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Relationship of refractive index to mass density and self-consistency of mixing rules for multicomponent mixtures like ambient aerosols

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Abstract

This paper focuses on two important yet poorly addressed aspects of ambient aerosols: relationship of refractive index to mass density (index–density relationship) and consistency of the mixing rules used to calculate these two quantities of a multicomponent mixture like ambient aerosols with the index–density relationship. Combined empirical and theoretical analyses show that a denser material generally tends to have a larger refraction index because the applied electric field induces a greater number of electric dipoles, and that the index–density relationship can be described reasonably well by the Lorentz–Lorenz relation. It is shown that the commonly used volume–mean mixing rule for calculating the effective mass density, the Lorentz–Lorenz mixing rule and the molar refraction mixing rule for calculating effective refractive index form a set of mixing rules that are consistent with the Lorentz–Lorenz relation. The molar fraction mixing rule and the Lorentz–Lorenz mixing rule are shown to be equivalent for the Lorentz–Lorenz mixture while the linear volume-mixing rule is an approximation of the Lorentz–Lorenz mixing rule for quasi-homogeneous mixtures wherein the refractive indices of the constituents do not differ much. The results highlight the need for consistency of the mixing rules for calculating the effective refractive index and mass density with the index–density relationship, which not only provides a theoretical guide for judiciously choosing the mixing rules to calculate effective properties of ambient aerosols but also poses new challenges to develop an effective medium theory that applies to more than one quantity. An empirical power-law expression is obtained from the published data that relates the effective specific refractive index to the effective mass density of aerosol particles.

Keywords: Refractive index; Particle density; Effective medium theory; Mixing rules; Aerosols

1. Introduction

Refractive index and mass density are two fundamental properties of aerosol particles that are often required together in many areas of aerosol research (Seinfeld & Pandis, 1997; Van de Hulst, 1957). For example, both refractive index and mass density of aerosol particles are needed in quantification of aerosol effects on climate, which calls for coupling aerosol dynamical models with aerosol optical models (Ghan & Schwartz, 2007). Knowledge of the two quantities is also useful for interpretation of aerosol measurements taken with instruments that are built on different physical principles (see McMurry, 2000 for a recent review). Some instruments such as impactors are based on aerosol dynamics and measure the “aerodynamic size” that depends on particle mass density, in addition to the geometrical size and geometrical shape. Other instruments such as DMA measure the electric mobility size that depends on particle shape

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and size, but not on particle mass density. Still others such as optical counters measure "optical sizes" that depend on refractive index. Measurements with different instruments can be very different, and converting one set of measurements to another requires information on particle refractive index and mass density, among other things.

Ambient aerosol particles are mixtures of multiple chemical species, and mixing rules are generally needed to calculate the effective mass density and effective refractive indices as functions of chemical composition. Distinct mixing rules have been developed, and often used without a clear physical basis to favor one approach over another. This situation is especially true for the calculation of effective refractive index. Therefore, understanding the applicability of various mixing rules and their mutual relationship is vitally important to further advancing representation of aerosol-related processes in climate models (Ghan & Schwartz, 2007).

Despite the need for accurate estimates of both the effective refractive index and the effective mass density, simultaneous measurements of these two aerosol quantities are very limited, and few studies have been made to examine their relationship. Furthermore, the mixing rules use to estimate effective refractive index and mass density, for the most part, have been developed separately, and the consistency of the mixing rules with respect to the index–density relationship has not been examined. The connections between the different mixing rules that have been commonly used to calculate effective refractive indices of aerosol particles, if any, have not been rigorously clarified. The objectives of this paper are to fill these gaps by (1) exploring the relationship between the effective refractive index and the effective mass density of aerosol particles, (2) examining the consistency of the mixing rules with the index–density relationship, and discerning the connections between the different mixing rules that have been commonly used to calculate effective refractive indices of aerosol particles, (3) establishing a self-consistent set of mixing rules for calculating effective refractive index and effective mass density, and (4) summarizing the fundamental physical principles that constrain the mixture characterized by these self-consistent mixing rules.

2. Relationship between refractive index and mass density of pure materials

2.1. Empirical investigation

As two fundamental material properties, refractive index (or dielectric constant) and mass density have been extensively investigated by researchers in diverse disciplines for various purposes since the early 20th century (e.g., Phillips, 1920 for carbon dioxide, Anderson & Schreiber, 1965 for minerals related to the Earth's mantle). A large amount of data on pure materials, including organics, inorganics and minerals, has been accumulated. To illustrate the general relationship between the refractive index and mass density, a comprehensive set of data for over 4000 pure materials published in literature, including organics, inorganics, and minerals, are collected and shown in Fig. 1. The overall increase of refractive index with increasing mass density is evident from the figure. The refractive index increases linearly with mass density when the mass density is much less than $1\,\mathrm{g\,cm^{-3}}$, but the linearity disappears for dense materials such as liquids and solids. Dense materials tend to exhibit relatively large scatter, suggesting that although the mass density is a primary determinant of the refractive index, other factors affect the index–density relationship as well (see the theoretical discussion below for details).

2.2. Theoretical expression

The theoretical basis of the relationship between reflective index and mass density is embedded in the so-called state equation of polarization, which relates macroscopic optical/electrical properties (dielectric constant and refractive index) to the corresponding microscopic molecular properties (e.g., molecular polarizability). Most of the theory was established in the late 19th and early 20th century, and constitutes a textbook content in electrostatics and molecular optics (e.g., Aspnes, 1982; Debye, 1929; Lorentz, 1960). However, the derivation of the theory is not easy to find in the literature on atmospheric aerosols. Also, the theory has been largely developed for pure materials of the same chemical species, and its extension to multicomponent mixtures such as ambient aerosols has not been well investigated. More importantly, as will be shown in Section 4, the theory for pure materials is critical for developing self-consistent mixing rules used to calculate effective quantities of multicomponent mixtures like ambient aerosols. For these reasons, the major steps of this theory are recapped below.

Briefly, consider a piece of pure material as a system of molecules that react to an incident electric field like electric dipoles. From the microscopic perspective, when a piece of dielectric is placed in an applied electric field, the electric

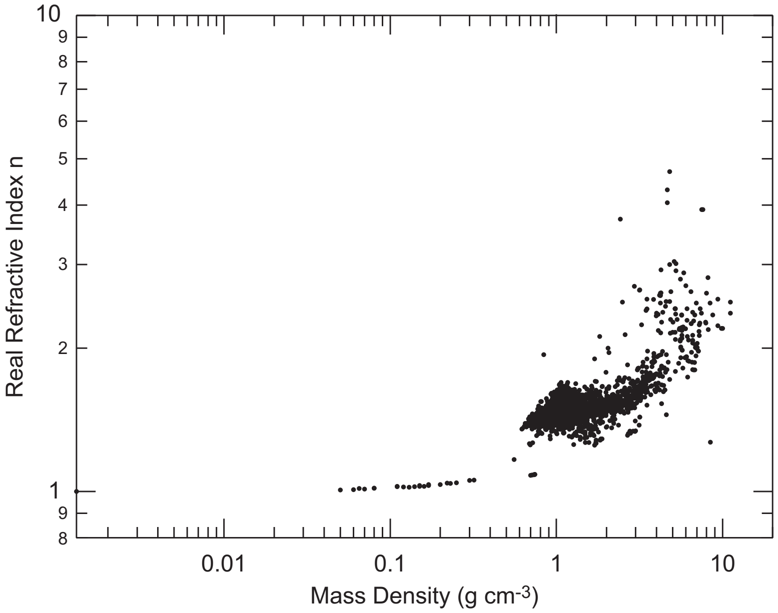

Fig. 1. Dependence of refractive index on mass density for pure materials compiled from various sources, including organic compounds, inorganic compounds and minerals.

polarization P (average electric dipole moment per unit volume) is given by

$$P = \rho\alpha\varepsilon_0 E_{\mathrm{loc}}, \tag{1}$$

where ρ is the number density of the material molecules, α is the mean molecular polarizability, ε_0 is the vacuum permittivity, and E_{loc} is the local electric field experienced by an individual molecule. From the macroscopic perspective, the electric polarization is related to the applied electric field E by

$$P = (\varepsilon - 1)\varepsilon_0 E, \tag{2}$$

where ε is the dielectric constant (also called relative permittivity) of the material. The equality of Eqs. (1) and (2) yields

$$\varepsilon = 1 + \alpha\rho\frac{E_{\mathrm{loc}}}{E}. \tag{3}$$

Elimination of E_{loc} and E using the Lorentz expression for the local electric field

$$E_{\mathrm{loc}} = E + \frac{P}{3\varepsilon_0} = \frac{1}{3}(\varepsilon + 2)E \tag{4}$$

yields the so-called Clausius–Mossotti relation

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{\rho\alpha}{3}. \tag{5}$$

Application of the Maxwell relation $\varepsilon = n^2$ to Eq. (5) yields the well-known Lorentz–Lorenz relation for the refractive index (n)

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{\alpha\rho}{3}. \tag{6}$$

In terms of the mass density ρ_m, which is related to the number density by $\rho_m = (M/N_{\mathrm{A}})\rho$, the Lorentz–Lorenz relation becomes

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{N_{\mathrm{A}}\alpha}{3M}\rho_m, \tag{7a}$$

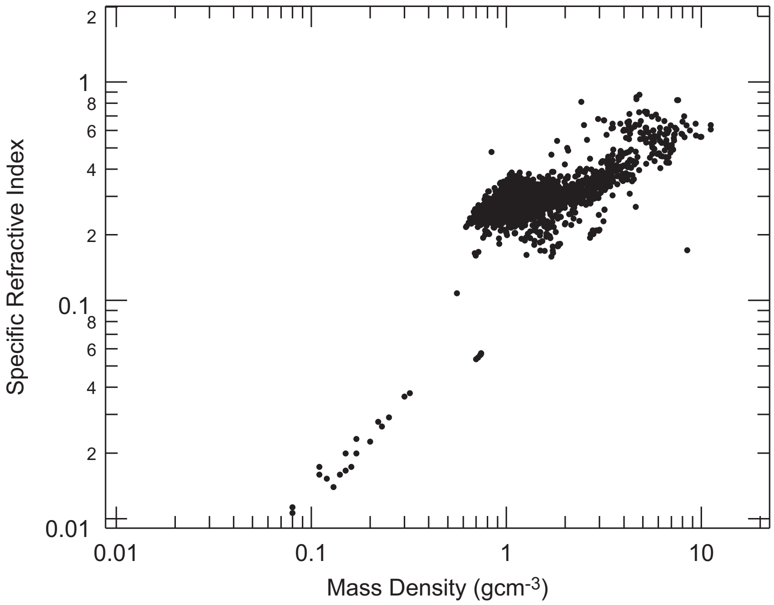

Fig. 2. Same as Fig. 1, except that it shows the dependence of the specific refractive index, instead of refractive index itself, on mass density.

where N_A is the universal Avagadro's number and M is the molecular weight of the chemical element of the material. Note that Lorentz (1960) actually derived Eq. (6) first and then reduced it to the Clausius–Mossotti relation using the Maxwell relation. Lorentz's work further related the molecular polarizability to the properties of the electrons, which is beyond the scope of this paper. Also noted is that the original Clausius–Mossotti equation was developed for the static or infinitely low frequency while the Lorentz–Lorenz relation was for electromagnetic waves of any frequency. Nevertheless, Oughstun and Cartwright (2003) generalized the original Clausius–Mossotti relation for any frequency. Therefore, the Lorentz–Lorenz relation is equivalent to the Clausius–Mossotti relation in essence; the former name is used in this work because refractive index is used more often than dielectric constant in aerosol research.

Eq. (7a) indicates that the functional relationship between refractive index and mass density is better represented with the reduced refractive index on the left-hand side as the dependent variable, instead of the refractive index itself. This reduced refractive index is often referred to as the specific refraction. This point is illustrated by Fig. 2, which redisplays the same data shown in Fig. 1, but in the form of the specific refraction against the mass density. Compared to Fig. 1, Fig. 2 clearly exhibits a better linearity.

Eq. (7a) also reveals that in addition to the mass density, refractive index depends on the molecular polarizability and the molecular weight as well. This additional dependency is likely responsible for the scatter of the data points shown in the previous two figures because different chemical species tend to have different values of molecular polarizability and molecular weight. As a result, the Lorentz–Lorenz relation has been used in other forms. One form of the Lorentz–Lorenz relation is rewriting Eq. (7a) as

$$\frac{(n^2-1)}{(n^2+2)\rho_m}=\frac{N_A\alpha}{3M}. \tag{7b}$$

It is obvious that this form of the Lorentz–Lorenz relation is useful when the right-hand side does not change. For example, according to the notion that the molecular weight and molecular polarizability of a given material do not change much with temperature and pressure, this form of the Lorentz–Lorenz relation has been used to infer the refractive index of the sulfuric acid in the stratosphere from the mass density measured at the same stratospheric environment, together with the refractive index and mass density obtained in room conditions under the assumption that the left-hand side is a constant (Massie, 1994; Yue & Deepak, 1981; Yue, Poole, Wang, & Chiou, 1994).

The other form of the Lorentz–Lorenz relation is given by

$$\frac{(n^2-1)M}{(n^2+2)\rho_m}=\frac{N_A\alpha}{3}, \tag{7c}$$

where the reduced quantity on the left-hand side is often referred to as the molar refraction (note the subtle difference with the specific refraction). The quantity on the right-hand side also has a name for itself, molar polarization (Debye, 1929). The Lorentz–Lorenz relation therefore means the equality of the molar refraction and molar polarization. As will be shown in Section 2b, Eq. (7b) is closely related to the so-called molar refraction mixing rule that has been widely used to calculate the effective refractive index of aerosol particles (Stelson, 1990).

A linear equation has also been used to describe the index–density relationship. As shown in Fig. 1, this linear relationship between refractive index and mass density approximately holds when the mass density $\ll 1$. Below we derive the linear equation from both a mathematical approximation of the Lorentz–Lorenz relation and a direct physical argument. For materials with small mass densities, the molecules are far apart from one another, the molecular interactions are weak, and the refractive index is close to 1. Under this condition, a Taylor expansion of the specific refraction at $n = 1$ gives

$$\frac{(n^2-1)}{(n^2+2)} \approx \frac{2}{3}(n-1). \tag{8}$$

By use of this approximation, Eq. (7a) can then be approximated by

$$n = 1 + \frac{N_A \alpha}{2M}\rho. \tag{9}$$

Eq. (9) proves the linear dependence of the refractive index on the mass density when the mass density $\ll 1$. From a physical perspective, Eq. (9) stems from the fact that the dipoles in dilute systems with the mass density $\ll 1$ are too far apart from one another to exert notable effects on the local electric field, i.e., the local electric field E_{loc} is equal to the applied field E (see Eq. (3)).

Obviously, the three different forms of the Lorentz–Lorenz relation are theoretically equivalent in describing the relationship refractive index, mass density, molecular polarizability and molecular weight, and should be equally capable in inferring one unknown quantity (e.g., refractive index) from the other three quantities (e.g., mass density, molecular polarizability, and molecular weight). Their difference lies primarily in practicality when not all the three necessary quantities are at disposal. The Lorentz–Lorenz relation in its various equivalent forms is more general than the linear relation, encompassing gases, liquids, and solids. The linear relation approximately holds for dilute systems where molecules are far apart from one another.

3. Self-consistent set of mixing rules for aerosol particles

3.1. Common mixing rules

Ambient aerosol particles are generally mixtures of different chemical constituents. A common approach to treating such inhomogeneous mixtures is the so-called effective medium theory whereby a mixture is considered a homogeneous material with the effective quantities that are calculated from some mixing rules (Heller, 1965; Ossenkopf, 1991). The commonly used mixing rule for calculating the effective mass density is the so-called volume-mixing rule whereby the effective mass density ρ_{me} is given by

$$\rho_{me} = \sum_i f_i \rho_{mi}, \tag{10}$$

where the summation is over all the constitutes of the mixture, and f_i and ρ_{mi} are the volume fraction and the partial mass density of the ith component of the mixture, respectively. The effective molecular weight M_e is just the apparent molecular weight of a mixture given by (Wallace & Hobbs, 2006)

$$\frac{1}{M_e} = \sum_i \frac{\phi_i}{M_i} = \left(\sum_i f_i \rho_{mi}\right)^{-1} \sum_i \frac{f_i \rho_{mi}}{M_i}, \tag{11}$$

where ϕ_i and M_i are the mass fraction and the partial molecular weight of the ith constitutes, respectively.

Unlike the calculation of effective molecular weight and effective mass density, several mixing rules have been proposed to calculate the effective refractive index, and there is little agreement on which one should be used. One of the mixing rules that has been commonly used in aerosol studies is the so-called linear volume average (or volume mixing rule hereafter for brevity) whereby the effective refractive index is simply the volume–mean refractive index given by

$$n_e = \sum_i f_i n_i, \tag{12}$$

where n_e and n_i are the effective refractive index and the partial refractive index of the ith component, respectively. This simple mixing rule has been widely used in studies of atmospheric aerosols by many researchers (e.g., Hand & Kreidenweis, 2002; Hanel, 1968; Hasan & Dzubay, 1983; Lowenthal, Watson, & Saxena, 2000; Ouimette & Flagan, 1982). The other common mixing rule is the so-called molar refraction-mixing rule whereby the molar refraction of a mixture is given by the linear average of the partial molar refraction of the individual components in the mixture weighted by their molar fraction

$$R_e = \sum_i x_i R_i, \tag{13}$$

where x_i is molar fraction (the fraction of the number of moles) of the ith component of the mixture. The molar fraction mixing rule was popularized in the aerosol community thanks to Stelson and Seinfeld (1982), Stelson (1990), Tang (1996), and Tang and Munkelwitz (1994). Note that unlike the volume-mixing rules and the Lorentz–Lorenz mixing rule introduced below, which only require the partial refractive indices to calculate the effective refractive index, estimation of the effective refractive index from the molar fraction mixing rule requires knowing mass density of each component and the effective mass density in addition to the partial refractive index.

The third mixing rule is the so-called Lorentz–Lorenz mixing rule given by (Heller, 1965)

$$r_e = \sum_i f_i r_i, \tag{14}$$

where r_e and r_i are the effective specific refraction and the partial specific refraction for the ith component of the mixture, respectively. The Lorentz–Lorenz mixing rule does not appears to be used as often as the other two in the aerosol community, although the Lorentz–Lorenz mixing is equally popular in other disciplines, and as will be shown next, it is equivalent to the molar refraction mixing rule and requires the same input as that required by the volume-mixing rule.

3.2. Self-consistency, additivity principles, and Lorentz–Lorenz mixture

The traditional effective medium theory, or the corresponding mixing rules, has dealt largely with a single quantity such as refractive index or mass density. However, according to the discussion in Section 2, mass density and refractive index, along with molecular weight and molecular polarizability, are closely connected to each other through the Lorentz–Lorenz relation. Therefore, all these quantities should be considered together in an effective medium theory, and the mixing rules for calculating the various effective quantities should be consistent with the Lorentz–Lorenz relation.

Despite the need for studying self-consistency, to the best of our knowledge, no mixing rules have been developed specifically for calculating the effective polarizability. Careful inspection of Eq. (1) reveals a major assumption underlying the Lorentz–Lorenz relation for pure materials discussed in Section 2.2: All the molecules of the material share the same molecular polarizability, which is equal to the average of all the molecules, i.e., the total polarizability divided by the total number of molecules. Extending this assumption to a multicomponent mixture, we obtain the mixing rule for calculating the effective polarizability from the partial polarizabilities of all the components,

$$\alpha_e = \frac{\sum_i N_i \alpha_i}{N} = \frac{\sum_i y_i N_\mathrm{A} \alpha_i}{y N_\mathrm{A}} = \sum_i x_i \alpha_i = \left(\sum_i \frac{f_i \rho_{mi}}{M_i}\right)^{-1} \sum_i \frac{f_i \rho_{mi}}{M_i} \alpha_i, \tag{15}$$

where α_e and α_i are the polarizabilities for the effective medium and the ith component of the mixture, respectively; y and y_i are the number of moles of the mixture and the ith component, respectively; x_i is mole fraction of the ith component of the mixture.

Eq. (15) deserves special emphasis because it presents another way to express the molar fraction mixing rule for calculating effective refractive index. According to Eq. (7c), which states that the molar refraction is equal to the molar polarization, Eq. (15) is equivalent to the molar fraction mixing rule given by Eq. (14). In other words, the commonly used molar fraction mixing rule for calculating refractive index in fact can be derived from the mixing rule for calculating the effective molecular polarizability.

With the mixing rules for all the quantities we are in a position to examine the issue of self-consistency. It is easily shown (see Appendix A) that if the effective refractive index, effective density, effective polarizability, and effective molecular weight are calculated from the corresponding mixing rules given by Eqs. (13), (10), (15), and (11), respectively, these effective quantities of the mixture satisfy the same Lorentz–Lorenz relation, i.e.,

$$r_e = \frac{n_e - 1}{n_e + 2} = \frac{N_{\mathrm{A}}\alpha_e}{3M_e}\rho_{me}. \tag{16}$$

The above analysis can also be understood in a different but equivalent way: if the effective density, effective polarizability, and effective molecular weight are calculated from the corresponding mixing rules given by Eqs. (10), (15), and (11) and the Lorentz–Lorenz relation holds for the effective medium, the effective refractive index is determined by the Lorentz–Lorenz mixing rule. To summarize, the set of the four mixing rules as given by Eqs. (13), (10), (15), and (11), along with the Lorentz–Lorenz relation, provides a self-consistent way to quantify the effective properties of the mixture. For convenience, the multicomponent mixture that satisfies these equations is defined as the Lorentz–Lorenz mixture.

The mathematical equations that describe the Lorentz–Lorenz mixture can be further distilled into some fundamental physical principles. Briefly, the volume mixing rule for calculating effective mass density derives from the additivity and conservation of the masses and volumes of the mixture (mass and volume additivity hereafter); the mixing rule for calculating effective molecular weight derives from the additivity and conservation of the number of moles or molecules (mole additivity hereafter); the molar-refraction mixing rule for calculating the effective refractive index derives from the additivity and conservation of the molecular polarizabilities of the different molecules in the mixture (polarizability additivity hereafter) and the Lorentz–Lorenz relation; the Lorentz–Lorenz mixing rule for calculating effective refractive index derives from the four principles of additivities of mass, volume, mole, and molecular polarizability, along with those underlying the Lorentz–Lorenz relation. These results suggest that from the physical point of view, for a Lorentz–Lorenz mixture, not only the masses, volumes, moles and molecular polarizabilities of the molecules composed of the mixture are additive or conserved during the process of formation of the mixture, but also they satisfy the Lorentz–Lorenz relation (see Appendix A for derivation). Because the additive properties are often associated with ideal mixtures and the Lorentz–Lorenz relation requires the Lorentz local electric field, the Lorentz–Lorenz mixture can be consider as the ideal mixture with the Lorentz local field.

3.3. Implications for the linear volume mixing rule for effective refractive index

As shown in Section 2, the nonlinear Lorentz–Lorenz relation becomes linear for dilute mixtures with mass density $\ll 1$. For such dilute mixtures, it is easy to show that the linear volume mixing rule for calculating the effective refractive index and the mixing rules for calculating effective mass density, molecular weight, and molecular polarizability forms a self-consistent set of the mixing rules. In fact, it can be shown as follows that the linear volume mixing rule for calculating effective refractive index is applicable to a more general class that only requires that the refractive indices of all the components have values close to each other (such materials is hereafter named as quasi-homogeneous mixture).

Without loss of generality, assume that the refractive indices of all the components of a quasi-homogeneous material—hence the effective refractive index as well—are close to a common value n_0. A Taylor expansion of the specific refraction around n_0 yields

$$r \equiv \frac{(n^2 - 1)}{(n^2 + 2)} \approx \frac{(n_0^2 - 1)(n_0^2 + 2) - 6n_0^2}{(n_0^2 + 2)^2} + \frac{6n_0}{(n_0^2 + 2)^2}n. \tag{17}$$

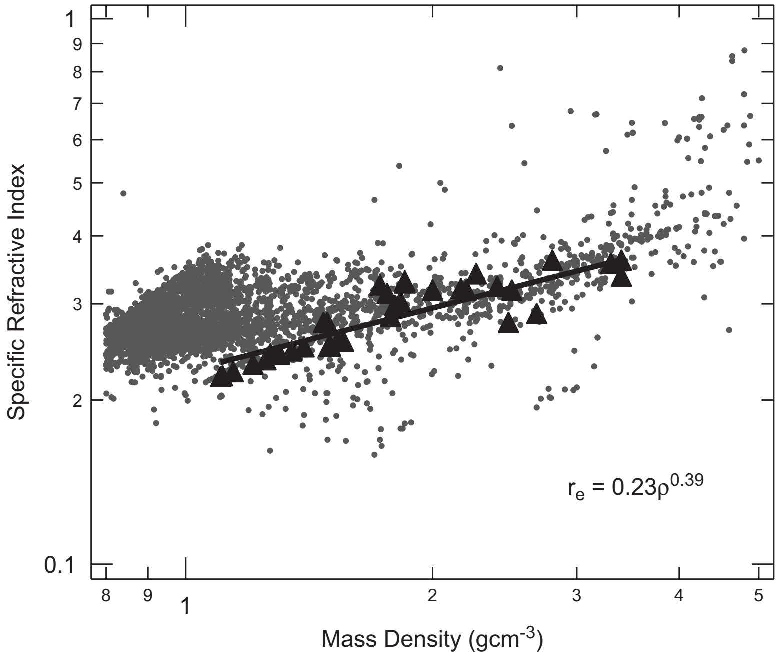

Fig. 3. Dependence of the effective refractive index on the effective mass density for aerosol particles (big black triangles). The aerosol data are from Hanel (1968), Tang and Munkelwitz (1994), Tang (1996), Hand and Kreidenweis (2002), and Guyon et al. (2003). Also shown as comparison are the data for pure materials for the mass density ranging from 0.8 to 5 g cm^{-3} (small grey dots).

Applying Eq. (17) to the effective specific refractive index and the corresponding partial specific refractive indices of all the components of the mixture and then substituting the results into the Lorentz–Lorenz mixing rule described by Eq. (13), we obtain the linear mixing rule given by Eq. (12).

The above derivation implies that the commonly used volume–mean mixing rule for calculating refractive index works only for quasi-homogeneous mixture where refractive indices of each component are similar. A mixture of dilute gases such as the air is a special quasi-homogeneous mixture with $n_0 = 1$.

It is noteworthy that in aerosol research, probably the two most commonly used mixing rules are the volume-mixing rule and the molar refraction mixing rule. According to the preceding analyses, the latter is evidently better than the former. However, the molar refraction mixing rule requires information on the mass density in addition to the partial refractive indices of the chemical components required by the volume-mixing rule, and the additional information is not always available. Lack of information on the mass density has been a reason for using the volume-mixing rule to calculate effective refractive index (review 2 comment). According to this work, when the information on mass density is not available, the Lorentz–Lorenz mixing rule should be used in general instead of the volume-mixing rule, which only approximates the Lorentz–Lorenz mixing rule for quasi-homogenous mixtures.

3.4. *Empirical expression for ambient aerosols*

The above theoretical analysis reveals that the effective refractive index of a mixture is related to the effective mass density by the Lorentz–Lorenz relation given by Eq. (16), and its precise quantification requires information on the effective molecular weight and effective polarizability in addition to the effective mass density. However, such complete data are not often available for aerosol particles. It is thus desirable to empirically examine the relationship of the effective refractive index to the effective mass density of aerosol particles to see if a practical approximation is possible. For this purpose, Fig. 3 displays the data that we have collected on aerosol particles or their major components, along with the data for pure materials within the mass density ranging from 0.8 to 5 g cm^{-3} as a reference. Evidently, similar to pure materials (small grey dots), aerosol particles (big black triangles) have a positively correlated relationship

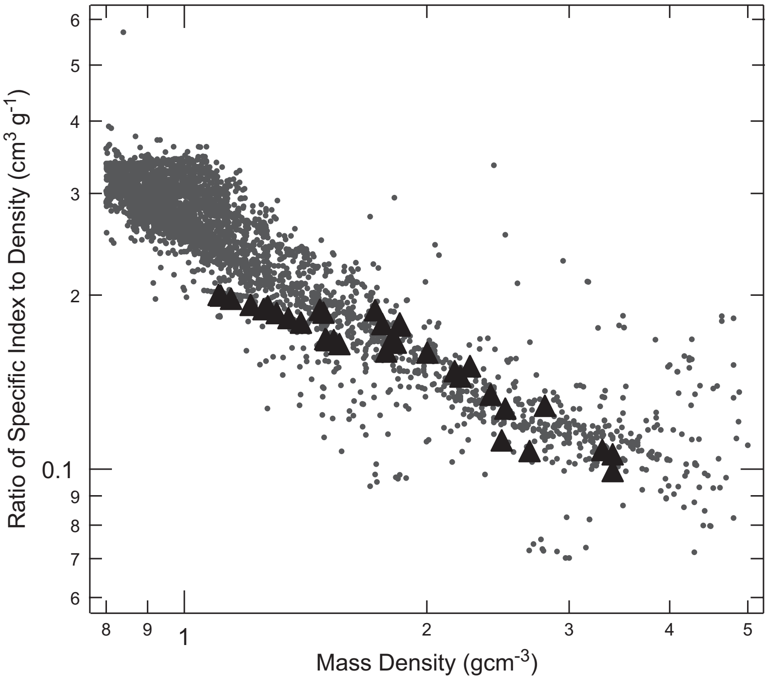

Fig. 4. Same as Fig. 3, except that it shows the dependence of the ratio of specific refractive index to mass density on mass density.

between the effective refractive index and effective mass density that can be well described by (black line)

$$r_e = \frac{n_e - 1}{n_e + 2} = 0.23\rho_{me}^{0.39}. \tag{18}$$

It is interesting to note that the aerosol data appear less "noisy" than those for pure materials. One on hand, the less scatter may be real because not all the pure chemicals belong to ambient aerosols. On the other hand, simultaneous measurements of effective refractive index and mass density have been very limited and rarely reported in aerosol literature (Guyon et al., 2003; Hand & Kreidenweis, 2002; Hanel, 1968; Tang, 1996; Tang & Munkelwitz, 1994). The less scatter may arise from the insufficient statistics as well.

The other noteworthy point is that the power exponent of 0.39 is less than 1, indicating from the Lorentz–Lorenz relation that the ratio of effective polarizability to effective molecular weight is a decreasing function of the mass density. The Lorentz–Lorenz equation as described by Eq. (7b) further indicates that the ratio of molecular polarizability to molecular weight is proportional to the ratio of specific refractive index to mass density. Therefore, the dependence of the ratio of molecular polarizability to molecular weight on mass density can be examined by plotting the ratio of specific index to mass density against the mass density (Fig. 4). It is evident from Fig. 4 that the ratio of the effective polarizability to the effective molecular weight decreases with increasing mass density for both aerosol particles and pure materials with the properties of similar ranges.

4. Concluding remarks

About 4000 pairs of published data on refractive index and mass density for pure materials (e.g., organics, inorganics, and minerals) and a few measurements for inhomogeneous mixtures including aerosols are compiled and first used to empirically examine the relationship between refractive index and mass density, which substantiates the general trend of refractive index and mass density increasing together. The Lorentz–Lorenz relation, which was originally developed to relate dielectric constant and refractive index to the molecular polarizability of a pure material, is then introduced to provide theoretical understanding and quantification of the relationship between refractive index and mass density for pure materials. The Lorentz–Lorenz relation reveals that refractive index in general depends on molecular weight and molecular polarizability as well as mass density. Nonetheless, the observational fact of refractive index and mass density generally increasing together suggests that the effect of the mass density on refractive index is dominant. This is physically understandable according to molecular optics because the refractive index results from the collective response of electric dipoles excited by the external applied field and the number of dipoles in a given volume is closely related to the mass density (Lagendijk, Nienhuis, van Tiggelen, & de Vries, 1997). The intimate relationship between the refractive index and mass density is also well reflected by the nickname of refractive index, optical density.

To seek application of the Lorentz–Lorenz relation to multicomponent mixtures like ambient aerosols, commonly used mixing rules for calculating effective refractive index, effective mass density, effective molecular weight and effective molecular polarizability are reviewed, and rigorously examined in the context of their consistency with the corresponding relationship between refractive index and mass density. It is shown that not only the Lorentz–Lorenz relation describes the relationship among these effective properties for the Lorentz–Lorenz mixture, but also the commonly used volume–mean mixing rule for calculating the effective mass density, the Lorentz–Lorenz mixing rule and the molar refraction mixing rule for calculating effective refractive index form a set of mixing rules that are consistent with the Lorentz–Lorenz relation. The theoretical analysis also reveals the connections among the linear volume mixing rule, Lorentz–Lorenz mixing rule, and molar fraction mixing rule for calculating effective refractive index. In calculation of the effective refractive index, the Lorentz–Lorenz mixing rule and the molar refraction mixing rule are physically equivalent and more general than the linear volume-mixing rule while the linear volume mixing rule is only an approximation of the Lorentz–Lorenz mixing rule when the refractive indices of individual components of the mixture are close to one another (or for quasi-homogeneous mixture).

An empirical power-law expression is obtained from the published data that relates the effective specific refractive index to the effective mass density of aerosol particles. The relationship is further examined in the context of the dependence of the ratio of molecular polarizability to molecular weight on the mass density. It is shown that this ratio generally decreases with increasing mass density, leading to a sublinear (the power-exponent < 1) dependence of the specific refractive index on the mass density. However, the data are very limited and more research is needed to substantiate this finding.

The results also point to several directions for future research. First, the result indicates that not only are refractive index and mass density related to each other, but also their relationship is pivotal for choosing the appropriate mixing rule for calculating effective refractive index of aerosol particles. For example, the self-consistent set of mixing rules discussed in this paper applies to the Lorentz–Lorenz mixture that satisfies the Lorentz–Lorenz relation and the four additivity principles of mass, volume, mole, and polarizability. If any of these conditions is violated, corresponding changes in mixing rules are necessary. For example, it is well known that the Lorentz–Lorenz relation holds when the host medium has refractive index of one. For a different host medium, the Lorentz–Lorenz relation changes, and the rule for calculating effective refractive index should change accordingly (Aspnes, 1982). Similar changes are necessary when the local electric field deviates from the Lorentz field due to, for example, the overlap field (Anderson & Schreiber, 1965). To answer the question as to whether or not ambient aerosols belong to the Lorentz–Lorenz mixture, concurrent measurements of the effective refractive index, mass density of ambient aerosol particles, and chemical compositions, along with information on molecular polarizability and molecular weight, are needed to validate the Lorentz–Lorenz relation and the set of mixing rules. The same data are also needed to examine how well the linear volume-mixing rule approximates the Lorentz–Lorenz mixing rule in calculation of effective refractive index. Unfortunately, such data are extremely limited to date. The single particle technique like that discussed by Moffet and Prather (2005) holds promise in this aspect. Second, a single value of refractive index is often assigned to aerosol particles regardless of their size. However, many studies have shown that some aerosol particles such as combustion aggregates often assume open, fractal-like structures with effective mass density depending on particle sizes (Olfert, Symonds, & Collings, 2007; Sorensen, 2001; Zelenyuk, Cai, Chieffo, & Imre, 2005). Mass densities of solid hydrometeors (e.g., snowflake, graupels and hailstone) are also found to depend on particle sizes (Pruppacher & Klett, 1997). The inherent dependence of refractive index on mass density discussed in this paper suggests that the effective refractive index of these particles should be size dependent as well. Third, refractive index and mass density are the major concerns of this paper because of their importance in determining the direct aerosol effect on climate. According to the discussion, molecular weight and polarizability are also needed to get deeper understanding of aerosol particles. The intensive research that has been performed to investigate the molecular polarizability in other fields may be useful for aerosol research in the future. Fourth, although this study is concerned mainly with the real part of the complex refractive index, the Lorentz–Lorenz relation, and various mixing rules are expected to hold for the complex refractive index. However, it is not clear to us how strong the dependence of the imaginary part (absorbing property) on the mass density is. This issue deserves special attention in view of the importance of the mixing state of absorbing aerosols in evaluating aerosol effects on climate (Ramanathan & Carmichae, 2008). Finally, aerosol properties other than mass density and refractive index are also important. For example, aerosol hygroscopicity is crucial for evaluating the ability of aerosol particles being activated into cloud droplets. The same guiding principle of self-consistency should be applied to develop the mixing rule for estimating the effective hygroscopicity.

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Appendix A. Relationship of mixing rules to additivity principles

Mass additivity states that the total mass of a mixture equals to the sum of all the components:

$$m = \sum_i m_i = \sum_i V_i \rho_{mi}. \tag{A.1}$$

Volume additivity states that the total mass of the mixture equals to the sum of all the components:

$$V = \sum_i V_i. \tag{A.2}$$

Dividing Eq. (A.1) by Eq. (A.2) yields the volume mixing rule to calculate the effective mass density

$$\rho_{me} = \frac{m}{V} = \frac{\sum_i V_i \rho_{mi}}{V} = \sum_i f_i \rho_{mi}. \tag{A.3}$$

Mole Additivity states that the total number of moles (y) equals to the sum of moles of each component (y_i):

$$y = \sum_i y_i. \tag{A.4}$$

The total mass of the mixture can also be given by

$$m = \sum_i m_i = \sum_i y_i M_i. \tag{A.5}$$

The effective molecular weight of the mixture is given by

$$M_e = \frac{m}{y} = \sum_i \frac{y_i}{y} M_i = \sum_i x_i M_i. \tag{A.6}$$

Using the relationship between the mole fraction, mass fraction, and volume fraction given by

$$f_i = \frac{\rho_e}{\rho_i}\phi_i = \frac{\rho_e M_i}{\rho_i M_e} x_i, \tag{A.7}$$

we can show that Eq. (A.6) is equivalent to Eq. (11).

Polarizability additivity states that the total of polarizability (polarization) of a mixture equals to the sum of the molecular polarizability of each component:

$$P = N\alpha_e = \sum_i N_i \alpha_i. \tag{A.8}$$

Table A1
Self-consistent mixing rules in terms of volume, mass, and mole fractions

Effective variables	Volume fraction f_i	Mass fraction ϕ_i	Mole fraction x_i
Molecular weight	$\frac{1}{M_e} = \frac{1}{\rho_e}\sum_i \frac{\rho_i f_i}{M_i}$	$\frac{1}{M_e} = \sum_i \frac{\phi_i}{M_i}$	$M_e = \sum_i x_i M_i$
Density	$\rho_{me} = \sum_i f_i \rho_{mi}$	$\frac{1}{\rho_{me}} = \sum_i \frac{\phi_i}{\rho_{mi}}$	$\frac{1}{\rho_{me}} = \frac{1}{M_e}\sum_i \frac{M_i x_i}{\rho_{mi}}$
Polarizability	$\alpha_e = \left(\frac{f_i \rho_{mi} \alpha_i}{M_i}\right)^{-1} \sum_i \frac{f_i \rho_{mi} \alpha_i}{M_i}$	$\alpha_e = \left(\sum_i \frac{\phi_i}{M_i}\right)^{-1} \sum_i \frac{\phi_i \alpha_i}{M_i}$	$\alpha_e = \sum_i x_i \alpha_i$
Specific refraction	$r_e = \sum_{i=1} f_i r_i$	$r_e = \left(\sum_{i=1} \frac{\phi_i}{\rho_{mi}}\right)^{-1} \sum_{i=1} \frac{\phi_i}{\rho_{mi}} r_i$	$r_e = \left(\sum_i \frac{x_i M_i}{\rho_{mi}}\right)^{-1} \sum_i \frac{x_i M_i}{\rho_{mi}} r_i$
Molar refraction	$R_e = \frac{M_e}{\rho_e}\sum_i \frac{f_i \rho_{mi}}{M_i} R_i$	$R_e = M_e \sum_i \frac{\phi_i}{M_i} R_i$	$R_e = \sum_{i=1}^{N} x_i R_i$

Therefore,

$$\alpha_e = \sum_i \frac{N_i}{N}\alpha_i = \sum_i \frac{y_i N_{\mathrm{A}}}{y N_{\mathrm{A}}}\alpha_i = \sum_i x_i \alpha_i. \tag{A.9}$$

Combination of Eq. (A.9) with Eq. (7b) leads to the molar refraction mixing rule for calculating effective refractive index,

$$R_e = \frac{N_{\mathrm{A}}\alpha_e}{3} = \frac{N_{\mathrm{A}}}{3}\sum x_i \alpha_i = \sum x_i R_i. \tag{A.10}$$

Assuming that the effective refractive index is n_e and it is related to the other effective quantities calculated from the above equations by the Lorentz–Lorenz equation, we obtain the Lorentz–Lorenz mixing rule such that

$$\frac{n_e - 1}{n_e + 2} = \frac{N_{\mathrm{A}}\alpha_e}{3M_e}\rho_{me} = \sum_i f_i \frac{n_i - 1}{n_i + 2}. \tag{A.11}$$

In other words, because the middle term in Eq. (11) equals to that on the right-hand side, the effective refractive index calculated from the Lorentz–Lorenz mixing rule satisfies the Lorentz–Lorenz relation.

In aerosol research, the volume, mass and molar concentrations are measured in different studies. It is therefore desirable to formulate the effective medium equations in terms of the mass fraction ϕ_i and the mole fraction x_i in addition to the volume fraction f_i. For convenience, the set of self-consistent mixing rules expressed in all the three fractions are summarized in Table A1.

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