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Particle Dispersion in a Gas[1]

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The dispersion mechanism of particles in a gas is discussed from the viewpoint of nonequilibrium thermodynamics and kinetic theory. A heuristic equation, based on the quasi-Lorentz model developed by Mason and other workers, for the particle velocity in the presence of a gradient of pressure and temperature is proposed for all values of a parameter s, where s is defined as the ratio of the particle radius r to a multiple of the mean free path, λ, of the gas medium. A schematic calculation demonstrates the conditions under which molecular diffusion could play a role in a realistic atmospheric pollution problem.

KEY WORDS: atmospheric pollution; diffusion coefficients; kinetic theory; nonequilibrium thermodynamics; particulate matter, quasi-Lorentz model; thermal diffusion factor.

1. INTRODUCTION

A heuristic equation for the diffusion of particles in a dilute gas, subjected to gradients of pressure and temperature, and under the influence of gravity is introduced in this paper. The objective is to see when molecular diffusion might be a significant contribution to particle dispersion, even in a convective field. The paper is intended as a tribute to Ed Mason, and, because of this, it is based on some of his ideas. Many of Mason's earlier papers [1] dealt with adroit applications of kinetic theory, and I think this problem would have appealed to his approach and philosophy.

The underpinning of the calculation here is Mason's work on the model quasi-Lorentzian gas [2]. A quasi-Lorentzian gas is a mixture in which the number fraction of one component is very small, but the mass of this component is far greater than the mass of the others. In this discus-

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sion, the system considered is a binary mixture of species a (gas molecules) and p (particles) at temperature T and pressure P such that

$$\begin{aligned} m_p &\gg m_a \\ n_p &\ll n_a \end{aligned} \tag{1}$$

where m_i is the mass of i and n_i is the number density. The number fractions are $x_i = n_i/n$, where n is the total number of particles, and $x_a \to 1$ from Eq. (1). The corresponding mass densities are $\rho_i = m_i n_i$, where $\rho = \rho_a + \rho_p$, with mass fractions $x'_i = \rho_i/\rho$.

The system is taken to be isotropic and the particles to be monodisperse. And although the system has gradients of temperature and pressure, it is assumed to be in local equilibrium and defined thermodynamically. It is not obvious that this assumption is always valid unless the sizes of the mixture components are of the same order, which is not realistic in view of Eq. (1). Accordingly, we first review the limiting cases that are compatible: Case a, in which the mean free path of the gas λ is much smaller than a characteristic particle dimension such as the particle radius r, $r/\lambda \gg 1$; and the antithetical Case b, for which $r/\lambda \ll 1$. For Case a, the local thermodynamic properties of the system are determined by the gas–gas interactions, but the particle motion will be dominated by external forces, such as gravity. Conversely, for Case b, the system approximates a thermodynamic two-component mixture with component a in excess. Hence the properties of the mixture will depend on the dynamics of the gas–particle collisions. Case b is clearly the more interesting in the context of this paper because diffusion forces will affect the particle distribution.

2. DISPERSION

The diffusive flux of a particle can be defined in terms of its velocity $\mathbf{u}_p$ with respect to an external coordinate system. It is better, however, to consider the flux $\mathbf{J}_p$, which is defined with respect to the local center of mass velocity $\mathbf{u}$, where $\rho\mathbf{u} = \rho_a\mathbf{u}_a + \rho_p\mathbf{u}_p$:

$$\mathbf{J}_p = \rho_p(\mathbf{u}_p - \mathbf{u}) \tag{2}$$

The starting point is to write the expression for this flux in the context of nonequilibrium thermodynamics [3]:

$$\mathbf{J}_p = -\frac{L_{pa}}{T}\, grad(\mu_p - \mu_a)_T - \frac{L_{pq}}{T^2}\, grad T \tag{3}$$

where μ_i is the chemical potential of i and L_{pa} and L_{pq} are the phenomenological Onsager coefficients; L_{pa} is the coefficient for diffusion and L_{pq} is the coefficient for the formal coupling between the mass flow of p and the temperature gradient. Transforming the gradient of chemical potential, Eq. (3) becomes, after some manipulation [4–5],

$$\mathbf{J}_p = -\frac{L_{pa}R}{m_a m_p x'_a x'_p W}\left[grad x'_p - W(m_p - m_a)\, x'_a x'_p \frac{gradP}{P} + \frac{L_{pq} m_a m_p x'_a x'_p W gradT}{L_{pa} R T^2} \right] \tag{4}$$

where

$$W = \frac{x'_p}{m_p} + \frac{x'_a}{m_a}$$

and it is assumed that the particles and gas make up an ideal dilute mixture. Defining coefficients by

$$\rho D'_{pa} = \frac{L_{pa}R}{m_a m_p x'_a x'_p W}$$

$$\alpha'_p = W(m_p - m_a)$$

$$\alpha'_T = \frac{L_{pq} m_a m_p W}{L_{pa} R T}$$

gives the equation

$$\mathbf{J}_p = -\rho D'_{pa}\left[grad x'_p - x'_a x'_p \alpha'_p \frac{gradP}{P} + x'_a x'_p \alpha'_T \frac{gradT}{T} \right] \tag{5}$$

which can be connected readily with kinetic theory when reformed in terms of number fractions:

$$n_p \mathbf{u}_p - n_p \mathbf{u} = -nD_{pa}\left[grad x_p - x_a x_p \alpha_p \frac{gradP}{P} + x_a x_p \alpha_T \frac{gradT}{T} \right] \tag{6}$$

where D_{pa} is the kinetic theory diffusion coefficient, α_p is the pressure diffusion factor, and α_T is the thermal diffusion factor [2, 6], also now $\mathbf{u} = (1/n)[n_a \mathbf{u}_a + n_p \mathbf{u}_p]$.

2.1. The Quasi-Lorentzian Limit

In the quasi-Lorentzian limit expressed by Eq. (1), Eq. (6) reduces to

$$n_p\mathbf{u}_p - n_p\mathbf{u} = -n_p\, D_{pa}\left[grad \ln n_p - \frac{m_p}{m_a}\, grad \ln P + \alpha_T\, grad \ln T \right] \tag{7}$$

since $x_a \rightarrow 1$ and $\alpha_p \approx m_p/m_a$. The appropriate quasi-Lorentzian expressions for the coefficients were derived by Mason and Chapman [2] and by Mason [7], who showed that, in the first approximation,

$$nD_{pa} = \frac{3}{16r^3}\sqrt{\frac{2kT}{\pi m_a}} \tag{8}$$

$$\alpha_T = \frac{5\sqrt{2}}{8}\left(\frac{r}{d}\right)^2 \tag{9}$$

where k is Boltzmann's constant and d is the radius of the species a, the gas molecule in this case.

3. VELOCITY OF A PARTICLE IN A GENERAL FORCE FIELD

As implied when the diffusion problem was outlined, there is no satisfactory way to derive a mass flow equation for all values of the parameter r/λ because the transition region between (in our notation) Case a and Case b cannot be defined unambiguously. All attempts to do this, therefore, must ultimately introduce some empiricism [8]. Here we propose a general relation and a general friction coefficient $\hat{\eta}$:

$$m_p n_p \dot{\mathbf{u}}_p = -\hat{\eta}(n_p\mathbf{u}_p - n_p\mathbf{u}) + \mathbf{F}_D + m_p n_p g \tag{10}$$

where $\mathbf{F}_D$ is the diffusive force and $m_p n_p g$ the gravity term. The relation is heuristic, but in the Case a limit, $m_p n_p g \gg \mathbf{F}_D$, it reduces to a Stokes' equation,

$$m_p n_p \dot{\mathbf{u}}_p = -6\pi r\eta(n_p\mathbf{u}_p - n_p\mathbf{u}) + m_p n_p g \tag{11}$$

and the friction coefficient is thus appropriately defined; η is the viscosity of the gas medium. In the Case b limit, however, provided the diffusion forces dominate, the expression becomes

$$m_p n_p \dot{\mathbf{u}}_p = -B(n_p\mathbf{u}_p - n_p\mathbf{u}) + \mathbf{F}_D \tag{12}$$

where now the friction coefficient should be

$$B=\frac{kT}{D_{pa}} \tag{13}$$

Provided that the acceleration $\dot{\mathbf{u}}_p$ becomes zero in a time short compared to the time a particle will travel a mean free path length, the diffusive force is

$$\mathbf{F}_D=-n_p kT\left[grad \ln n_p-\frac{m_p}{m_a} grad \ln P+\alpha_T grad \ln T\right] \tag{14}$$

from Eq. (7).

The most straightforward expression for $\hat{\eta}$ which is a smooth function of the particle radius r and which will approach the Case a and Case b limiting values is

$$\hat{\eta}=\frac{6\pi r\eta B}{[6\pi r\eta+B]} \tag{15}$$

This relation, therefore, is postulated as the general coefficient for Eq. (10).

A small modification to Eqs. (10) and (15) links them more closely with experiment. Some time ago Hanley and Steele [9] studied the flow of a gas through a capillary to determine how the diffusion coefficients varied with respect to the ratio l/λ, where l is the capillary radius. If the ratio l/λ is very large, the flow is Poiseuille flow. If the ratio is small, the flow is Knudsen. If the ratio is intermediate, the flow is known as slip, and Hanley and Steele observed that slip flow corresponded roughly to the region in which $l/\lambda \approx 10$. Clearly the limiting conditions of the capillary flow problem are very similar to the quasi-Lorentzian limits discussed in this paper. The flow, in fact, can be modeled in terms of the Lorentzian variant in which the large particles are fixed in space and act as a membrane [2, 10]. We, therefore, carry the analogy further and define an arbitrary but convenient dimensionless radius whose value should delineate between Case a and Case b, namely

$$s=r/(10\lambda) \tag{16}$$

The diffusion and viscosity coefficients of Eqs. (10) and (15) are now defined in terms of s but the change is trivial, for example, the diffusion coefficient becomes

$$nD_{pa}=\frac{3(10\lambda)^{-2}}{16s^2}\sqrt{\frac{2kT}{\pi m_a}} \tag{17}$$

and so on. [That this parameter s makes sense is reinforced when s is substituted into Eq. (15) and $\hat{\eta}$ plotted against. ln $\hat{\eta}$ varies smoothly, as it should, but the slope changes markedly around $s = 1$. Note that the parameter is a redefinition of the conventional Knudsen number, $Kn = 2\lambda/r$ [8].]

Equation (10) has one final modification: the diffusion term is qualified by a damping factor, $\exp(-s)$ because as $\hat{\eta} \rightarrow 6\pi r\eta$, $\mathbf{F}_D \rightarrow 0$ on physical grounds. Provided, then, that $\dot{\mathbf{u}}_p$ is zero, the equation for the particle dispersion becomes

$$\hat{\eta}(\mathbf{u}_p - \mathbf{u}) = \exp(-s)\, kT\left[grad \ln n_p - \frac{m_p}{m_a}\, grad \ln P + \alpha_T\, grad \ln T \right] + m_p g \tag{18}$$

which is the final expression. The diffusive flow of p will, in principle depend on the gradients of number density, pressure, and temperature, which could either reinforce or counterbalance each other, depending on the sign and magnitude of the gradients. Note, however, that the thermal diffusion factor is positive for the hard-sphere-like particles considered here, but it could be positive or negative for large real molecules, depending on the temperature [6].

3.1. Dispersion in an Atmospheric Temperature Inversion Layer

The paper concludes with a brief and symbolic discussion. A very real problem in Boulder, Colorado, is to understand better the dispersion and distribution of submicrometer-sized pollutants over the city. Like many other cities, Boulder can suffer from a brown cloud when a temperature inversion layer hangs overhead. Inversions are most common on sunny winter days when the ground temperature is around freezing. A typical inversion temperature gradient extends to a height (h) of about 900 m above the surface and is of the order $\Delta T/T \sim 0.13$. The atmospheric pressure at Boulder is about 0.083 MPa and drops to about 0.074 Mpa at the higher elevation. Is the contribution of molecular diffusion significant to the particle dispersion, even though there is a consensus that molecular diffusion would be overwhelmed by convection and turbulence in a real atmosphere? It is, of course, true that the latter factors must dominate in most cases [11]. Nevertheless, there is evidence that molecular diffusion should not be ruled out. For example, there is the historical fact, which goes back at least to Tyndall [12], that a temperature gradient definitely affects the motion and distribution of dust or soot in a gas. And it is well-known that molecular diffusion can couple with convection: a phenomenon that was exploited to extract the uranium isotopes needed to manufacture the atomic bomb.

Consider Eq. (18) and assume (a) that the air is a single-species gas, (b) that the inversion layer is at a steady state, and (c) that the gradients vary along the h-coordinate only and are defined as positive if the higher value is at $h = 0$. Set **u** to zero and vary the ratio s while keeping all other terms in the equation fixed. If the values of the gradient terms are of the order of (or even one order less than) the value of the gravity contribution for a particular choice of s, we can argue as a rule of thumb that a diffusion mechanism should be considered when investigating the dispersion of particles of reduced size s. Given the data in Table I [13], we estimate that diffusion may contribute if $s \leqslant 0.05$ or, in other words, if the particle radii are less than about 50 nm. Particles of this dimension are classed under the general headings of aerosols and small particulate matter [14]. Hence, according to our simple criteria, molecular diffusion is significant to the dispersion of particles of this size. The thermal diffusion term is the interesting contribution since the direction of the temperature gradient (with a positive thermal diffusion factor) implies that the heavier particles will migrate downwards and, hence, reinforce the effects of the pressure gradient and gravity. As an aside, note that the calculations were based on the Boulder elevation approximation for the air mean free path $\lambda = 10^{-7}$ m. But the mean free path will increase substantially with height. At stratospheric heights, the dispersion of even micrometer-sized particles could be strongly influenced by the diffusion mechanism.

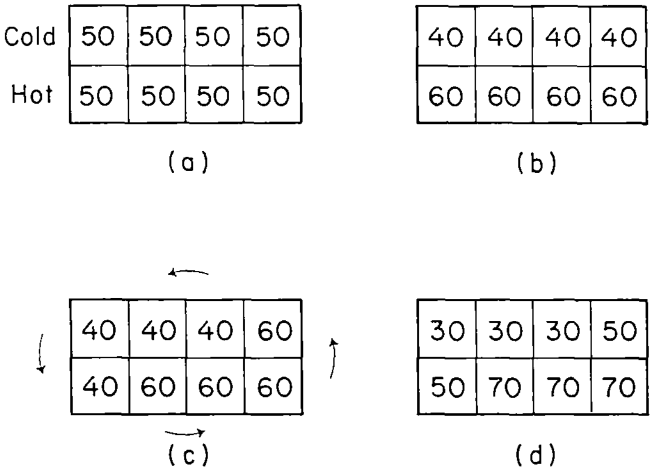
Setting **u** to zero is a severe approximation since it excludes the effects of convection and turbulence from the calculation, but it does not necessarily follow that molecular diffusion would be overruled if these factors were included. The pictorial explanation of Grew and Ibbs [6] illustrates how diffusion and convection may couple. It is as follows. Con-

Table I. Approximate Values of the Parameters of Eq. (18) Corresponding to a Temperature Inversion Above Boulder, CO

Air mean free path, λ	10^{-7} m
Reduced particle size, s, for particles of radius r	$10^{6} r$
Total density, n	10^{25} molecules · m^{-3}
Mass of air molecule, m_a	5×10^{-23} g
Mass of pollution particle, radius, r, and density = 2 kg · m^{-3}	$(4 \times 10^{-12} s^3)$ g
Radius of air molecule, d	10^{-10} m
Viscosity of air, η	2×10^{-3} Pa · s
Average temperature, T	300 K
Average pressure, P	0.08 MPa
Height of the system, h	900 m
Factor $\Delta P\ Ph$	10^{-4} m^{-1}
Factor $\Delta T\ Th$	-2×10^{-4} m^{-1}

sider a two-dimensional system divided into volume segments, each in local equilibrium. Figure 1 displays eight of the segments. The concentration of a given component is set constant throughout the system at an initial time, at 50% for convenience (Fig. 1). A temperature gradient is imposed on the system. The gradient will induce convections but will also set up the mechanism of thermal diffusion. Coupling will occur if the diffusion of particles from the segments can take place faster than convection can displace the segments with respect to each other. For example, suppose the system diffuses to the state shown in Fig. 1b. Convection acts and the segments are dislocated (Fig. 1c). Then diffusion leads to Fig. 1d. Convection follows, and so on. Using the numbers in Table I, and using that a dimension of a segment in a real atmosphere should be at least $(10 s\lambda)$ m, we estimate that intersegmental diffusion would take place over 10^{-2} to 1 s. Hence, unless the segments are displaced by rapid and violent turbulence or convection, molecular diffusion can well be the trigger for an ultimately large particle gradient.

In conclusion, how convection and molecular diffusion combine to influence particle dispersion in a system as complex as the real atmosphere is a very difficult problem and we have not addressed it quantitatively. But we have at least demonstrated that molecular diffusion should not be dismissed out of hand.



Cold	50	50	50	50
Hot	50	50	50	50

(a)

40	40	40	40
60	60	60	60

(b)

40	40	40	60
40	60	60	60

(c)

30	30	30	50
50	70	70	70

(d)

Fig. 1. Schematic pattern showing the combined effect of diffusion and convection. The system is divided into eight segments, initially all with uniform composition (a). Diffusion causes a separation of one component, represented by (b). Convection displaces the segments (c), allowing diffusion to enhance the separation (d).

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