Second-law limitations on particle size distribution functions

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The size distribution of particles in dispersions is an important property that is usually measured. In many cases, however, theoretical or semi-empirical models are developed to predict these distributions. The models, none the less, come with subtle constraints that limit the régimes of their applicability. At present, there is no systematic approach for identifying these limitations, which, if ignored, can lead to serious flaws. In this work we introduce an entropy-related property of the dispersion, and demonstrate that this property, which is intensive, and, therefore, independent of system size and configuration, can be used to pinpoint where these limitations lie.

1. Introduction

Particle size distributions have long been used to characterize dispersion systems. In some cases, the size distributions vary with time, as in continual coagulation or fragmentation, whereas in many others, they maintain a steady state.

For reasons that these distributions are crucial to industrial applications and academic research, a vast number of theoretical and experimental works focusing on explaining and predicting their forms (and evolution, in the case of time-dependent systems) have been generated over the years. Also, the fact that size distributions can be measured fairly accurately and easily has helped investigators put to test many of the proposed theories. Consequently, some major contributions in the area of predicting particle size distribution functions in dispersions have arisen. These include, to name just a few, the Rosin–Rammler distribution in crushing (Rosin & Rammler 1934), Smoluchowski's distribution for the binary coagulation process, and Friedlander's self-preserving distribution (Friedlander & Wang 1966), which extends Smoluchowski's theory to long-time limits when the average particle sizes become large.

Having mentioned some of the well-known distributions found in common day-to-day physical processes, the existence of many others, namely the Poisson, normal, log-normal, beta, etc., must not be overlooked. These, however, are more general and mathematical in nature, and are useful because their forms can be made to fit relevant data by way of empirical adjustments.

Therefore, many choices of distribution functions are available for representing particle sizes. What these, and most others not listed here, have in common is that they all contain certain superficial qualities. For instance, the range of particle sizes for the Rosin–Rammler distribution covers from zero to infinity, and this is certainly not realistic.

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Furthermore, there are severe limitations on the ranges of validity of many of these distributions. For example, Smoluchowski's theory of coagulation by binary collisions, beginning with a fully dispersed initial condition, retains its validity up to short times. After this, Friedlander's self-preserving distribution, which is applicable only after a certain 'large average particle size' is reached, takes over. However, exactly what this 'large average particle size' represents cannot be established from the derivation of the asymptotic theory. Thus, a systematic way, based on some well-accepted principle(s), is needed to identify such régimes quantitatively and accurately. Presenting such an approach, and demonstrating its potential applications in evaluating particle size distributions in dispersions, is the primary objective of this work.

2. Problem formulation

As mentioned above, this work is aimed at introducing an approach that would enable one to accurately identify the limits of validity of particle size distribution functions. In the interest of space, we shall, for illustrative purposes, refer to only a few examples of well-known size distributions. Narrowing this work down to these does not limit the applicability of the proposed method. Rather, the approach is general, and, therefore, remains useful for exploring the limitations of almost any size distribution function of interest.

To begin, we consider a dispersion in which the particles are clusters consisting of elementary particles. The number of these particles in a cluster shall represent the cluster size, i. Hence, a dispersion comprising a number of clusters of different sizes is subject to the following constraints

$$N_0 = \sum_i iN_i, \tag{1}$$

$$N = \sum_i N_i, \tag{2}$$

where N_i is the number of clusters of size i, N is the total number of clusters, and N_0 is the total number of elementary particles. In a closed system, therefore, N_0 remains constant, while N and N_i may or may not vary with time.

For convenience, we define the dimensionless quantities

$$\tilde{N} \equiv N/N_0 \quad \text{and} \quad \tilde{N}_i \equiv N_i/N_0 \tag{3a, b}$$

to represent the number ratios. Note that $1/\tilde{N}$ is also the average cluster size, i_{ave}. Hence, equations (1) and (2), respectively, can be written as

$$\sum_i i\tilde{N}_i = 1 \tag{4}$$

and

$$\sum_i \tilde{N}_i = \tilde{N} = 1/i_{\mathrm{ave}}. \tag{5}$$

Finally, if we define the degeneracy, $\Omega(N_1, N_2, N_3, \ldots)$, to signify the number of ways a dispersion containing N_0 primary particles can be arranged to consist of N_1 clusters of $i = 1$, N_2 clusters of $i = 2$, N_3 clusters of $i = 3$, and so on, then (Cohen 1991)

$$\Omega(N_1, N_2, N_3, \ldots) = N_0!/\prod_i N_i![i!]^{N_i}. \tag{6}$$

Using equations (1)–(5), and noting that typical cases involve moderate to very large N_i and N_0, the above can be rearranged as

$$\frac{\ln(\Omega)}{N_0} = (1-\tilde{N})[\ln(N_0)-1] - \sum_i \tilde{N}_i \ln(\tilde{N}_i) - \sum_i \tilde{N}_i \ln(i!) \tag{7}$$

upon incorporating Stirling's approximation for $\ln(N_i!)$ and $\ln(N_0!)$, i.e. $\ln(x!) \approx x\ln(x) - x$ for moderate to large x. This, of course, can raise questions concerning the applicability of equation (7) to very wide distributions because, in some of these cases, the moderate to very large-N_i criterion necessary for Stirling's approximation to hold may be violated. Therefore, for what follows hereafter, we shall consider only situations for which equation (7) is suitable, which means that for all i, N_i ranges from moderate to very large.

With the above in mind, we now introduce a property, σ, of the dispersion, and define it as

$$\sigma \equiv \ln(\Omega)/N_0 - (1-\tilde{N})[\ln(N_0)-1]. \tag{8}$$

Based on this, equation (7) becomes

$$\sigma = -\sum_i \tilde{N}_i \ln(\tilde{N}_i) - \sum_i \tilde{N}_i \ln(i!). \tag{9}$$

This property possesses two important qualities. First, it is related to the entropy of the distribution since $\ln(\Omega)$ is directly proportional to the statistical definition of entropy. Second, it is an *intensive* property of the system because $\tilde{N}_i$, which is the governing parameter in equation (9), is a number *ratio* (as defined in equation (3*b*)), and, therefore, it is independent of system size. To prove this, if we let $\forall$ be the volume of the system, then dividing numerator and denominator of equation (3*b*) by $\forall$ makes $\tilde{N}_i$, and subsequently σ, dependent only on concentrations, which themselves are intensive properties. The significance of σ being intensive is that equation (9) becomes applicable to the particle size distribution function of any system, regardless of its volume or configuration.

Next, with the aid of Lagrange multipliers we extremize σ while subjecting it to the constraints of equations (4) and (5). This is written as

$$\frac{\partial}{\partial \tilde{N}_i}\left[\sigma + \lambda_1 \sum_i i\tilde{N}_i + \lambda_2 \sum_i \tilde{N}_i\right] = 0, \tag{10}$$

where λ_1 and λ_2 are the Lagrange multipliers. Inserting equation (9) into the above, differentiating with respect to $\tilde{N}_i$, and evaluating λ_1 and λ_2 using equations (4) and (5), we find that σ is maximized when

$$\tilde{N}_i = \exp(-\mu)\,\mu^{i-1}/i!, \tag{11a}$$

where μ is related to $\tilde{N}$, or the average cluster size, $i_{\text{ave}}(i_{\text{ave}} = 1/\tilde{N})$, through

$$\tilde{N} = (1-e^{-\mu})/\mu. \tag{11b}$$

To avoid any unnecessary repetition, much of the derivation leading to equation (11*a*, *b*) has been left out of here because the steps are very similar to those in Cohen (1991). Of importance, however, is that upon inserting equation (11*a*) into equation (9), and utilizing equations (4), (5), and (11*b*), we obtain the maximum possible value that σ can attain. This shall be denoted by $\sigma_{\max}$. Further manipulation yields the following

$$\sigma_{\max} = \tilde{N}\ln[(e^{\mu}-1)/\tilde{N}] - \ln\mu, \tag{12}$$

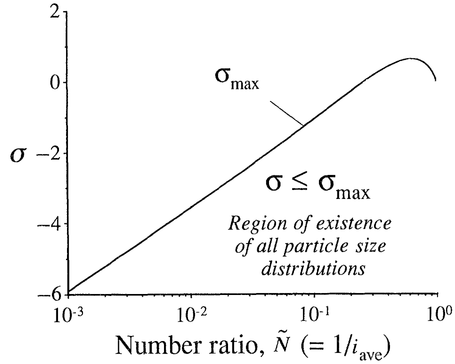

Figure 1. Equation (12) plotted as σ_{max} against $\tilde{N}$. No size distribution function, theoretical or experimental, can exist above the curve.

whose behaviour is depicted in Figure 1. It is also necessary to note that since equation (11a) is the Poisson distribution (multiplied by a factor of μ^{-1}), then σ is maximized when the size distribution, $\tilde{N}_i$, is formed entirely by random behaviour.

A crucial implication arising from this is that, for all $\tilde{N}$ ranging between $0 < \tilde{N} \leqslant 1$ (or $\infty > i_{ave} \geqslant 1$), virtually no particle size distribution can acquire a value of σ greater than σ_{max}. By this reasoning, therefore, if we introduce the differential $\Delta\sigma$ as

$$\Delta\sigma \equiv \sigma_{max} - \sigma, \tag{13}$$

we get the inequality

$$\Delta\sigma \geqslant 0. \tag{14}$$

Simply stated, equation (14) is the second law (of thermodynamics) applied to particle size distributions. Consequently, if a size distribution function is proposed that acquires a value of $\Delta\sigma < 0$ at some $\tilde{N}$, then it simply violates the second law, and, hence, cannot exist at that specific $\tilde{N}$. Examples of such violations are presented next.

3. Applications of the inequality $\Delta\sigma \geqslant 0$ to some physical situations

Upon substituting equations (9), (12), and (13) into (14), we obtain

$$\Delta\sigma = \tilde{N}\ln\left[\frac{e^{\mu}-1}{\tilde{N}}\right] - \ln(\mu) + \sum_i \tilde{N}_i \ln(\tilde{N}_i) + \sum_i \tilde{N}_i \ln(i!) \geqslant 0. \tag{15}$$

Therefore, if $\tilde{N}_i$ is provided for a dispersion, $\tilde{N}$ and μ can then be evaluated from equations (5) and (11b), respectively, after which $\Delta\sigma$ can be computed using equation (15).

It is important to note that because σ is an intensive property, the inequality imposed by equation (15) is general, and, consequently, it can be used to assess the limitations of almost any proposed particle size distribution function. In the interest of space, however, we shall restrict this work to distributions arising from some well-known physical phenomena, namely those described by Smoluchowski, and Friedlander & Wang (1966), and Brown (1989), where the latter was introduced relatively recently to model fragmentation processes. In addition to these, equation (15) shall also be used to examine some experimental cluster size distributions measured in continuous flow.

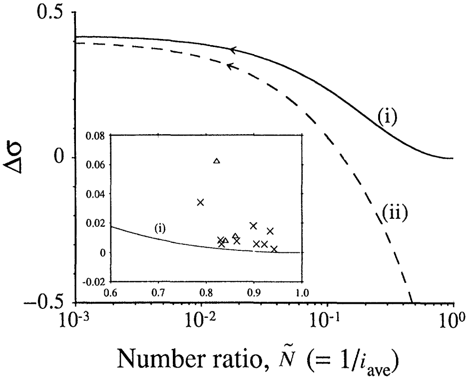

Figure 2. $\Delta\sigma$ against $\tilde{N}$, illustrating the paths of two time-dependent distributions. Curve (i) belongs to Smoluchowski's coagulation equation (equation (16)), which is valid for initial times when $\tilde{N} \approx 1$. Curve (ii) is Friedlander's self-preserving distribution (equation (18)) applicable to later times when $\tilde{N} \ll 1$. The arrows mark the direction of the coagulation process. Inset shows the data of Chen *et al.* (1991) (crosses) and Graham & Bird (1984) (triangles), collected from their continuous flow systems.

(*a*) *Application to Smoluchowski's theory of coagulation by binary collisions*

Following the nomenclature adopted here, the result of Smoluchowski's theory of coagulation by binary collisions at initial times can be summarized as

$$\tilde{N}_i = \tilde{N}^2[1-\tilde{N}]^{i-1}. \tag{16}$$

In equation (16), $\tilde{N}$ is related to time, t, through the expression

$$\tilde{N} = 1/(1+t/t_c), \tag{17a}$$

where t_c is the coagulation time, which, for a brownian process, is given by

$$t_c = 3\hat{\mu}/4\kappa T c_0. \tag{17b}$$

In the above, κ is Boltzmann's constant, T is the absolute temperature, $\hat{\mu}$ is the viscosity of the continuous phase, and c_0 is the primary particle concentration, equal to $N_0/\forall$.

Substituting equation (16) into (15), utilizing the relation between μ and $\tilde{N}$ in equation (11*b*), and finally (numerically) computing $\Delta\sigma$, yields curve (i) in figure 2. Curve (ii) and the data points, also appearing in this figure, shall be discussed shortly.

Beginning at $t = 0$ when $\tilde{N} = 1$ (by equation (17*a*)), which denotes the fully dispersed initial condition, the path of equation (16) follows curve (i) from right to left in the $\Delta\sigma$–$\tilde{N}$ plane. Evidently, the curve is at first asymptotic to the $\Delta\sigma = 0$-axis near $\tilde{N} = 1$, then deviates from it by slowly rising in the $\Delta\sigma > 0$ direction, to finally reach another asymptote when $\tilde{N}$ becomes small.

The asymptote to the ($\Delta\sigma = 0$)-axis near $\tilde{N} = 1$ results from the fact that, in this region, Smoluchowski's theory of coagulation by binary collisions is limited by stochastic behaviour. The reason for this is attributed to the homogeneity of the dispersion at the fully dispersed initial condition, when all particles are identical (Cohen 1992). Also, the fact that no portion of this curve lies in the $\Delta\sigma < 0$ half-plane indicates that equation (16) does not violate the second law anywhere. This is because the form of equation (16) enables it to adjust to any range of widths (in cluster size, i), from the infinitely narrow shape of the initial fully dispersed distribution ($\tilde{N} = 1$), to the very wide, as $\tilde{N}$ progressively becomes smaller. Thus, as we shall see shortly, it is the ability of a function to accommodate this variation of distribution widths, while simultaneously satisfying the constraints of equations (4) and (5), that determines whether it violates the second law or not.

(b) Application to the self-similar particle size distribution in brownian coagulation

We should mention that the relation between entropy and the self-similar distribution in brownian coagulation has been investigated earlier by Rosen (1984). Upon incorporating an expression analogous to the first summation appearing in our equation (9), Rosen demonstrated how the second law can be used (in the context of information theory) to obtain reasonable approximations for the self-similar distribution. Our scope, however, differs in that we intend to use the second-law principles, based exclusively on equation (9), to explore the limitations and behaviours of particle-size distribution functions, in general.

For the case of brownian coagulation at later times (or when average cluster sizes become large), we follow our notations and express Friedlander's self-preserving distribution as

$$\tilde{N}_i = \tilde{N}^2 \psi(\xi_i), \tag{18}$$

where

$$\xi_i \equiv i/i_{\text{ave}} = \tilde{N}i, \tag{19}$$

with $\psi(\xi_i)$ satisfying

$$\int_0^\infty \xi\psi(\xi)\,\mathrm{d}\xi = 1 \tag{20}$$

and

$$\int_0^\infty \psi(\xi)\,\mathrm{d}\xi = 1. \tag{21}$$

Equations (20) and (21), respectively, are the constraints of equations (4) and (5) presented in Friedlander's transformed coordinates.

Equation (18) suggests that the size distribution function, when the coagulation process has sufficiently developed, achieves a self-preserving status, dependent only on the size ratio, i/i_{ave}, or $\tilde{N}i$. The function $\psi(\xi_i)$, which has been calculated both numerically and asymptotically, is available in Friedlander & Wang (1966). Although the limit of applicability of equation (18) is known to be $\tilde{N} \ll 1$, its exact bounds remain to be identified.

To determine these bounds, we substitute equation (18) into (15). Before doing so, however, it is essential that the summations be expressed as integrals because the former equation is valid when the average cluster sizes are large. Hence, upon incorporating equations (18) and (19), and utilizing Stirling's approximation for $\ln(i!)$, the summations in equation (9) reduce to

$$\sum_i \tilde{N}_i \ln(\tilde{N}_i) + \sum_i \tilde{N}_i \ln(i!) = \tilde{N}[2\ln(\tilde{N}) + c_1] + c_2 - \ln(\tilde{N}) - 1, \tag{22}$$

where we have used equations (4), (5), (20), and (21), and applied the necessary transformations to convert the discrete sums to integrals. In the above

$$c_1 \equiv \int_0^\infty \psi \ln(\psi)\,\mathrm{d}\xi \approx -1.00 \quad \text{and} \quad c_2 \equiv \int_0^\infty \xi\psi \ln(\xi)\,\mathrm{d}\xi \approx 0.403, \qquad (23\,a, b)$$

both of which were calculated numerically from the information provided in Friedlander & Wang (1966).

Finally, substituting equation (22) into (15) and manipulating, we obtain $\Delta\sigma$ for the self-similar distribution of Friedlander. This turns out to be

$$\Delta\sigma = \tilde{N}\ln[\tilde{N}(e^{\mu}-1)] - \tilde{N} - \ln(\mu\tilde{N}) - 0.597. \tag{24}$$

With the relationship between μ and $\tilde{N}$ given by equation (11*b*), equation (24) is plotted as $\Delta\sigma$ versus $\tilde{N}$, and depicted by curve (ii) in figure 2. The direction of the process is, once again, from right to left, indicating coagulation.

Obviously, the régime of validity of the self-preserving distribution, based on this analysis, is between $0 < \tilde{N} \leqslant 0.133$, which is where the curve lies in the positive portion of the $\Delta\sigma$–$\tilde{N}$ plane. This is in contrast to the original work, and to all subsequent ones, that provide only a qualitative range of applicability for equation (18), that is $\tilde{N} \ll 1$. Also, the fact that curve (ii) crosses the $(\Delta\sigma = 0)$-axis at $\tilde{N} \approx 0.133$ indicates that at this particular value of $\tilde{N}$, the self-preserving coagulation mechanism comes closest to displaying random behaviour.

It is necessary now to explain why this violation occurs because it is for similar reasons that many proposed size distribution functions, theoretical and semi-empirical, fail to satisfy the second law at some range of $\tilde{N}$. To do so, we refer to equation (18) and recall that it expresses the particle size distribution at some time after the coagulation process has sufficiently progressed. A characteristic of this distribution function, which is portrayed graphically (and also tabulated) in Friedlander & Wang (1966), is that its range in ξ is infinite for any value of $\tilde{N}$. Thus, this function cannot be adjusted to simulate the infinitely narrow shape of the fully dispersed distribution at $t = 0$ (or $\tilde{N} = 1$), which is precisely why its applicability does not include $\tilde{N} = 1$ and its vicinity. In short, therefore, a size distribution function fails to satisfy the second-law principle at a certain $\tilde{N}$ if it cannot reproduce the necessary range of size width without violating the conservation constraints of equations (4) and (5) (or, in this case, equations (20) and (21)).

Regarding how the two curves approach one another in the small-$\tilde{N}$ limit, it appears to be asymptotic. This is testimony to Hidy's finding (Hidy 1965) that the two limiting theories of coagulation come together at a certain time (or $\tilde{N}$).

As to the transition time, in terms of dimensionless time, t/t_c, needed for Smoluchowski's solution to attain Friedlander's form, Hidy calculated a value of approximately 12 (Hidy 1965). Based on figure 2 of our work, however, $\tilde{N}$ is roughly on the order of 0.02, which, after implementing the relationship between $\tilde{N}$ and t/t_c in equation (17*a*), translates to $t/t_c \approx 50$. The discrepancy between our prediction and Hidy's, which is by a factor of about 4, can be attributed to the fact that curve (i) (based on equation (16)) does not incorporate the proper expression for the coagulation frequency when particles of different sizes collide. Hidy's numerical computations, however, do. This should also explain why the two lines in figure 2 are not closer to each other, as they ought to be, in the small-$\tilde{N}$ limit. Allowing for the proper coagulation frequency in our calculations would most probably narrow the gap between the two curves, thereby yielding better agreement between our transition time and Hidy's. None the less, the overall results point to another potential application of the method – to determine more systematically if two time-dependent size distribution functions do ultimately approach one another asymptotically, and if so, at approximately what $\tilde{N}$ (or time)?

(c) Application to some experimental size-distribution data in flowing systems

Of interest, also, is the application of this work to actual experimental data, especially to determine their location on the $\Delta\sigma$–$\tilde{N}$ plane. The inset in figure 2 displays the results of two unrelated experiments on continuous flow of suspensions of solid particles. The crosses belong to the sedimentation tests of Chen *et al.* (1991), and the triangles refer to the continuous shear flow experiments of Graham & Bird (1984).

We have selected these experiments specifically because the data were supplied in terms of $\tilde{N}_i$, thus eliminating the need for any empirical parameters at arriving at the values of $\Delta\sigma$. Obviously, judging from figure 2, all points lie in the positive portion of $\Delta\sigma$, further confirming the inequality relation of equation (15). In addition, the proximity of many of the points to the $(\Delta\sigma = 0)$-axis reflects the near-random behaviour of the experimental data, a matter that has been discussed in more detail in Cohen (1992).

(d) Application to particle size distributions arising from sequential fragmentation

Particles formed by crushing have, for some time, been known to follow the Rosin–Rammler distribution (Rosin & Rammler 1934). Recently, however, a more general distribution function suitable to sequential fragmentation was proposed (Brown 1989). This function, which has the flexibility to also represent the Rosin–Rammler, as well as many others, can be recast into

$$\tilde{N}_i = K\tilde{N}^2 f(\gamma, K\xi_i), \tag{25a}$$

where

$$f(\gamma, K\xi_i) = (K\xi_i)^\gamma \exp[-(K\xi_i)^{\gamma+1}/(\gamma+1)], \tag{25b}$$

upon utilizing our nomenclature. In the above, $\xi_i = \tilde{N}i$, as defined in equation (19), and K is given by

$$K = K(\gamma) \equiv (\gamma+1)^{1/(\gamma+1)}\,\Gamma((2+\gamma)/(1+\gamma)), \tag{26}$$

where $\Gamma(\alpha)$ is the complete gamma function. By adjusting the only empirical parameter, γ, in equation (25), good fits with sequential fragmentation data collected from a number of different physical processes, ranging from iron ground in ball mills to stellar masses, were obtained (Brown 1989). In such processes, γ lies between -1 and 0, where $\gamma \approx -1$ signifies very few sequential fragmentation events, and as the number of events increases, γ approaches 0.

Briefly, substituting equation (25*b*) into (25*a*), and the result into equation (15), yields

$$\Delta\sigma = \tilde{N}\ln(K\tilde{N}[e^\mu - 1]) + \tilde{N}c_3 - \ln(\mu K\tilde{N}) + c_4/K - 1 \tag{27}$$

for Brown's distribution. In the above, c_3 and c_4 represent

$$c_3 = c_3(\gamma) \equiv \int_0^\infty f\ln(f)\,\mathrm{d}(K\xi) \quad \text{and} \quad c_4 = c_4(\gamma) \equiv \int_0^\infty [K\xi] f\ln(K\xi)\,\mathrm{d}(K\xi) \tag{28a, b}$$

(with $f = f(\gamma, K\xi)$, coming from equation (25*b*)), both of which happen to be functions of the adjustable parameter, γ. Note the similarity between equations (27) and (24).

The parameters $K(\gamma)$, $c_3(\gamma)$, and $c_4(\gamma)$ were evaluated for several values of $\gamma \leqslant 0$ and substituted into equation (27), and the result is plotted in figure 3 as $\Delta\sigma$ against $\tilde{N}$. The integrals leading to $c_3(\gamma)$, and $c_4(\gamma)$ were computed numerically.

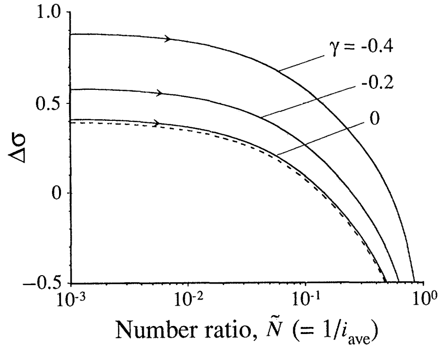

Figure 3. $\Delta\sigma$ against $\tilde{N}$, illustrating the regimes of validity of the size distribution function represented by equation (25). The arrows mark the direction of the sequential fragmentation process. The broken line, which is taken from figure 2, is the path of the self-preserving distribution in brownian coagulation.

Figure 3 shows that corresponding to any γ, there exists a unique curve that moves from left to right. This direction indicates fragmentation. Moreover, each curve is limited to a certain range of $\tilde{N}$, which can be extracted by simply considering the region $\Delta\sigma \geqslant 0$.

An immediate conclusion of this analysis is that as γ decreases, the maximum allowable $\tilde{N}$ approaches unity (i.e. i_{ave} becomes smaller). Thereby, functions characterized by smaller values of γ can accommodate narrower particle size distributions before they fail to exist (since the particle size distribution at $\tilde{N} = 1$ is infinitely narrow). Moreover, the fact that none of the solid lines in figure 3 crosses $\Delta\sigma = 0$ at $\tilde{N} = 1$ indicates that, according to equation (25), continuous fragmentation in a dispersion of clusters, at least for the range of γ considered here, does not guarantee a fully dispersed state at the end, even if the process carries on indefinitely (represented by the case $\gamma = 0$).

For comparison, figure 3 also includes the coagulation curve of Friedlander (broken line), as it appears in figure 2. Interestingly, a value of $\gamma = 0$ produces a good fit for all $\tilde{N}$ between the distributions of Brown & Friedlander. This implies that sequential fragmentation characterized by $\gamma = 0$ is entropically, and perhaps even microscopically, similar to the binary coagulation process, except that it moves in the opposite direction. This is not surprising because inserting $\gamma = 0$ into equations (25) and (26) yields

$$f(\xi) = \exp(-\xi), \tag{29}$$

which is identical to what has been obtained using the maximum entropy principle (Rosen 1984). Hence, for γ ranging between -1 and 0, the closest that equation (25) can get to mimicking the self-preserving distribution in brownian coagulation is when $\gamma = 0$.

4. Summary and conclusions

A number of distribution functions have, over the years, been proposed and applied to describe size distributions of particles and particle clusters in dispersions. What all of these have in common is that certain restrictions limit their régimes of validity. To date, these régimes, if provided at all, have been expressed only qualitatively. This is probably because, as far as we are aware, no systematic approach for determining them has been made available in related literature.

In this work, with the aid of a newly introduced property, a way to identify these limitations is proposed. Since this property is closely related to the entropy of the system, the approach then comes down to simply checking whether the function violates the second law of thermodynamics; and if it does, where does the violation occur?

Furthermore, by analysing the paths that time-dependent size distributions traverse on the $\Delta\sigma$–$\tilde{N}$ plane, one can ascertain if such distribution functions do approach one another asymptotically. To illustrate the notion, the two limiting size distribution functions arising from Smoluchowski's theory of coagulation were chosen as examples.

In conclusion, the use of the proposed method appears to be relatively simple and straightforward, as we have demonstrated here by applying it to a few well-known size distribution functions. The approach is none the less general, and can be used to find the limitations and test the validity of almost any particle size distribution function of interest (possibly except for very wide ones, as discussed in the statement following equation (7)), be it theoretical or empirical.

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