

Ensemble Averaging

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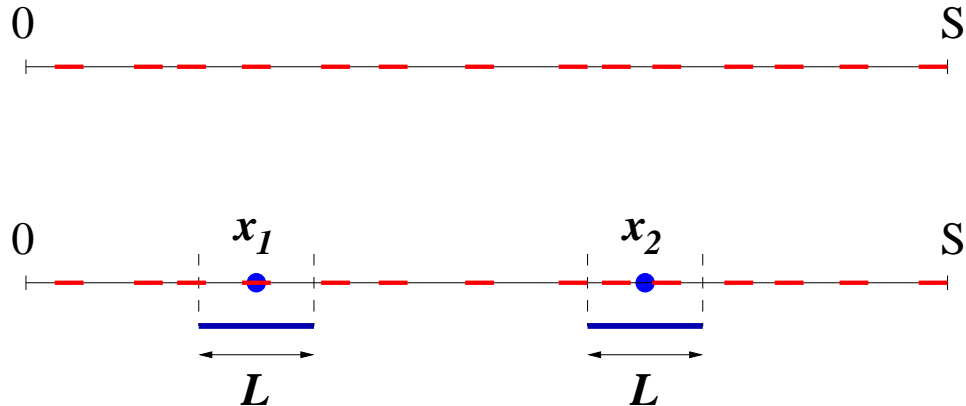


Figure 1: Definition of “length fraction” by volume averaging.

1 Averaged equations: the need and the challenge

- Consider a batch of sedimenting particles: average settling velocity might be sufficient and one can do experiments, simple modelling or (in principle) numerical simulations to calculate it.
- But now take the particles in a complicated flow: how do they behave? do they cluster? do they deposit? how do they affect the flow? These questions cannot be answered as before or, if they can for one flow type, a different flow type would require a new *ex novo* effort. If we had averaged equations which we could solve for the new boundary conditions, we could predict the new flow.
- Any averaging process leads to loss of information, but some of that information needs to be reintroduced to formulate a closed set of equations. Example: ice crystals in a cloud cool the cloud, but the heat taken away by each ice crystal depends on the temperature in the immediate vicinity of the crystal, which can be quite different from the average temperature of that region of the cloud. This is the **closure problem** that afflicts all attempts to formulate averaged equations.

2 Volume and ensemble averaging

To illustrate the difference between volume and ensemble averaging let us consider a random arrangement of N short segments, which we call “particles”, on a segment of length S (figure 1). Define a *length fraction* as the local fraction of the line occupied by particles. According to the “volume averaging” rule – which here is really just a “length averaging” – to define the length fraction at x_1 we would take a segment of length L , place it around x_1 , and form the fraction

$$\beta(x_1) = \frac{\text{total length of } L \text{ inside particles}}{L} \quad (1)$$

We would repeat the same process to define the length fraction at x_2 .

It is evident that this procedure depends – at least to some extent – on the choice of L . If L is too short, the measure is either not representative (e.g., it might be 100% if L is shorter than the particles), or strongly fluctuates. If L is too long, β so defined fails to give a faithful representation of the particle distribution in the neighborhood of x_1 . A writer on the subject remarks:

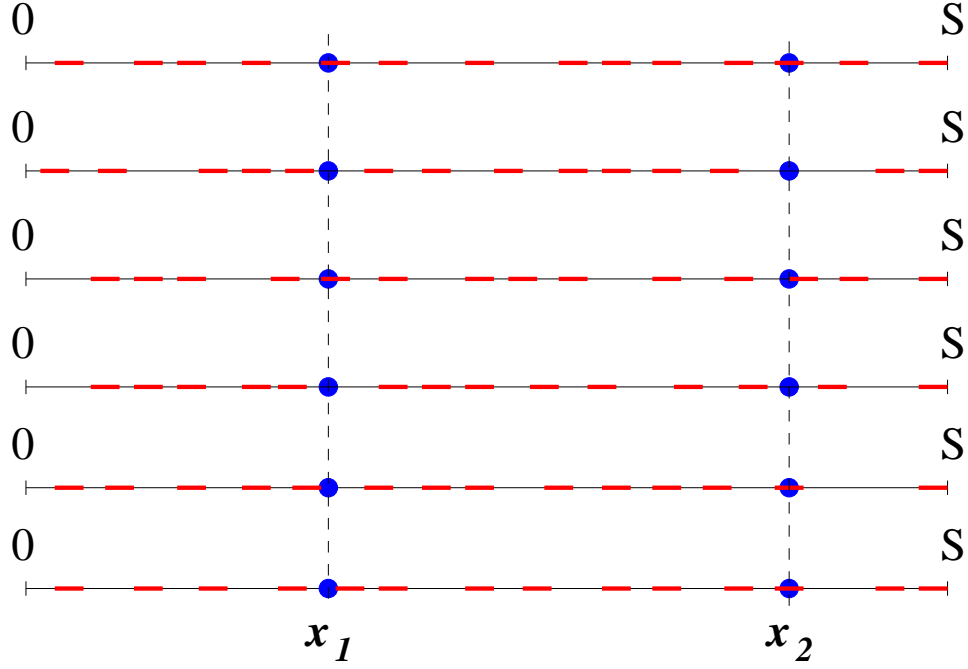


Figure 2: Definition of “length fraction” by ensemble averaging.

Implicit in the idea of volume averaging is the existence of “an elementary macro-volume ... the characteristic linear dimensions of which are many times greater than the nonuniformities (diameters of drops, bubbles, particles, pores, distances between them, film thicknesses, etc.), but at the same time much less than the characteristic macrodimension of a problem (length and diameter of a nozzle, pipe, the characteristic disturbance attenuation distance, its length and so on)” (Nigmatulin 1979)

In other words, volume averaging presupposes the notion of local uniformity, which in turn implies a **separation of scales**: the particle scale must be much smaller than the macroscale.

For a random process, the fluctuations around a mean count \bar{n} is of the order of $\Delta n \simeq \sqrt{\bar{n}}$. Let the total number of particles be N ; then, if the total length of the interval is S , a length L will contain an average number of particles given by

$$\bar{n} = \frac{L}{S} N \quad (2)$$

and the fluctuation would then be of the order of

$$\Delta n \simeq \sqrt{(L/S) N} \quad (3)$$

If the particles have length a , the length fraction obtained by the previous procedure would then be

$$\beta(x_1) = \frac{[(L/S) N \pm \sqrt{(L/S) N}] a}{L} = \frac{Na}{S} \left[1 \pm \sqrt{\frac{S}{LN}} \right] \quad (4)$$

The average length fraction over the entire segment is given by

$$\bar{\beta} = \frac{Na}{S} \quad (5)$$

and, therefore, we can write the previous result as

$$\beta(x_1) = \bar{\beta} \left[1 \pm \sqrt{\frac{S}{LN}} \right] = \bar{\beta} \left[1 \pm \sqrt{\frac{a}{L \bar{\beta}}} \right] \quad (6)$$

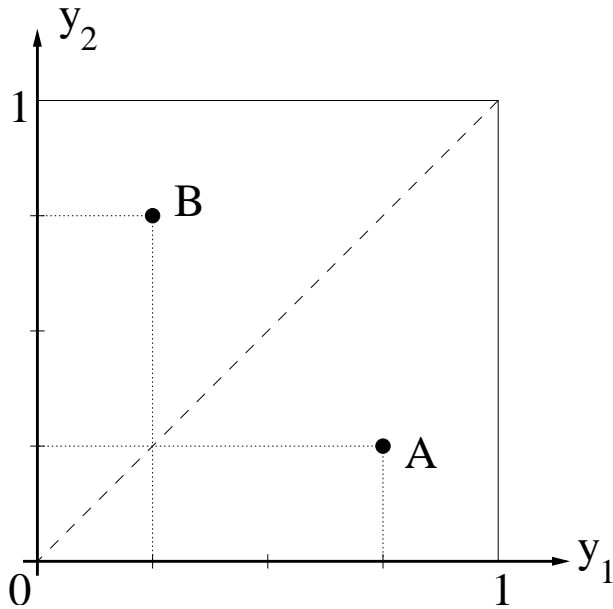


Figure 3: Phase space for two particles constrained to be on the unit segment

If we take an L such that $\bar{\beta}L = a$, we see that the expected fluctuations are of the order of 100%. But even if we increase L , the magnitude of the fluctuations decreases slowly since square roots are weak functions of their argument: one has to quadruple L to decrease it by 1/2. The problem is evidently more severe for smaller $\bar{\beta}$.

But what if the particles are distributed non uniformly? e.g., a particle-rich thin layer, surrounded by much more sparse particle distributions? Or the geometry is such that there are regions of very strong temperature gradients? Here lies the power of ensemble averaging which is **always** defined irrespective of any condition of local uniformity or separation of scales.

To calculate $\beta(x_1)$ by ensemble averaging on the previous example, we imagine a large numbers of replicas of the system, all macroscopically equal (e.g., with the same number of particles), but different in their microscopic details according to some specified probability distribution. We call this collection of replicas of the system the *ensemble*, with each replica a *realization*, and then count the fraction of realizations such that the point x_1 lies in a particle (figure 2).

3 Probabilities

Consider an ensemble consisting of \mathcal{N} realization of a system of two particles, 1 and 2, confined to the segment $[0, 1]$ of a line. We define the probability density $P(y_1, y_2)$ so that

$$\frac{d\mathcal{N}}{\mathcal{N}} = P(y_1, y_2) dy_1 dy_2 \quad (7)$$

is the fraction of realizations of the ensemble in which particle 1 is between y_1 and $y_1 + dy_1$ and particle 2 is between y_2 and $y_2 + dy_2$. Each realization of this system can be represented by a point in the phase space of the system (actually, in this case, the configuration space) consisting of the unit square (figure 3).

To normalize P we need to sum over all possible states of the system. If, for the particular purpose at hand – whatever it may be – the two particles have identical effects, considering the two states marked A and B in figure 3 as distinct would be wrong. To deal with this situation one could define the probability density in such a way that $P(y_1, y_2)$ represents the probability of finding *either* particle around y_1 and y_2 , but this complicates things. The simplest way to avoid the double counting is to count the two states as

distinct, and then divide by 2!:

$$\frac{1}{2!} \int_0^1 dy_1 \int_0^1 dy_2 P(y_1, y_2) = 1 \quad (8)$$

This rule is readily generalized to N particles, in which case we would write

$$\frac{1}{N!} \int_0^1 dy_1 \int_0^1 dy_2 \dots \int_0^1 dy_N P(y_1, y_2, \dots, y_N) = 1 \quad (9)$$

Similarly, if the particle position is in some region of space \mathcal{V} instead of the line, we write¹

$$\frac{1}{N!} \int_{\mathcal{V}} dy_1^3 \int_{\mathcal{V}} d^3 y_2 \dots \int_{\mathcal{V}} d^3 y_N P(\mathbf{y}_1, \mathbf{y}_2, \dots, \mathbf{y}_N) = 1 \quad (10)$$

or, more concisely

$$\frac{1}{N!} \int d\mathcal{C}^N P(N) = 1 \quad (11)$$

In general, we use the word *configuration* and the symbol \mathcal{C}^N to indicate the set of values of a number of quantities sufficient to specify uniquely the state of the N -particle system which, in addition to position, may involve velocities etc.

In addition to $P(N)$ we shall make use of the reduced 1-particle probability distribution which specifies the configuration (e.g., position) of particle 1 wherever the other particles are. In this case we need to sum over all the distinct states of the other particles and therefore we have

$$P(y_1) = P(1) = \frac{1}{(N-1)!} \int dy_2 \dots dy_N P(y_1, y_2, \dots, y_N) = \frac{1}{(N-1)!} \int d\mathcal{C}^{N-1} P(y_1, N-1) \quad (12)$$

By using the normalization condition we see that

$$\int dy_1 P(y_1) = N \quad (13)$$

which justifies interpreting $P(y_1)$ as the *particle number density* n . In a similar way we can define

$$P(y_1, y_2) = P(2) = \frac{1}{(N-2)!} \int d\mathcal{C}^{N-2} P(y_1, y_2, N-2) \quad (14)$$

and

$$\int dy_1 \int dy_2 P(y_1, y_2) = N(N-1) \quad (15)$$

and so on.

The probability of having a certain configuration of the last $N-1$ particles given that particle 1 has configuration y_1 defines the *conditional probability* $P(N-1|y_1)$. Since the probability of two events is the product of the respective probabilities, it is evident that

$$P(N) = P(y_1) P(N-1|y_1) \quad (16)$$

with

$$\int d\mathcal{C}^{N-1} P(N-1|y_1) = (N-1)! \quad (17)$$

¹After this equation, we will not bother to indicate the vector nature of \mathbf{y}_k simply writing y_k and dy_k in place of $d^3 y_k$. However, where necessary for clarity, we will reinstate the explicit indication of the vector nature of a quantity by using bold face.

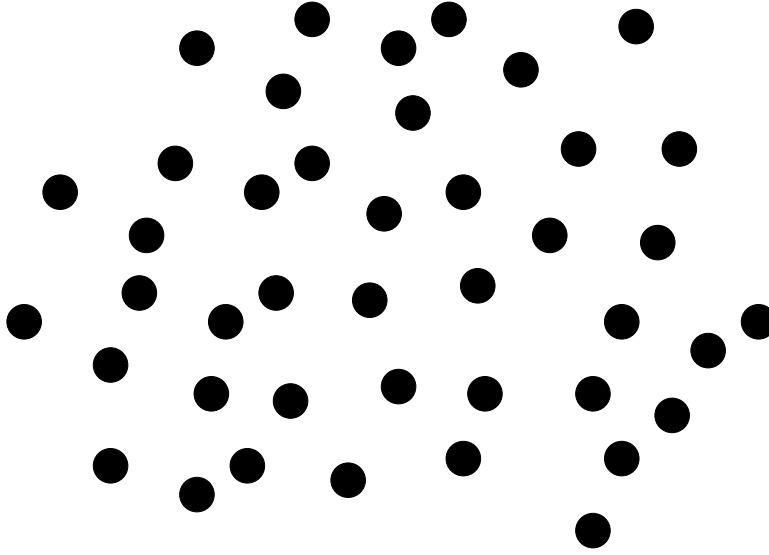


Figure 4: A composite consisting of equal spherical inclusions in a homogeneous matrix

4 Volume fractions and number density

Consider a composite medium consisting of equal spherical inclusions of radius a in a homogeneous matrix (figure 5). Let the *indicator function* of the disperse phase, i.e., the spheres, be defined by

$$\chi_D(\mathbf{x}; N) = \begin{cases} 1 & \text{if } \mathbf{x} \in \text{a sphere, given the configuration } N \\ 0 & \text{otherwise} \end{cases} \quad (18)$$

and, similarly for the continuous phase, i.e. the matrix:

$$\chi_C(\mathbf{x}; N) = \begin{cases} 1 & \text{if } \mathbf{x} \notin \text{a sphere, given the configuration } N \\ 0 & \text{otherwise} \end{cases} \quad (19)$$

Since the sphere surfaces have 0 measure

$$\chi_D + \chi_C = 1 \quad (20)$$

We define the *volume fraction* β_D of the disperse phase at \mathbf{x} as the fraction of realizations of the ensembles for which the point \mathbf{x} is in a sphere:

$$\begin{aligned} \beta_D &= \frac{1}{\mathcal{N}} \sum \Delta \mathcal{N}(\mathbf{x} \in \text{ sphere}) \\ &= \sum_{\text{all } \Delta \mathcal{N}} \chi_D(\mathbf{x}|N) \frac{\Delta \mathcal{N}}{\mathcal{N}} \\ &= \frac{1}{N!} \int \chi_D(\mathbf{x}; N) P(N) d\mathcal{C}^N . \end{aligned} \quad (21)$$

and similarly for the continuous phase

$$\beta_C(\mathbf{x}) = \frac{1}{N!} \int d\mathcal{C}^N P(N) \chi_C(\mathbf{x}; N) . \quad (22)$$

Clearly, by (20),

$$\beta_C + \beta_D = 1 \quad (23)$$

For equal spherical particles of radius a , χ_D can be explicitly represented as

$$\chi_D(\mathbf{x}; N) = 1 - \chi_C(\mathbf{x}, N) = \sum_{\alpha=1}^N H(a - |\mathbf{x} - \mathbf{y}^\alpha|), \quad (24)$$

where H is the Heaviside step function and we can use this representation to calculate β_D ; from the definition (21)

$$\beta_D = \frac{1}{N!} \int d\mathcal{C}^N P(N) \sum_{\alpha=1}^N H(a - |\mathbf{x} - \mathbf{y}^\alpha|). \quad (25)$$

Since the particles are identical, each one gives an equal contribution to this sum and we can then just consider the contribution of particle 1 and multiply by N . If we also use the definition (16) of conditional probability we have

$$\begin{aligned} \beta_D &= \frac{1}{N!} \int dy_1 N P(y_1) H(a - |\mathbf{x} - \mathbf{y}_1|) \int d\mathcal{C}^{N-1} P(N|y_1) \\ &= \int dy_1 P(y_1) H(a - |\mathbf{x} - \mathbf{y}_1|) \frac{1}{(N-1)!} \int d\mathcal{C}^{N-1} P(N|y_1) \end{aligned} \quad (26)$$

The inner integral equals $(N-1)!$ by the normalization (17) so that

$$\beta_D = \int dy_1 N P(y_1) H(a - |\mathbf{x} - \mathbf{y}_1|) = \int_{|\mathbf{x}-\mathbf{y}|\leq a} dy P(y) = \int_{|\mathbf{x}-\mathbf{y}|\leq a} dy n(y) \quad (27)$$

where $n(y)$ is the number density, given by $P(y)$ as noted before. If n is uniform over the scale of a particle radius, we find

$$\beta_D(\mathbf{x}) = vn(\mathbf{x}) \quad (28)$$

If n is not uniform, we can expand in Taylor series

$$n(\mathbf{y}) = n(\mathbf{x}) + (\mathbf{y} - \mathbf{x}) \cdot \nabla n + \frac{1}{2} (\mathbf{y} - \mathbf{x})(\mathbf{y} - \mathbf{x}) : \nabla \nabla n + \dots \quad (29)$$

to find

$$\beta_D(\mathbf{x}) = vn(\mathbf{x}) + \frac{a^2}{10} \nabla^2(vn) + \dots \quad (30)$$

We can now define the *phase average* of any quantity f belonging to either phase; for example, for the disperse phase,

$$\beta_D(\mathbf{x}) \langle f_D \rangle(\mathbf{x}) = \frac{1}{N!} \int d\mathcal{C}^N P(N) \chi_D(\mathbf{x}; N) f_D(\mathbf{x}; N). \quad (31)$$

We can strengthen the previous interpretation of $P(y)$ as particle number density as follows. Just as (24) is the characteristic function for the particle material, we can define a characteristic function for the particle centers as

$$\sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{y}^\alpha) \quad (32)$$

Then the number density at \mathbf{x} is the average number of particles with center at \mathbf{x} :

$$n(\mathbf{x}) = \frac{1}{N!} \int d\mathcal{C}^N P(N) \sum_{\alpha=1}^n \delta(\mathbf{x} - \mathbf{y}^\alpha) \quad (33)$$

The same steps as before lead us to

$$n(\mathbf{x}) = \int dy P(y) \delta(\mathbf{x} - \mathbf{y}) = P(\mathbf{x}) \quad (34)$$

Upon comparison with (27) we see that we transition from the number density to the volume fraction by “inflating” the particles from 0 radius (the “volume” of their centers) to a finite volume,

For future reference we note the result

$$\nabla\chi_C = -\nabla\chi_D = \sum_{\alpha=1}^N \delta(a - |\mathbf{x} - \mathbf{y}_\alpha|) \frac{\mathbf{x} - \mathbf{y}_\alpha}{a}. \quad (35)$$

5 Application: Conduction of heat in a composite

Consider a composite medium consisting of equal spherical inclusions of radius a in a homogeneous matrix. Inside the inclusions and inside the matrix the heat flux is given by

$$\mathbf{q}_D = -k_D \nabla T_D, \quad \mathbf{q}_C = -k_C \nabla T_C \quad (36)$$

respectively, where $k_{D,C}$ are the thermal conductivities. The mean heat flux \mathbf{q}_m in the composite is given by the weighted average of the heat fluxes in the two phases:

$$\begin{aligned} \mathbf{q}_m(\mathbf{x}) &= \frac{1}{N!} \int d\mathcal{C}^N P(N) [\chi_C \mathbf{q}_C(\mathbf{x}; N) + \chi_D \mathbf{q}_D(\mathbf{x}; N)] \\ &= -\frac{1}{N!} \int d\mathcal{C}^N P(N) [\chi_C k_C \nabla_x T_C(\mathbf{x}; N) + \chi_D k_D \nabla_x T_D(\mathbf{x}; N)] \\ &= -k_C \beta_C \langle \nabla_x T_C \rangle - k_D \beta_D \langle \nabla_x T_D \rangle = -k_C [\beta_C \langle \nabla_x T_C \rangle + \beta_D \langle \nabla_x T_D \rangle] - (k_D - k_C) \beta_D \langle \nabla_x T_D \rangle \end{aligned} \quad (37)$$

where we have affixed the subscript x to the gradient to stress that the gradient is taken at the point where the average is evaluated. The mean temperature is

$$T_m = \frac{1}{N!} \int d\mathcal{C}^N P(N) [\chi_C T_C + \chi_D T_D] \quad (38)$$

and

$$\begin{aligned} \nabla T_m &= \frac{1}{N!} \int d\mathcal{C}^N P(N) [\chi_C \nabla T_C + \chi_D \nabla T_D] + \frac{1}{N!} \int d\mathcal{C}^N P(N) [(\nabla \chi_C) T_C + (\nabla \chi_D) T_D] \\ &= \beta_C \langle \nabla T_C \rangle + \beta_D \langle \nabla T_D \rangle + \frac{1}{N!} \int d\mathcal{C}^N P(N) (T_D - T_C) \nabla \chi_D \end{aligned} \quad (39)$$

But, according to (35), $\nabla \chi_D$ localizes the integral over the surface of the particles, where the temperature is continuous so that $T_C = T_D$, and therefore we conclude that

$$\nabla T_m = \beta_C \langle \nabla T_C \rangle + \beta_D \langle \nabla T_D \rangle \quad (40)$$

so that we can write (37) as

$$\mathbf{q}_m = -k_C \nabla T_m - (k_D - k_C) \beta_D \langle \nabla T_D \rangle \quad (41)$$

The task is then to calculate

$$\beta_D \langle \nabla_x T_D \rangle = \frac{1}{N!} \int d\mathcal{C}^N P(N) \chi_D(\mathbf{x}; N) \nabla_x T_D(\mathbf{x}; N) \quad (42)$$

We use the representation (24) and the identity of the particles to obtain a result similar to (26), namely

$$\beta_D \langle \nabla_x T_D \rangle = \int dy_1 P(y_1) H(a - |\mathbf{x} - \mathbf{y}_1|) \frac{1}{(N-1)!} \int d\mathcal{C}^{N-1} P(N|y_1) \nabla_x T_D(\mathbf{x}; y_1, N-1) \quad (43)$$

Note that, because of the factor $H(a - |\mathbf{x} - \mathbf{y}_1|)$ we are guaranteed that the point \mathbf{x} is inside particle 1. Thus we see that the inner integral can be interpreted similarly to the phase average (31) with the difference that,

instead of integrating over the position of all the particles, we integrate over the position of the remaining $N - 1$, given that particle 1 is at y_1 . This defines the (1-particle) *conditional average*, which we write for the special case in which we know that \mathbf{x} is inside a particle so that we do not need a χ_D in the integrand:

$$\langle \nabla_x T_D \rangle_1(\mathbf{x}|\mathbf{y}_1) = \frac{1}{(N-1)!} \int d\mathcal{C}^{N-1} P(N|\mathbf{y}_1) \nabla_x T_D(\mathbf{x}; \mathbf{y}_1, N-1). \quad (44)$$

Thus, we have found that

$$\beta_D \langle \nabla_x T_D \rangle = \int_{|\mathbf{x}-\mathbf{y}| \leq a} d^3y P(\mathbf{y}) \langle \nabla_x T_D \rangle_1(\mathbf{x}|\mathbf{y}) \quad (45)$$

No progress can be made without further assumptions or approximations. Let us assume therefore that the density of particles in the composite is fairly small (dilute limit). It is then reasonable to assume that one can calculate $\langle \nabla_x T_D \rangle_1$ assuming that there is a single particle immersed in the average medium. The result of such a calculation is

$$T_D = T_m(\mathbf{y}) + \frac{3}{2+\lambda} (\mathbf{x} - \mathbf{y}) \cdot \nabla T_m \quad (46)$$

in which

$$\lambda = \frac{k_D}{k_C} \quad (47)$$

is the ratio of the conductivities. Thus

$$\langle \nabla_x T_D \rangle_1(\mathbf{x}|\mathbf{y}) \simeq \frac{3}{2+\lambda} \nabla T_m \quad (48)$$

so that

$$\beta_D \langle \nabla_x T_D \rangle \simeq \frac{3}{2+\lambda} \int_{|\mathbf{x}-\mathbf{y}| \leq a} d^3y P(\mathbf{y}) \nabla T_m \quad (49)$$

If P and ∇T_m are constants over a volume with the dimensions of the particle volume this is just

$$\beta_D \langle \nabla_x T_D \rangle \simeq \frac{3}{2+\lambda} n v \nabla T_m = \frac{3}{2+\lambda} \beta_D \nabla T_m \quad (50)$$

and, substituting into (37), we find

$$\mathbf{q}_m(\mathbf{x}) = -k_C \nabla T_m - (k_D - k_C) \frac{3}{2+\lambda} \beta_D \nabla T_m \quad (51)$$

from which

$$\mathbf{q}_m(\mathbf{x}) = -k_C \left[1 + 3 \frac{\lambda - 1}{\lambda + 2} \beta_D \right] \nabla T_m \quad (52)$$

We thus conclude that the *effective* thermal conductivity of the composite is given by

$$k_{eff} = k_C \left[1 + 3 \frac{\lambda - 1}{\lambda + 2} \beta_D \right] \quad (53)$$

Obviously, if $\lambda = 1$, $k_{eff} = k_C$.

If, however, $P(y)$ is not a constant, we can use the series expansion (54)

$$n(\mathbf{y}) = n(\mathbf{x}) + (\mathbf{y} - \mathbf{x}) \cdot \nabla n + \frac{1}{2} (\mathbf{y} - \mathbf{x})(\mathbf{y} - \mathbf{x}) : \nabla \nabla n + \dots \quad (54)$$

to find

$$\beta_D \langle \nabla_x T_D \rangle \simeq \frac{3}{2+\lambda} \left[n v + \frac{a^2}{10} \nabla^2 (n v) \right] \nabla T_m \quad (55)$$

with a different result for k_{eff} .

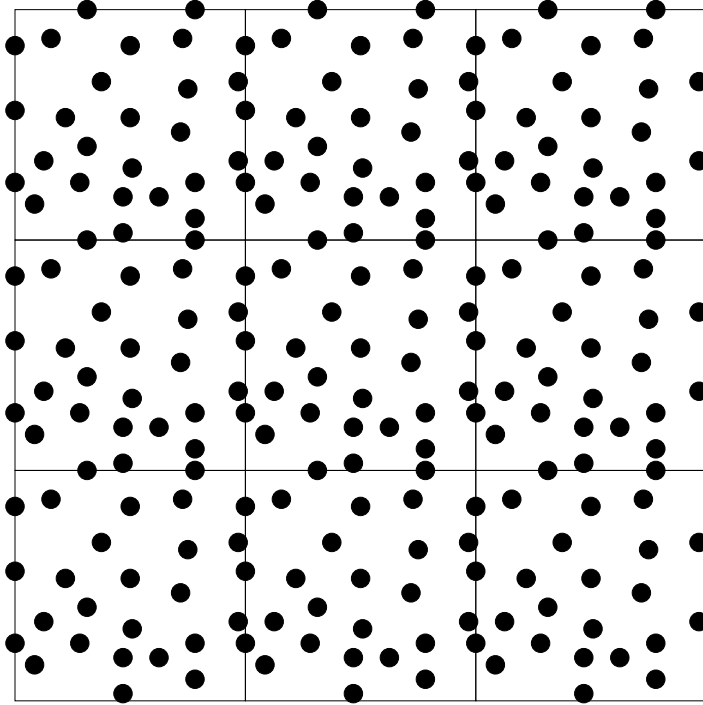


Figure 5: Approximation of a very large piece of composite by the periodic repetition of a unit cell.

6 Heat conduction in a dense uniform composite

To approximate a region of the composite containing a very large number of inclusions, we consider a cubic cell of side L in which we arrange N equal spherical particles, and imagine filling up the entire space with exact replicas of this cell. In order to transfer heat, it is necessary to impose some temperature difference, which we can do by writing the exact microscopic temperature field in either phase in the form

$$T_{D,C}(\mathbf{x}) = T_\infty(\mathbf{x}) + \tilde{T}_{D,C}(\mathbf{x}) \quad (56)$$

Here $T_\infty(\mathbf{x})$ is an imposed non-random temperature field and \tilde{T} is a fluctuating part which is the same in each cell, i.e., it is periodic. We assume that T_∞ is a linear function: if \mathbf{X}_K is the position of a reference point for cell K and \mathbf{x} is the position of a generic point in the cell relative to \mathbf{X}_K , we write

$$T_\infty = \mathbf{G} \cdot (\mathbf{X}_K + \mathbf{x}) = \mathbf{G} \cdot \mathbf{X}_K + \mathbf{G} \cdot \mathbf{x} \quad (57)$$

The first term is different from cell to cell, but it is a constant and does not influence the heat flux (which is given by ∇T_∞). The second term is the same in all cells and it is therefore periodic, and so will be \tilde{T} which represents the response of the particles to the presence of the imposed temperature gradient.

The mean temperature gradient is given by

$$\nabla T_m = \frac{1}{N!} \int d\mathcal{C}^N P(N) [\chi_C \nabla T_C + \chi_D \nabla T_D] = \nabla T_\infty + \frac{1}{N!} \int d\mathcal{C}^N P(N) (\chi_C \nabla \tilde{T}_C + \chi_D \nabla \tilde{T}_D) \quad (58)$$

The last term must be calculated numerically. To this end we note that, if the system is statistically homogeneous, ∇T_m is actually a constant so that

$$\nabla T_m = \frac{1}{V} \int_{cell} \nabla T_m dV \quad (59)$$

or

$$\nabla T_m = \nabla T_\infty + \frac{1}{N!} \int d\mathcal{C}^N P(N) \left[\frac{1}{V} \int_{cell} (\chi_C \nabla \tilde{T}_C + \chi_D \nabla \tilde{T}_D) dV \right] \quad (60)$$

and also

$$\beta_{C,D} \langle \nabla \tilde{T}_{C,D} \rangle = \frac{1}{N!} \int d\mathcal{C}^N P(N) \left[\frac{1}{V} \int_{cell} \chi_{C,D} \nabla \tilde{T}_{C,D} dV \right] \quad (61)$$

The procedure is then the following:

1. Generate an ensemble of configurations each consisting of a random arrangements of N spheres in a cell;
2. For each configuration so generated solve numerically the steady energy equation in the cell (both in the matrix and in the particles)

$$\nabla^2 \tilde{T}_{C,D} = 0 \quad (62)$$

subject to the condition of continuity of temperature and normal heat flux on the particle surfaces and to periodicity conditions on the cell surface;

3. Calculate the two inner volume integrals in (61);
4. Repeat for each configuration and average the values of these volume integrals, which amounts to a Monte Carlo calculation of the probability integral (the factor $N!$ is just a renumbering of the particles and can be ignored).

The numerical results of point 3 are vectors, and therefore they must be functions of the vectors specified in the problem statement, which in this case reduce to the single vector \mathbf{G} . Hence it must be that

$$\beta_{C,D} \langle \nabla \tilde{T}_{C,D} \rangle = \Lambda_{C,D} \mathbf{G} \quad (63)$$

where the constants $\Lambda_{C,D}$ are the result of the simulations. The mean heat flux is given by

$$\begin{aligned} \mathbf{q}_m &= \frac{1}{N!} \int d\mathcal{C}^N P(N) [-k_C \chi_C \nabla T_C - k_D \chi_D \nabla T_D] \\ &= -(k_C + k_D) \nabla T_\infty - \int d\mathcal{C}^N P(N) [-k_C \chi_C \nabla \tilde{T}_C - k_D \chi_D \nabla \tilde{T}_D] \end{aligned} \quad (64)$$

Hence we have

$$\mathbf{q}_m = -(k_C + k_D) \mathbf{G} - \Lambda_C k_C \mathbf{G} - \Lambda_D k_D \mathbf{G} = -[k_C(1 + \Lambda_C) + k_D(1 + \Lambda_D)] \mathbf{G} \quad (65)$$

and also

$$\nabla T_m = (\Lambda_C + \Lambda_D) \mathbf{G} \quad (66)$$

The only quantity which is problem-specific is \mathbf{G} , but we can find a constitutive relation valid beyond this specific problem by eliminating it between these two expressions to find

$$\mathbf{q}_m = -\frac{k_C(1 + \Lambda_C) + k_D(1 + \Lambda_D)}{\Lambda_C + \Lambda_D} \nabla T_m \quad (67)$$

which shows that the effective conductivity is given by

$$k_{eff} = \frac{k_C(1 + \Lambda_C) + k_D(1 + \Lambda_D)}{\Lambda_C + \Lambda_D} \quad (68)$$

If the cell size L is not large enough, the result may depend on it. In order to find a result reasonably independent of this size, we can repeat the above calculation for different ensembles consisting of cells of different size and containing different numbers of particles, but all having the same volume fraction, plot the results as function $1/L$, and take the limit $1/L \rightarrow 0$.

7 Heat conduction in a dense non-uniform composite

How can we adapt the previous approach to a non-uniform particle distribution? The philosophy is similar: we specify a non-uniform particle distribution in terms of certain parameters, solve the problem numerically, eliminate the problem-specific parameters and find relations that – hopefully – are valid also in other situations. The first task is to develop a useful non-uniform probability.

7.1 Non-uniform probability

Consider a volume $\Delta\mathcal{V}$ of the configuration space of the system. The fraction of systems of a uniform ensemble contained in $\Delta\mathcal{V}$ is given by

$$\int_{\Delta\mathcal{V}} d\mathcal{C}^N P_0(N), \quad (69)$$

where here we designate by P_0 the same statistically uniform probability distribution used in the previous section. Subject now the center \mathbf{y}^α of each sphere to a small displacement $\mathbf{y}^\alpha \rightarrow \mathbf{y}^\alpha - \epsilon \mathbf{F}(\mathbf{y}^\alpha)$ where \mathbf{F} is a given deterministic vector function and ϵ a small parameter. The fraction of systems in $\Delta\mathcal{V}$ then becomes

$$\begin{aligned} & \int_{\Delta\mathcal{V}} d\mathcal{C}^N P_0(N) + \epsilon \int_{\Delta\mathcal{S}} d\mathcal{C}^N P_0(N) \mathbf{N} \cdot \left(\sum_{\alpha=1}^N \mathbf{F}(\mathbf{y}^\alpha) \right) \\ &= \int_{\Delta\mathcal{V}} d\mathcal{C}^N P_0(N) \left[1 + \epsilon \sum_{\alpha} \nabla_{\alpha} \cdot \mathbf{F}(\mathbf{y}^\alpha) \right], \end{aligned} \quad (70)$$

where \mathbf{N} is the unit normal in phase space outwardly directed with respect to the surface $\Delta\mathcal{S}$ of $\Delta\mathcal{V}$, the divergence theorem has been used to obtain the second form, and ∇_{α} denotes differentiation with respect to the coordinate \mathbf{y}^α of the α -th particle. We thus see that the ensemble generated by the displacement of the particles has the probability density

$$P(N) = P_0 [1 + \epsilon \Phi(N)], \quad (71)$$

where

$$\Phi(N) = \sum_{\alpha=1}^N \nabla_{\alpha} \cdot \mathbf{F}(\mathbf{y}^\alpha). \quad (72)$$

This is of course a well-known result in the theory of probability. Its utility here is twofold. In the first place, it enables us to obtain a specific non-uniform probability density $P(N)$ starting from the readily generated uniform probability $P_0(N)$. Secondly – and more importantly – the presence of the small parameter ϵ enables us to readily identify in all the equations the terms due to the spatial nonuniformity of the suspension. The feature plays a key role in our ability to single out the effects of the spatial non-uniformity.

In order for $P(N)$ to be periodic it is necessary that \mathbf{F} have the same spatial periodicity as the fundamental cell. We take

$$\nabla \cdot \mathbf{F}(\mathbf{y}) = \sin \mathbf{k} \cdot \mathbf{y} \quad (73)$$

where the direction of \mathbf{k} is along one of the sides of the fundamental cell and its modulus k equals 2π divided by the length L of the side of the cell in that direction. With this choice the ensemble average of a generic quantity f is not independent of \mathbf{x} and, due to the linearity of the problem, can be represented over the fundamental cell as

$$\beta_{C,D} \langle f_{C,D} \rangle(\mathbf{x}) = f_{C,D}^0 + \epsilon [f_{C,D}^s \sin \mathbf{k} \cdot \mathbf{x} + f_{C,D}^c \cos \mathbf{k} \cdot \mathbf{x}] \quad (74)$$

with f^0 and $f^{s,c}$ given by the standard Fourier rules:

$$f^0 = \frac{1}{V} \int_{cell} \beta_{C,D} \langle f_{C,D} \rangle(\mathbf{x}) dV = \frac{1}{N!} \int d\mathcal{C}^N P(N) \left[\frac{1}{V} \int_{cell} \chi_{C,D} f_{C,D} dV \right] \quad (75)$$

$$f^s = \frac{2}{V} \int_{cell} \beta_{C,D} \langle f_{C,D} \rangle(\mathbf{x}) \sin \mathbf{k} \cdot \mathbf{x} dV = \frac{1}{N!} \int d\mathcal{C}^N P(N) \left[\frac{2}{V} \int_{cell} \chi_{C,D} f_{C,D} \sin \mathbf{k} \cdot \mathbf{x} dV \right] \quad (76)$$

$$f^c = \frac{2}{V} \int_{cell} \beta_{C,D} \langle f_{C,D} \rangle(\mathbf{x}) \cos \mathbf{k} \cdot \mathbf{x} dV = \frac{1}{N!} \int d\mathcal{C}^N P(N) \left[\frac{2}{V} \int_{cell} \chi_{C,D} f_{C,D} \cos \mathbf{k} \cdot \mathbf{x} dV \right] \quad (77)$$

In particular, one finds

$$\beta_{C,D}(\mathbf{x}) = \beta_{C,D}^0 + \epsilon \beta_{C,D}^s \sin \mathbf{k} \cdot \mathbf{x} \quad (78)$$

7.2 The average heat flux

If we write again $T_{C,D}$ as before in (56), now the problem specification includes 2 vectors, \mathbf{G} and \mathbf{k} and, therefore every numerically calculated vector must be a linear combination of these two. It proves convenient to introduce the two equivalent combinations

$$\mathbf{G}^{\parallel} = (\mathbf{G} \cdot \mathbf{m}) \mathbf{m}, \quad \mathbf{G}^{\perp} = (\mathbf{I} - \mathbf{m} \mathbf{m}) \cdot \mathbf{G} \quad \text{where} \quad \mathbf{m} = \frac{\mathbf{k}}{k} \quad (79)$$

Skipping all the details (which can be found in M. Marchioro & A. Prosperetti, *Proc. R. Soc. Lond.* **455**, 1483-1508, 1999), after proceeding as before we find results that can be written as follows

$$\begin{aligned} \mathbf{q}_m &= -Q^0(\beta_D^0) \mathbf{G} - \epsilon Q^s \mathbf{G}^{\perp} \sin \mathbf{k} \cdot \mathbf{x} \\ &= -(Q^0 + \epsilon Q^s \sin \mathbf{k} \cdot \mathbf{x}) \mathbf{G} + \epsilon Q^s \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \end{aligned} \quad (80)$$

Q^0 is a function of the particle volume fraction β_D and, therefore

$$Q^0(\beta_D) = Q^0(\beta_D^0 + \epsilon \beta_D^s \sin \mathbf{k} \cdot \mathbf{x}) \simeq Q^0(\beta_D^0) + \epsilon \beta_D^s \frac{dQ^0}{d\beta_D} \sin \mathbf{k} \cdot \mathbf{x} \quad (81)$$

A first test of the entire approach is then that one should have the equality

$$Q^s = \beta_D^s \frac{dQ^0}{d\beta_D} \quad (82)$$

The numerical results show that this is satisfied very accurately. Thus, so far, correct to $O(\epsilon)$, we have

$$\mathbf{q}_m = -Q^0(\beta_D) \mathbf{G} + \epsilon Q^s \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \quad (83)$$

We also find, numerically,

$$\nabla T_m = \mathbf{G} - \epsilon H^s \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \quad (84)$$

We can eliminate \mathbf{G} to find

$$\begin{aligned} \mathbf{q}_m &= -Q^0 \left[\nabla T_m + \epsilon H^s \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \right] + \epsilon Q^s \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \\ &= -Q^0 \nabla T_m - \epsilon (Q^0 H^s - Q^s) \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \end{aligned} \quad (85)$$

On setting $\epsilon = 0$ it is evident that $Q^0 = k_{eff}$ is the effective thermal conductivity of the uniform composite. But this is not yet a constitutive relation because it still contains problem-dependent quantities. In our search for another term that can be used to eliminate the ϵ contribution we find that

$$\nabla [\beta_D (T_m - \langle T_D \rangle)] = \epsilon \Lambda \mathbf{G}^{\parallel} \sin \mathbf{k} \cdot \mathbf{x} \quad (86)$$

Thus, we can write a problem-independent relation in the form

$$\mathbf{q}_m = -k_{eff} \nabla T_m + \frac{Q^0 H^s - Q^s}{\Lambda} \nabla [\beta_D (T_m - \langle T_D \rangle)] \quad (87)$$

in which a new ‘‘thermal conductivity’’ arises: a non-uniform composite does not behave like a homogeneous medium with a Fourier-like law of conduction. It can be shown that, if the composite is uniform, $T_m = \langle T_D \rangle$ so that this relation reduces to the previous one (67) as it should.