1 \frac{dt\, t^2}{\sqrt{(1 - xt^2)(1 - yt^2)}}.$$

2. Cylinders with the length H and the diameter $2R$ (the $D_{\infty h}$ symmetry group).

$$\Omega_1 = \Omega_2 = \frac{H}{2\sqrt{4R^2 + H^2}}, \tag{35}$$

$$\Omega_3 = 1 - \frac{H}{\sqrt{4R^2 + H^2}}. \tag{36}$$

   Note that $\Omega_1 + \Omega_2 + \Omega_3 = 1$.
3. Cones with the height H and the base diameter $2R$ (the $C_{\infty v}$ symmetry group).

$$\Omega_1 = \Omega_2 = \int_0^H \frac{(zR/H)^2 dz}{4r^2}, \tag{37}$$

$$\Omega_3 = \frac{1}{2} - \frac{H}{2\sqrt{16R^2 + H^2}} + \int_0^H \frac{(3H/4 - z)R^2 z dz}{2H^2 r^3}, \tag{38}$$

where $r^2 = (zR/H)^2 + (3H/4 - z)^2$.

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