

The energy level of size distribution probability functions

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ABSTRACT

The size distribution probability (SDP) is, among other functions, an important fingerprint of dispersions. Here we demonstrate that, associated with every size distribution function, there is an energy level, which could as well serve as the system's fingerprint. An advantage of using the energy level in conjunction with the SDP function is that, in addition to quantifying the 'energy' of the distribution, one can easily determine whether a proposed theoretical SDP function can exist or not.

§ 1. INTRODUCTION

Representing systems of particles by their size distribution probability (SDP) functions is common practice in many science and engineering fields, ranging from environmental studies of particulate-caused pollution to the applications of powder processing and technology in materials science and engineering. As a result, a number of theoretical SDP functions have been proposed over the years to account for the different types of distributions observed.

It was recently shown that theoretical SDP functions might be subject to entropic limitations, which could otherwise render them useless in practice (Cohen 1993). Our objectives here are firstly to introduce and derive, with the aid of concepts from statistical mechanics, an energy-related property of such functions, and secondly to demonstrate its uses in quantifying the 'energetics' of some typical cases, and in assessing their suitability and limitations in representing actual particle-size distributions.

§ 2. PROBLEM FORMULATION

Consider a system consisting of a total of N_0 primary units or building blocks. These can be arranged into clusters of different sizes, satisfying at any instant in time the following relations:

$$N_0 = \sum_i iN_i, \quad (1)$$

and

$$N = \sum_i N_i, \quad (2)$$

where N is the total number of clusters, i is the cluster size and N_i is the number of clusters of size i . In typical situations, N_0 remains constant (i.e. total mass is conserved), while N_i and N may or may not vary with time.

We now assume that the probability for a SDP function to lie in a particular 'energy level', with N_1 clusters of size $i = 1$, N_2 clusters of size $i = 2$, etc., satisfying the mass conservation constraint of eqn. (1), follows the Boltzmann distribution $\mathcal{P}(N_1, N_2, N_3, \dots)$, given by

$$\mathcal{P}(N_1, N_2, N_3, \dots) = \Omega(N_1, N_2, N_3, \dots) \exp\left(-\sum_i N_i \phi_i^*\right) / \Xi, \quad (3)$$

where $\Omega(N_1, N_2, N_3, \dots)$ is the degeneracy, which shall be discussed shortly, ϕ_i^* ($i = 1, 2, 3, \dots$) is the dimensionless energy state of an individual cluster of size i , and the sum $\sum_i N_i \phi_i^*$, which is carried out over the N_i values satisfying eqn. (1), is the 'energy level' of the SDP function. Moreover, Ξ , which represents the canonical ensemble, can be expressed by

$$\Xi \equiv \sum_{\substack{\text{all } N_i \text{ satisfying} \\ N_0 = \sum_i i N_i}} \Omega(N_1, N_2, N_3, \dots) \exp\left(-\sum_i N_i \phi_i^*\right). \quad (4)$$

Relations similar to eqn. (3) have been used earlier in modelling floc formation (Cohen 1989), and equilibrium linear clustering (Cohen 1988). The energy ϕ_i^* , implemented there, however, was specified as a Derjaguin, Landau, Verwey and Overbeek (DLVO) type interaction potential with a secondary minimum, and the goal was to predict certain properties related to floc structure, equilibrium-cluster size distribution, and capture of Brownian particles on rough surfaces. Our intention here, however, is to work backwards, in that we seek to extract the energetic properties, given a particle-size distribution function.

We proceed by assuming that every distribution of particles (or clusters) is in a state that is perturbed from the random distribution. It will become clear later that the major cause for this perturbation is an energy parameter, which would in fact be the energy level of the distribution. In addition to being useful as a signature of the system, this property may also be of potential value for quantifying the nature of the process leading to the distribution function.

With its energy level always being at an extremum, as it will be proven shortly, the random distribution could subsequently be implemented as the standard against which all other size distribution functions can be compared. Therefore, given that the degeneracy of random clustering is (Levine 1987, Cohen 1990)

$$\Omega(N_1, N_2, N_3, \dots) = N_0! / \prod_i N_i! [i!]^{N_i}, \quad (5)$$

the most probable size distribution of the clusters in the system can thus be derived by maximizing $\ln \mathcal{P}$ in eqn. (3), using eqn. (5) for the degeneracy, and imposing, with the help of Lagrange multipliers, eqns. (1) and (2) as constraints. Avoiding the details, which are straightforward, the final result can be shown to be

$$\frac{N_i}{N} = \frac{[\mu^i \exp(-\phi_i^*)]/i!}{Q} \quad (i = 1, 2, 3, \dots), \quad (6)$$

where μ , which shall be evaluated next, is a constant, independent of i , and Q , the partition function, is given by

$$Q \equiv \sum_i \mu^i \exp(-\phi_i^*)/i! \quad (i = 1, 2, 3, \dots). \quad (7)$$

On substituting eqn. (7) into eqn. (6), and the result into eqns. (1) and (2), the ratio N_0/N , being the average size i_{ave} , of the distribution, becomes

$$\frac{N_0}{N} = \sum_i \frac{i\mu^i \exp(-\phi_i^*)}{i!} \bigg/ \sum_i \frac{\mu^i \exp(-\phi_i^*)}{i!} \quad (i = 1, 2, 3, \dots), \quad (8a)$$

which, after further manipulation, can be written as

$$\frac{N_0}{N} = \frac{\mu}{Q} \frac{\partial Q}{\partial \mu} = \frac{\partial(\ln Q)}{\partial(\ln \mu)}. \quad (8b)$$

We now observe that, while the average cluster size N_0/N is computable given the SDP function, the parameters ϕ_i^* and μ needed to satisfy eqn. (8a), remain unknown. A way to obtain these is to treat *all but one* of them as independent, and the remainder dependent. Since this selection happens to be arbitrary, we could then very conveniently take all the ϕ_i^* to be the independent parameters and assign each a value of zero, that is let $\phi_i^* (i = 1, 2, 3, \dots) = 0$ and, at the same time, let μ be the dependent variable. In view of this, eqn. (7) reduces to

$$Q = \exp \mu - 1, \quad (9)$$

because $\sum_i \mu^i / i!$, with $i = 1, 2, 3, \dots$, is the Taylor expansion of $\exp \mu - 1$. Since eqn. (8b) must also be satisfied, then on utilizing eqn. (9) we obtain

$$\frac{N_0}{N} = \frac{\mu}{1 - \exp(-\mu)}, \quad (10)$$

which relates μ with the average size N_0/N . Although the choice of $\phi_i^* = 0$ (for all $i \geq 1$) to obtain Q and μ by virtue of eqn. (9) and (10) above represents only one of the many possibilities, it does possess certain implications and consequences, some of which will become obvious as we proceed with the analysis.

We now return to eqn. (6) and solve for the cluster energy ϕ_i^* , which should correspond to the distribution of interest. This leads to

$$\phi_i^* = -\ln \left(\frac{\mu \exp \mu}{\mu^i} \right) - \ln(\tilde{N}_i i!) \quad (11)$$

upon incorporating eqns. (9) and (10), and introducing \tilde{N}_i as

$$\tilde{N}_i \equiv \frac{N_i}{N_0} \quad (12)$$

to represent the actual distribution. With ϕ_i^* being the energy state of a single cluster of size i , the *total* energy level Φ_T^* of the given distribution is therefore

$$\Phi_T^* = \sum_i N_i \phi_i^*. \quad (13)$$

Inserting eqn. (11) into eqn. (13), and normalizing with respect to N_0 , that is letting $\phi_{N_0}^* \equiv \Phi_T^*/N_0$, where $\phi_{N_0}^*$ denotes the energy level per unit of building block (or per unit mass), yields

$$\phi_{N_0}^* = -\sum_i \tilde{N}_i \ln \left(\frac{\mu \exp \mu}{\mu^i} \right) - \sum_i \tilde{N}_i \ln(\tilde{N}_i i!), \quad (14)$$

which, in association with eqns (1), (2) and (10), reduces to

$$\phi_{N_0}^* = - \left[\tilde{N} \ln \left(\frac{\exp \mu - 1}{\tilde{N}} \right) - \ln \mu + \sum_i \tilde{N}_i \ln (\tilde{N}_i i!) \right] \quad (15)$$

upon letting $\tilde{N} \equiv N/N_0$. Alternatively, if we define the mean energy level ϕ_N^* per cluster to represent the ratio Φ_1^*/N , we obtain

$$\phi_N^* = - \left[\tilde{N} \ln \left(\frac{\exp \mu - 1}{\tilde{N}} \right) - \ln \mu + \sum_i \tilde{N}_i \ln (\tilde{N}_i i!) \right] / \tilde{N}. \quad (16)$$

Thus, beginning with a given SDP function, which may very well be available in terms of the ratio N_i/N , the parameters $N_0/N (= \sum_i i N_i/N)$, $\tilde{N}_i (= N_i/N_0)$ and μ (from eqn. (10)) can be computed, from which $\phi_{N_0}^*$ and ϕ_N^* can be evaluated using eqns. (15) and (16).

More important is that, on using eqns. (1) and (2) as constraints, eqns (15) and (16) are maximized at $\phi_{N_0}^*$ and $\phi_N^* = 0$. As a result, the inequalities

$$\phi_{N_0}^* \text{ and } \phi_N^* \leq 0 \quad (17)$$

must always be obeyed. The quantity within the large square brackets in eqns. (15) and (16) is identical with the previously derived parameter $\Delta\sigma$, which happens to signify the entropy level of the size distribution function (Cohen 1993). A more thorough derivation of the inequality $\Delta\sigma \geq 0$, leading to those given by eqn. (17) above, is available there.

An important implication of the preceding paragraph is that the random distribution, whose degeneracy is describable by eqn. (5), and which acquires energies of ϕ_i^* (for all $i \geq 1$), $\phi_{N_0}^*$ and ϕ_N^* all to equal zero, attains the maximum energy level. As a result, it could also serve appropriately as the absolute standard against which all SDPs are to be compared. In other words, all SDP functions are, in one way or another, perturbed forms of the random distribution, and their energy levels are signatures of this perturbation.

§ 3. ANALYSIS AND EXAMPLES

Here we shall consider and examine the suitability of three types of distribution for representing actual SDP functions. These are in addition to those analysed by Cohen (1993), whereby owing to the similarity between eqn. (15) and the distribution entropy $\Delta\sigma$, defined there, the conclusions reached therein should apply equally here.

As an additional note, since $\phi_{N_0}^*$ and ϕ_N^* are intensive properties, their application is not limited to these examples only. They are general and should be valid for representing the energy levels of almost any SDP function.

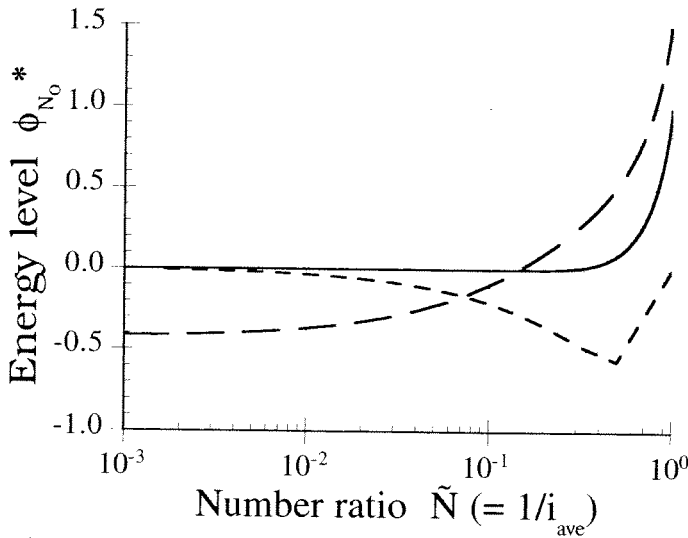
3.1. The Poisson size distribution probability function

This distribution function, which has its uses in describing random phenomena, can be expressed by the following relationship (Miller and Freund 1965):

$$P(i) = \exp(-i_{\text{ave}}) \frac{(i_{\text{ave}})^i}{i!} \quad \text{for } i = 0, 1, 2, 3, \dots \quad (18)$$

In our nomenclature, $P(i)$, i and i_{ave} respectively, would be the SDP function given by N_i/N , the cluster size and the average cluster size, that is

$$i_{\text{ave}} = \frac{N_0}{N} \equiv \tilde{N}^{-1}, \quad (19)$$



Energy level $\phi_{N_0}^*$ plotted against the number ratio \tilde{N} which is equal to the reciprocal of the average size, i_{ave} : (—), the Poisson SDP function (eqn. 20); (---), exponential SDP function (eqn. (22)); (- - -), monodisperse SDP function (eqn. (25)).

where the number ratio \tilde{N} has been defined in the statement following eqn. (15). In view of this, eqn. (18) can be rewritten as

$$\tilde{N}_i = \tilde{N} \exp(-\tilde{N}^{-1}) \frac{(\tilde{N}^{-1})^i}{i!} \quad \text{for } i = 0, 1, 2, 3, \dots \quad (20)$$

Substituting eqn. (20) into eqn. (15) yields the following expression for the energy level per unit mass:

$$(\phi_{N_0}^*)_{\text{Poisson}} = 1 + \ln(\mu\tilde{N}) - \tilde{N} \ln(\exp \mu - 1), \quad (21)$$

where μ and \tilde{N} are related through eqn. (10). The behaviour of the above is depicted by the solid curve in the figure.

It is interesting to note that the curve does not satisfy the inequality of eqn. (17) for all \tilde{N} , covering the range $0 < \tilde{N} \leq 1$. The same is true also for $\phi_{N_0}^*$. Basically, this means that the Poisson distribution, as expressed by eqn. (18) or (20), can *never* be proposed as a suitable function for describing particle-size distributions. The reason for this is simply that the Poisson distribution includes $i = 0$ (see eqn. (20)), which is meaningless when clusters are concerned. However, since the curve does approach zero quite rapidly as \tilde{N} decreases, this distribution can be put to use only as an approximation when relatively small values of \tilde{N} , corresponding to average cluster sizes of about five and larger, are involved.

3.2. The exponential distribution function

The maximum entropy principle, in the context of information theory, has been employed as a powerful tool for predicting particle-size distributions generated by coagulation (Rosen 1984), as well as by fragmentation (Englman, Rivier and Jaeger 1988). On applying this method, in association with the two constraints given by

eqns. (1) and (2) here, the following result can be derived (Rosen 1984):

$$\bar{N}_i = \bar{N}^2 \exp(-\xi_i) \quad \text{for } 0 \leq \xi_i < \infty, \quad (22)$$

where ξ_i is the continuous counterpart of the product $i\bar{N}$. While the above merely represents the most elementary size distribution function obtained in this way, other more elaborate forms have been developed by simply adding to the number of constraints (Englman *et al.* (1988), and some references therein).

A major outcome of these studies is the appearance of an exponential factor, identical with eqn. (22), in all the final results. Hence, an examination of the energy level pertaining to this basic expression should provide clues to the general behaviour of the energy levels of SDP functions derived from the entropy maximization method.

Noting that the exponential SDP function is continuous rather than discrete, appropriate transformations must be made prior to substituting eqn. (22) into eqn. (15) and solving. However, since eqn. (15) is similar to an earlier result (Cohen 1993), we shall, in the interest of space, avoid all the calculation details, take the result and display it here as the broken curve (long dashes) in the figure. In examining this curve, it is obvious that the regime of existence of the exponential SDP function, as provided above, is restricted to the region $0 < \bar{N} \leq 0.144$. Hence, SDP functions of this type should, in general, be limited in their range of applicability, meaning that one should be careful in applying them to practical situations.

3.3. The monodisperse size distribution probability function

Using our notation, this function, which is a distribution of clusters having identical sizes, is representable by

$$N_i = \frac{N_0}{i} \delta(i - i_{\text{ave}}) \quad \text{for } i = 1, 2, 3, \dots \quad (23)$$

where $i_{\text{ave}} = \bar{N}^{-1}$, as defined earlier, and

$$\delta(x) = \begin{cases} 1, & \text{if } x = 0, \\ 0, & \text{if } x \neq 0. \end{cases} \quad (24)$$

It therefore follows that eqn. (23) can be expressed as

$$\bar{N}_i = \bar{N} \delta(i - \bar{N}^{-1}). \quad (25)$$

Inserting this into eqn. (16) yields

$$(\phi_{N_0}^*)_{\text{monodisperse}} = \ln \mu - \bar{N} \ln [(\exp \mu - 1)(\bar{N}^{-1})] \quad (26)$$

the behaviour of which is displayed by the broken curve (short dashes) in the figure.

As expected, this SDP function can be defined for the full range of \bar{N} , lying between zero and unity (or $1 \leq i_{\text{ave}} < \infty$). The minimum at $\bar{N} = 0.5$, which represents a collection of dimers, implies that, configurationally, such systems are at their lowest energy level, suggesting that a system of dimers is perturbed farthest away from total randomness. In addition, one can also infer that beginning with a system of dimers only, characterized by $\bar{N} = 0.5$, the effort required to break all of them to form monomers is more than that needed to form trimers or other larger clusters. While this might be an obvious conclusion, eqn. (26), nevertheless, quantifies it.

§ 4. CONCLUSIONS

The 'energy level' of SDP functions has been introduced here as a possible fingerprint of dispersion systems. In addition to showing that this property can be used to determine the extent to which a given SDP function deviates from total randomness, we have demonstrated that it has potential uses in pinpointing the limitations of size distribution functions, in general. The latter conclusion follows directly from the similarity between the current results and those presented earlier (Cohen 1993).

We chose here as examples the Poisson, exponential and monodisperse SDP functions and calculated their respective energy levels $\phi_{N_0}^*$ (per unit mass). Among the conclusions reached are

- (1) the Poisson distribution can never be applied to represent actual SDP functions although for average sizes i_{ave} greater than about five, it could serve as a viable approximation,
- (2) the exponential SDP function, as given by eqn. (22) and other similar proposals, is limited to certain ranges of average sizes and
- (3) energetically some SDP functions are more difficult to form than others.

For instance, it requires less energy to generate an exponential SDP function with, say, $\tilde{N} = 10^{-2}$ (or $i_{ave} = 100$), than a monodisperse distribution of clusters having cluster sizes of 100, whereas the contrary is true when $i_{ave} = 10$. This simply follows from the figure, where the differences in the energy levels between the two SDP functions, evaluated at the two average sizes of 10 and 100, are shown. Once again, for the reason that the energy level introduced here is an intensive property, its application is general.

REFERENCES

- COHEN, R. D., 1988, *J. statist. Phys.*, **51**, 559; 1989, *J. Chem. Soc., Faraday Trans. II*, **85**, 1487; 1990, *J. Chem. Soc., Faraday Trans.*, **86**, 2133; 1993, *Proc. R. Soc. A*, **440**, 611.
- ENGLMAN, R., RIVIER, N., and JAEGER, Z., 1988, *Phil. Mag. B*, **56**, 751.
- LEVINE, R. D., 1987, *The Physics of Structure Formation*, edited by W. Guttinger and G. Dangelmayr (Berlin: Springer), pp. 78–86.
- MILLER, I., and FREUND, J. E., 1965, *Probability and Statistics for Engineers* (Englewood Cliffs, New Jersey: Prentice-Hall).
- ROSEN, J. M., 1984, *J. Colloid Interface Sci.*, **99**, 9.



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