

## A Brief Guide to Appendix F

Appendix F appears in a popular-level book intended to illustrate, among other things, the depth and fullness of science and the devotion of most scientists to the discovery of universal truth. Because this appendix includes a summary from scratch of elementary statistical mechanics, it is somewhat lengthy and tedious to read, and unnecessary to read completely if one is already familiar with the topic.

However, some of the early material is vital to later, original material because the method used in deriving novel results is illustrated and justified in deriving the well-known canonical distribution. This method is called the *Maxent* method, short for *maximization of system information entropy subject to constraints characteristic of a system type, or even of a particular system*. Maxent provides a most probable distribution characterizing each type of system. It surely applies to equilibrium systems and it is supposed that it also applies to stationary systems that are not in equilibrium. It may well even apply to quasi-stationary systems. In every case, the resulting distribution corresponds to maximum system information (Boltzmann) entropy and, therefore, presumably to the most probable system state. Maxent thus appears to provide a powerful capability for characterizing nonequilibrium systems and processes. Theories like the present one will provide tests of the principle.

In Section 2 the Boltzmann entropy and Boltzmann's H theorem are described (old news). Section 3 contains a summary of results of the Maxent method for various system types. Sections 4 and 5 describe derivations of the microcanonical and canonical distributions. None of these results are original but Section 5 is useful in introducing and illustrating the Maxent method.

Original results start in Section 6 and continue through Section 8 based on results derived in Section 6. The core physics of the paper are thus described in Section 6 in which the velocity distribution of dilute (perfect) gas molecules is derived for a gas containing a stationary, nonuniform, temperature field. As in Section 5, the problem is posed and solved. Novelty of Section 6 lies in the fact that the local velocity distribution of molecules in a closed, stationary-but-nonequilibrium system applies at specified temperature *and* at specified temperature gradient.

The two key results of Section 6 are the nonequilibrium velocity distribution in a temperature gradient, given by Equation [F4], and a balancing *counterflow velocity* required to conserve mass or number of molecules, given by Equation [F7a]. These are the core physics, the critical results, used in the remainder of the paper.

In Section 7 the standard problems of heat, momentum, and mass transfer are addressed. While the problems are standard, the results are not. In the heat transfer result two coupled terms appear, one proportional to temperature gradient and one to concentration gradient. This result predicts the Dufour or diffusion thermo effect. This effect has previously been invisible in any treatment of such simplicity. One virtue of the method is therefore that it faithfully represents complex processes by means of a simple theory. And, when compared to "rigorous" or Chapman-Enskog theory, simplicity is a highly desired quality because some results of the Chapman-Enskog theory are very complex and appear to be fundamentally incorrect, a property previously lost in their complexity.

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Section 7 also contains results for momentum and mass transfer. The former result, Equation [F9], does not differ fundamentally from previous results but the latter does. In Equations [F11] we obtain a pair of coupled transport equations, one for each component of a binary mixture, which contain all coefficients explicitly defined. This result is new, with previous results having been misdirected by assumptions dating back to the origins of Chapman-Enskog theory. Such assumptions and much complexity are avoided here by using dependent variables  $\zeta_\phi(z)$ ,  $n(z)$ , and  $T(z)$ , with  $\zeta_\phi$  the local number fraction of species- $\phi$  molecules,  $n(z) = P/kT$  the local number concentration of all molecules, and  $T(z)$  the local temperature. Then, local concentration of species- $\phi$  molecules,  $n(z)\zeta_\phi(z)$ , contains its complete temperature dependence in  $n(z)$  and its complete concentration dependence in  $\zeta_\phi(z)$ . Complexity and confusion in writing gradients are thus removed, avoiding past errors.

In Equations [F11] both molecular and thermal diffusion emerge, the first due to a concentration gradient and the second due to a temperature gradient. Again we find the simple theory producing a subtle effect, in this case the Soret or thermal diffusion effect, invisible in other theories of comparable simplicity. And again the coefficients for coupled molecular diffusion and thermal diffusion are explicitly defined. These results replace long-standing, widely-used standards that are 50 years old, but incorrect in that coefficients are either incorrectly or not defined.

Diffusion and thermal diffusion are the worst-predicted processes of the rigorous theory. Errors in past analyses have been corrected here by (1) using quantities  $n(z)$ ,  $\zeta_\phi(z)$ , and  $T(z)$  as variables in the transport equations, (2) including transient and stationary counterflow velocity necessary for correct characterization of all transport, and (3) basing the theory on an apparently reliable foundation: maximization of system information entropy with required physical constraints. Indeed, this last feature may be regarded as the fundamental cause of all transport and many other nonequilibrium phenomena and equilibrium properties.

Finally the thermophoresis and diffusiphoresis processes are addressed, the former being migration of individual particles in a temperature gradient in a suspending gas and the latter their migration in a concentration gradient in the gas.

To predict phoretic migrations, the molecular velocity distribution [F4] must be adapted to apply to individual, isolated particles (or molecules) instead of numerous, distributed gas molecules. The adaptation is simple and intuitive and provides correct results, exact within 50 % at worst and maybe outright exact. While molecules are driven by thermal diffusion in the direction of the temperature gradient, suspended particles are driven in the opposite direction. For particles suspended in a gas mixture, a stationary migration of particles is proportional to concentration gradient of a gas species thus predicting the diffusiphoretic effect. One final result, Equation [F20], gives migration velocity of a suspended particle due to both a temperature and a concentration gradient, a combined phoretic velocity.

That all these generally-applicable results, previously underived with all their coefficients explicitly defined, are derived directly from a simple molecular velocity distribution is rather remarkable and, if they agree with observation, they will serve to support the validity of the nonequilibrium velocity distribution in particular and the Maxent method in general.

## Appendix F

### Thermodynamics, Statistical Mechanics, and Kinetic Theory

#### 1. Thermodynamic Laws, Systems, and Entropy

In Chapter 10 we described the first law of classical or macroscopic thermodynamics as the conservation of energy in a system in which heat  $Q$  is recognized as a form of energy. In its most general form the *first law of thermodynamics* is written

$$Q = \Delta E + m_{\text{in}} \times E_{\text{in}} - m_{\text{out}} \times E_{\text{out}} - W,$$

where  $Q$  is heat addition to the system,  $\Delta E$  is energy increase of the system,  $m_{\text{in}}$  and  $m_{\text{out}}$  are masses added to and extracted from the system,  $E_{\text{in}}$  and  $E_{\text{out}}$  are the energy contents per unit mass of the added and extracted masses, and  $W$  is work energy extracted from the *thermodynamic system*.<sup>1</sup> This form of the law applies for an *open system* in which mass, heat, energy, and work may all be exchanged. For a *closed system*, no mass exchange occurs and the law applies but with  $m_{\text{in}} = m_{\text{out}} = 0$ . For an *isolated system*, no mass or heat or energy or work exchange occurs. However, energy may be internally converted into heat for which process  $\Delta E = \Delta E_i + Q_i = 0$ .

We also mentioned in Chapter 10 that Rudolf Clausius *et al* discovered an equilibrium-state property of a system that he eventually named *entropy*. Change in entropy of a system due to heat  $Q$  transferred to the system is  $\Delta S = Q/T + I$ , where  $T$  is the absolute temperature of the heat (source) and  $I$  is the irreversibility of the process due to, say, friction or electrical resistance or .... In ideal processes  $I = 0$  and  $\Delta S = Q/T$ , the only classical-thermodynamics type of process in which entropy change is exactly defined. For a real process wherein  $I \geq 0$  we write  $\Delta S \geq Q/T$ .

Clausius stated the *second law of thermodynamics* as follows: “No spontaneous process in an isolated system causes system entropy to decrease.” This law has been stated in other forms and we soon consider a famous one due to L. Boltzmann.

The universe exemplifies an *isolated system*, i.e., no transfer of energy, work, heat, or matter to or from the system. In such systems, evolution toward maximum entropy proceeds by internal processes by which, in the vicissitudes of spontaneous energy fluctuations even in the vacuum, some energy is inexorably converted to heat, a form of energy from which there is never a full or reversible return to any other. This universal, at-least-partially mono-directional process is relentless in its effect: isolated systems ever evolve toward their only possible stationary or equilibrium state, referred to as a “heat-death,” in which system entropy is maximized and all system energy is unusable heat.<sup>2</sup> Clausius’ (and Boltzmann’s) statement conveys the relentless nature of entropy production in spontaneous generation and exchange of heat.

Entropy extended the scope of thermodynamics, especially beginning in the 1870s when Austrian physicist Ludwig Boltzmann (1844-1906) began developing powerful statistical mechanics thereby extending James Clerk Maxwell’s introduction of statistical methods to physics in his 1859 and 1864 kinetic theories of gases.

Traditional classical thermodynamics considers *macroscopic* characterization of systems by their *bulk* properties, such as system volume  $V$ , pressure  $P$ , and energy  $E$ . But in statistical mechanics we seek deeper understanding at a more fundamental, *microscopic* level in characterization of systems by *atomic* (or even subatomic) properties, such as atom velocities. Moreover, we seek a methodology in statistical mechanics useful for small numbers of atoms and for nonequilibrium systems, possibilities not contemplated in traditional, macroscopic thermodynamics.

## 2. Entropy in Statistical Mechanics

Throughout Boltzmann's life most scientists held a preconception against the atomic theory of matter (illustrated by J. J. Waterston's experience described in Appendix A). Continuum theories of matter and energy were favored as superior to atomic theories. Moreover, since Newton's mechanics are fully reversible in time, i.e., any solution for forward flowing (positive) time applies equally for backward flowing (negative) time, physicists objected to the concept of a thermodynamic property, entropy, that only increases in time until it reaches a stationary, maximum value. How could such a process be consistent with the fully reversible mechanics of the atoms involved? To justify the atomic-molecular theory of matter and the existence of an entropy-like property in time-reversible mechanics, Boltzmann sought and discovered a gas property he called  $H$  that continually decreases in time until it reaches a stationary, minimum value. *Boltzmann's H-theorem* states that the time-rate-of-change of  $H$  is less than or equal to zero, i.e.,  $dH/dt \leq 0$ , with  $H$  defined by<sup>3</sup>  $H = \sum_j p_j \log_e(p_j)$ . In this sum, index  $j$  indicates a *system state*. The sum includes all states accessible to the system, corresponding to many *microscopic configurations* or *microscopic states* or *microstates* consistent with its bulk-properties state (i.e., everything we know about the system). Each such microstate is assumed to be equally probable. The probability  $p_j$  that the system is in its  $j^{\text{th}}$  discrete microstate is regarded as equal to the fraction of an *ensemble* – a huge number of (imaginary) identical replications of a prototype system – in microstate  $j$  or the fraction of time the prototype system is in microstate  $j$ .

In quantum statistical mechanics all possible exchanges of identical atoms are counted as a single configuration (page 573), such exchanges being conceptually beyond any capability to detect. In addition, when system energy does not vary with position of an atom in system volume  $V$ , many geometric configurations form different but bulk-property-equivalent states. The number of possible microstates of a system is usually much larger than the number of atoms in the system.<sup>4</sup>

By its above definition and because probability  $p_j$  must satisfy  $0 \leq p_j \leq 1$  and  $p_j \log_e(p_j) = 0$  when  $p_j$  is zero or one and is otherwise negative,  $H$  is always negative. Boltzmann's  $H$  and entropy  $S$  for a dilute (or perfect) gas are related by

$$S = -kH = -k \sum_j p_j \log_e(p_j) \geq 0,$$

with  $k$  the Boltzmann constant. Boltzmann's version of the second law, derived from his reversible-mechanics analysis of the evolving state of perfect-gas atoms, is that isolated-system entropy only increases until it reaches a maximum value, i.e.,

$$dS/dt \geq 0.$$

In 1902, American engineer-physicist Josiah Willard Gibbs (1839-1903) entered the statistical-mechanics story.<sup>5</sup> He introduced the powerful concept of the ensemble as a superior foundation of statistical mechanics (see endnote 11 of Chapter 2) and utilized it to correct and extend Boltzmann's results. While Boltzmann ignored atomic interactions, Gibbs included them. Thus, Boltzmann's results apply only for a perfect gas while Gibbs' sometimes identical expressions, such as the one for entropy of a system, are derived from the superior conceptual basis that allows their application to real gases, liquids, and solids in which strong molecular interactions occur.<sup>6</sup>

To illustrate the nature of entropy and the value of Gibbs' approach, consider a closed thermodynamic system containing a solution in which a crystal (with strong atomic bonding) is forming. In a closed system, heat and energy but not matter may transfer into or out of the system.<sup>1</sup> A crystal represents a highly ordered state with the crystal atoms purified and fixed in a regular structure. Before crystallization, solute atoms are neither purified nor fixed (distinguishable) but are mixed and randomly drifting about in the solution. When crystal growth is slow and system temperature remains nearly fixed, the crystallization is essentially reversible. Nevertheless, *system entropy decreases in such spontaneous crystallization*, a claim justified in endnote 7.

What happened? Isn't entropy supposed to increase in spontaneous processes? Have we encountered an enigma? A reader might say "We were led to believe" (by the reader's induction) "that a spontaneous process should always give a positive  $\Delta S$ , either when heat is indirectly generated by inefficiency (irreversibility) in use of energy or generated directly from energy. But  $\Delta S$  is negative in this crystallization-of-solute-atoms illustration! What kind of swindle is going on here?"

No one is being swindled because the system is not isolated. For the closed system in our illustration no net internal-heat increase occurs. Heat slowly generated by crystallization *in* the system is slowly transferred *out of* the system so that system entropy decreases. But entropy of the universe inevitably increases by more than system entropy decreases because, for outward heat flow, the system-boundary temperature  $T_b$  is slightly smaller than internal system temperature  $T$  and environmental (universe) entropy increase  $\Delta S_e = Q/T_b > |Q/T| = |\Delta S|$ . In applying thermodynamics, and especially the second law, it is essential to take account of system *type* as well as the process. Otherwise one quickly finds him- or her-self in deep tapioca (pudding).

Our crystallization example illustrates a general principle: *entropy change represents change in information required to fully specify a system state*. Specifying a system of atoms fixed in a regular crystal structure requires less information than atoms randomly drifting in solution. In general, uncertainty in system state increases with heating ( $Q = T\Delta S > 0$ ) and *vice versa* with cooling. Heating extends the range of accessible microstates thus requiring more information to specify the system. Cooling reduces accessible microstates, ultimately to a single, ground state. But with increase of energy content of matter or space, energy content of other matter or space decreases, so a general implication of heating or cooling is not obvious except within an isolated system such as the universe. In information and communication theory an *information entropy* identical to Boltzmann's entropy emerges and provides an identical function

in specifying an information-system state.<sup>8</sup> Entropy, then, is a measure of information required to specify a rather-generally-defined-system state.

Using entropy, consequences of exchange or use of heat and related processes in systems may be characterized in illuminating ways. Clausius' and Boltzmann's versions of the second law for isolated systems and their variations for other systems introduce subtle but powerful means for analyzing thermodynamic processes and predicting conditions when they occur naturally and spontaneously.

The nature of thermodynamics and use of entropy with its common pitfalls are further indicated or implied in the microscopic-scale theories and mathematical tools provided by statistical-mechanics or -thermodynamics we next describe.

### 3. Characteristic Properties and Equilibrium Distributions

We have already described three types of thermodynamic systems. (1) In an isolated system (no transfer of energy or matter), increase in system entropy  $dS$  occurs when incremental heat  $dQ_i = -dE_i \cong TdS$  is internally generated at absolute temperature  $T$  at cost of internal system energy  $dE_i$ . (2) In a closed system (energy or work but not matter may enter or leave the system), heat may be generated in or transferred into or out of the system causing system entropy change  $\Delta S \cong Q/T$ . (3) In an open system, entropy may additionally be changed by transfer of matter into or out of the system. The most common cause of confusion and error connected with entropy occurs in use of correct principles or expressions but for a wrong system type.

Therefore, in our sketch of thermodynamics we utilize *a principle valid for all systems* and already suggested by the second law: *a stationary, equilibrium, or most-probable state occurs at a maximum of system information entropy subject to constraints characteristic of each type of system.*<sup>9</sup> Maximization of system entropy or "Maxent" subject to these characteristic constraints or *fixed properties* results in a *characteristic thermodynamic property* for each type of system which is minimum at equilibrium, providing a useful criterion for the equilibrium or most-probable state.

Characteristic properties for various system types, determined by maximization of system entropy subject to the fixed-properties constraints, are listed in the following table.<sup>9,10</sup> For isolated systems of volume  $V$ , containing  $N$  atoms and fixed system energy  $E$ , the characteristic property is  $-S$  so that equilibrium corresponds to maximum  $S$ . For closed systems at fixed volume  $V$ , containing  $N$  atoms at absolute

System Type	Traditional Name in Statistical Mechanics	Fixed Properties	Characteristic Function (Partition Function)	Characteristic Property
Isolated	Microcanonical	$N, V, E$	$Z = \Omega$ (see text)	$-S = -k \log_e(Z)$
Closed	Canonical	$N, V, T$	$Z = \sum_j \exp(-\beta E_j)$	$F = -kT \log_e(Z)$
Open	Grand Canonical	$\mu, V, T$	$Z = \sum_i \sum_j \exp(\beta[n_j \mu - E_i])$	$-PV = -kT \log_e(Z)$
Open	Isothermal-Isobaric	$N, P, T$	$Z = \sum_i \sum_j \exp(-\beta[PV_j + E_i])$	$G = -kT \log_e(Z)$

system temperature  $T$ , the characteristic property is the *Helmholtz free energy* defined as  $F = E - TS$  so that equilibrium corresponds to minimum  $F$ . For open systems at fixed  $V$ ,  $T$ , and *chemical potential*  $\mu$  (Greek “mu” =  $\mu = G/N$ ) the characteristic property is  $-PV$ , with  $P$  the pressure, so that equilibrium corresponds to maximum  $PV$ . For open systems at fixed  $N$ ,  $P$ , and  $T$ , the characteristic property is the *Gibbs free energy* defined by  $G = E + PV - TS$  so that equilibrium corresponds to minimum  $G$ .

Let distribution  $\mathbf{p} = \{p_1, p_2, p_3, \dots, p_j, \dots\}$  be defined as the *probability distribution* of a system over its possible discrete *quantum states* denoted by quantum number  $j = 1, 2, 3, \dots, j, \dots$  for which each state has discrete system energy  $\mathbf{E} = \{E_1, E_2, E_3, \dots, E_j, \dots\}$ . Specification of *vectors* (i.e., quantities containing multiple values or elements)  $\mathbf{p}$  and  $\mathbf{E}$  statistically specifies the *microscopic state* of a system, i.e., a complete description of its statistical distribution over exact properties on a microscopic, and therefore also macroscopic, level of detail. In contrast, specifying only bulk properties such as  $N$ ,  $V$ , and  $E$  or  $T$  specifies only the *macroscopic state* of the system, i.e., its state fully defined on only a bulk or macroscopic level of detail.

To derive an equilibrium distribution vector  $\mathbf{p}$  we employ the above-stated “Maxent” principle that at equilibrium a system’s Boltzmann or information entropy is a maximum subject to imposed constraints (or, equivalently, the characteristic system property is minimum). We derive distribution  $\mathbf{p}$  for both isolated and closed systems as illustrations of statistical-mechanics methodology for all systems.

In the following illustrations we utilize important contributions of Boltzmann, Gibbs, American physicist Edwin T. Jaynes (1922-1998), and many others.<sup>9</sup> While Boltzmann and Gibbs lived in the age of classical physics, we use the more correct quantum physics in our illustrations but include classical-physics results when valid. In the interest of simplicity and brevity, we must ignore many interesting details.

#### 4. Equilibrium or Most-probable Distribution for the Isolated System

The isolated system has characteristic property  $-S$  so its most probable state occurs at maximum  $S$  (equivalent to minimum  $-S$ ) subject to fixed  $N$ ,  $V$ , and  $E$ . This agrees with the statements of Clausius and Boltzmann that maximum  $S$  corresponds to the stationary, equilibrium condition or  $dS/dt \geq 0$ . Thus, we seek the distribution  $\mathbf{p}$  that maximizes system entropy subject to fixed  $N$ ,  $V$ , and  $E$ .

For an isolated system with  $N$ ,  $V$ , and  $E$  fixed, many (imagined) macroscopically-identical replications of the system (the Gibbs ensemble of the system) contain many different microscopic *configurations* or *states*, each having the same macroscopic state, i.e., identical macroscopic or bulk properties. Each microstate, being equally consistent with the known bulk properties, is regarded as equally probable, a fundamental assumption in statistical mechanics called *the assumption of equal a priori probabilities*. Let  $\Omega$  (upper case Greek “omega”) be the *number of microstates* giving  $N$ ,  $V$ , and  $E$ . Thus,  $\Omega$  is a measure of the degree of ignorance of the system’s microstate. That is, the probability of observing any one microstate is  $\mathbf{p} = \{p_1 = p_2 = \dots = p_j = 1/\Omega\}$  and the information entropy of the ensemble is

$$S = -k \sum_{j=1}^{\Omega} p_j \log_e(p_j) = -k \sum_{j=1}^{\Omega} (1/\Omega) \log_e(1/\Omega) = k \log_e(\Omega).$$

But an ensemble is, equivalently, a single system at many different times. Thus, an *ensemble average of a system property is a time average of the property*<sup>11</sup> and  $S$  is the *experimental system entropy*. When  $\Omega = \exp(S/k) = 1$ , the system microstate is fully known and  $S = 0$ . At large number of system microstates  $\Omega$  the system microstate is poorly known. That is, entropy of an isolated system, even one with fully known bulk properties  $N$ ,  $V$ , and  $E$ , is a measure of uncertainty in its microstate.

Equation  $S = k \log_e(\Omega)$  is *Boltzmann's principle*, so named by Albert Einstein even though it was first written by Max Planck in 1906, the year Boltzmann died. This equation was carved on Boltzmann's headstone in the Central Cemetery in Vienna.

### 5. Equilibrium or Most-probable Distribution for the Closed System

Consider now an ensemble for a closed system of fixed  $N$ ,  $V$ , and  $T$ . A system energy  $E_j$  may vary between different accessible  $E_j$  values because system energy varies over the ensemble systems or in one system over time with mean variance  $\sigma_E^2$ . (We shall shortly write an expression for  $\sigma_E^2$ .) A description of system-quantum-state distribution  $\mathbf{p}$  must include dependence on  $T$  and  $E_j$ , with  $E = \langle E \rangle = \sum_j p_j E_j$  the average or "expectation value" of the prototype-system energy. We maximize the information entropy of the ensemble subject to this energy constraint ( $E = \sum_j p_j E_j$ ) and "normalization" ( $\sum_j p_j = 1$ ) to find the most-probable distribution  $\mathbf{p}$  for the ensemble of systems over their accessible states consistent with the known bulk properties of the prototype system (everything we actually know about the system). We find the Maxent condition using Lagrange's method of undetermined multipliers.<sup>12</sup> In Lagrange's method we form a sum  $\Lambda$  (upper case Greek "lambda") containing the quantity to be maximized (information entropy) and the constraints to be applied, each multiplied by a Lagrange multiplier  $\lambda_i$  (lower case Greek "lambda" sub  $i$ ),

$$\Lambda = -k \sum_j p_j \log_e(p_j) + \lambda_1 \{\sum_j p_j - 1\} + \lambda_2 \{\sum_j p_j E_j - \langle E \rangle\}.$$

By Lagrange's method, the Maxent or most-probable distribution  $\mathbf{p}$  occurs when

$$\partial \Lambda / \partial p_j = 0 \quad \text{for all } j \quad \text{and} \quad \partial \Lambda / \partial \lambda_i = 0 \quad \text{for } i = 1 \text{ and } 2.$$

Distribution  $\mathbf{p}$  must therefore satisfy

$$-k \{\log_e(p_j) + 1\} + \lambda_1 + \lambda_2 E_j = 0 \quad \text{or} \quad p_j = \exp(-\alpha - \beta E_j),$$

with new constants  $alpha = \alpha = 1 - \lambda_1/k$  and  $beta = \beta = -\lambda_2/k$ . The first constraint requires that  $\exp(-\alpha) \sum_j \exp(-\beta E_j) = 1$  from which  $\exp(\alpha) = Z = \sum_j \exp(-\beta E_j)$  and the maximally-probable (equilibrium) distribution  $\mathbf{p}$  is, for every state  $j$ ,

$$[F1] \quad p_j = \exp(-\beta E_j) / Z.$$

The value of  $\beta$  is determined using the energy constraint  $\sum_j p_j E_j = \langle E \rangle$  together with entropy  $S = -k \sum_j p_j \log_e(p_j)$  and Helmholtz free energy  $\bar{F} = E - TS$ . We write

$$\begin{aligned} F = E - TS &= \sum_j E_j \exp(-\beta E_j) / Z + kT / Z \sum_j \exp(-\beta E_j) \{\log_e[\exp(-\beta E_j)] - \log_e(Z)\} \\ &= \langle E \rangle - \beta kT \langle E \rangle - kT \log_e(Z). \end{aligned}$$

But  $F$  and  $E$  are independent thermodynamic properties; the result holds if and only if

$$\beta = 1/kT \quad \text{and} \quad F = -kT \log_e(Z).$$

The most-probable or equilibrium distribution  $p$  for a closed system is, for every  $j$ ,

$$p_j = \exp(-E_j/kT) / Z, \quad \text{with} \quad Z = \sum_j \exp(-E_j/kT).$$

$Z$  is called the *partition function*. It describes the partitioning of ensemble systems over their accessible energy states. When the system is one molecule,  $Z$  describes the partitioning of ensemble molecules over their accessible energy levels.  $Z$  may be evaluated by replacing summation with integration using the equality (page 202)  $dx dp_x dy dp_y dz dp_z = h^3$  to obtain the  $\mu$ -space (“mu”-space is 6-dimensional single-molecule space) element  $h^3 = dx dy dz dp_x dp_y dp_z$  with state- $j$  energy

$$E_j = E_{j \text{ translation}} + E_{j \text{ internal}} + 1/N \sum_{k \geq j} \sum_{m \geq n} \sum_n \phi_{mnjk}(r_{mn}), \quad \text{with} \quad \phi_{nnjj}(r_{nn}) = 0.$$

$E_{j \text{ translation}} = (p_x^2 + p_y^2 + p_z^2)/2m$ ,  $E_{j \text{ internal}}$  is energy contained in rotation, vibration, and electronic excitation of a molecule, and  $\phi_{mnjk}(r_{mn})$  is the atomic interaction potential energy for atom pair  $j$ - $k$ , in which atom- $n$  in molecule  $j$  is separated from atom- $m$  in molecule  $k$  by  $r_{mn}$ , with  $m$  and  $n = 1, 2, 3, 4, \dots$ . For dilute, noble-gas atoms,  $E_{j \text{ internal}} = 0$  for absolute temperature  $T < 10,000$  K and  $\phi_{mnjk}$  is negligible. For a single such atom

$$Z_1 = h^{-3} \int_{\text{over volume } V} dx dy dz \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp\{-\beta(p_x^2 + p_y^2 + p_z^2)/2m\} = V (2\pi mkT/h^2)^{3/2}.$$

When  $\phi_{mnjk}$  is negligible, the  $N$  gas atoms of the system behave independently (except during brief collisions) in system volume  $V$  so that the partition function is  $Z = Z_1^N$  or

$$Z = \sum_j \exp(-E_j/kT) = \{(2\pi mkT/h^2)^{3/2} V\}^N / N!.$$

$N!$  ( $N$  factorial) is introduced to obtain the correct quantum statistics in the classical limit, i.e., to correct for  $N!$  exchanges of  $N$  identical atoms giving the same quantum microstate. For interacting molecules (non-negligible  $\phi_{mnjk}$ ),  $Z$  is more complicated.

Partition function  $Z$  fully characterizes the equilibrium-system state, i.e.,

$$P = 1/\beta \partial \log_e(Z) / \partial V, \quad E = -\partial \log_e(Z) / \partial \beta, \quad F = -kT \log_e(Z), \\ S = -\beta^2 \partial [k/\beta \log_e(Z)] / \partial \beta, \quad \text{and} \quad C_v = k\beta^2 \partial^2 [\log_e(Z)] / \partial \beta^2 = k\beta^2 \sigma_E^2,$$

with  $P$  the system pressure,  $C_v$  its specific heat at constant system volume  $V$ , and  $\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$  the *mean variance in fluctuations of system energy*  $E$ .

Mixing of discrete and continuous variables in the preceding derivation and a following one is not consequential for the usual case when  $N$  is large.

The above distribution  $p$  is justified only for the equilibrium state because we have invoked a thermodynamic relation to evaluate  $\beta$ . While thermodynamics strictly applies only to stationary, equilibrium systems, we suppose that the Maxent or maximum-entropy-at-most-probable-distribution principle may be used to determine most-likely, stationary distributions over accessible states for stationary, nonequilibrium systems as well. Adopting this principle to define a most-likely distribution in nonequilibrium systems, wherein deviations or fluctuations

from equilibrium may be neither rare nor relatively small, provides probability distributions over even rarely-populated microscopic states.<sup>13</sup> Characterization of nonequilibrium systems allows characterization of nonequilibrium processes and provides most-probable *transition pathways* over an energy or other barrier inhibiting formation of a new equilibrium state as it becomes more stable than a previously more-stable one. Common transport processes and most-probable process pathways and even rate constants for transition processes have been and can be determined from such distributions, capabilities beyond the scope of equilibrium thermodynamics. Example processes so characterized by statistical mechanics include transport of heat, momentum, and mass, phase-change nucleation kinetics, such as formation of droplets or crystals in vapors, liquids, or solids, and chemical reactions.<sup>13</sup>

## 6. Velocity Distribution of Gas Particles in a Temperature Gradient

We illustrate the utility of statistical mechanics by deducing a microscopic, statistical, *nonequilibrium velocity distribution for gas molecules* (that is, for atoms, molecules, and particles suspended in a gas). Nonequilibrium systems lie beyond the scope of thermodynamics. In his 1859 and 1864 kinetic theories of gases, James Clerk Maxwell deduced the equilibrium velocity distribution of gas atoms and molecules. While his methods are direct and elegant, they only apply for gases in equilibrium. But nonequilibrium gases can be in a stationary state characterized by a stationary distribution. Using Maxent with quantum and classical statistical mechanics we deduce the molecular velocity distribution for a one-species gas and for all species in a multicomponent gas mixture in a stationary temperature gradient.

Consider a closed system containing  $N$  particles of dilute or perfect gas in volume  $V = A \times L$ , with  $A$  the uniform,  $x$ - $y$ -plane cross section of the system of  $z$ -direction height  $L$  lying between  $z = 0$  and  $z = z_1 = L$ . We impose a  $z$ -direction temperature gradient  $\gamma_T$  (Greek “gamma” sub  $T$ ) =  $(dT/dz)_z$  so that gas temperatures at altitudes  $z \pm \delta$  (Greek “delta”) for small  $\delta$  are  $T(z \pm \delta) = T_{z \pm \delta} = T_z (1 \pm \delta \gamma_T / T_z)$ . Likewise,  $n(z \pm \delta) = n_{z \pm \delta} = n_z (1 \mp \delta \gamma_T / T_z)$ . We assume gas pressure to be  $P = n_z k T_z = n(z) k T(z)$  with  $n_z$  the local *number density* of all gas particles at altitude  $z$ ,  $T_z$  the temperature at the same altitude, and  $k$  the Boltzmann constant. For mechanical stability we require uniform pressure  $P$ , i.e., an *isobaric* system.

The *probability* any selected gas particle is between planes  $z$  and  $z+dz$  is

$$p(z) dz = n_z A dz / N = PV / NkT_z dz / z_1 = \langle T \rangle / T_z dz / z_1.$$

*Probability density*  $p(z)$  is probability per unit altitude  $z$  (or, in other cases, per unit change in another property, e.g., a molecular velocity component  $u$  written  $p(u)$ ).

Average kinetic energy of a species- $\phi$  gas molecule at  $z$ ,  $\langle \epsilon_{\phi z} \rangle$  (Greek “epsilon” sub “phi”  $z$ ), is due to random-thermal and systematic motions,  $u, v, w - V_{\phi z}$  and  $V_{\phi z}$ , i.e.,

$$\langle \epsilon_{\phi z} \rangle = m_{\phi} \langle u_{\phi}^2 + v_{\phi}^2 + (w_{\phi} - V_{\phi z})^2 \rangle / 2 + m_{\phi} V_{\phi z}^2 / 2 = 3kT_z / 2 - m_{\phi} \langle w_{\phi} \rangle V_{\phi z} + m_{\phi} V_{\phi z}^2,$$

where index  $\phi = 1, 2, 3, \dots$  indicates the gas-molecule species of mass  $m_{\phi}$ . Then gas kinetic energy due to random thermal motions of each species is  $3kT_z / 2$ . This

assumption defines local, nonequilibrium-gas temperature  $T_z$ .<sup>14</sup>

We impose two constraints on each gas-molecule species at every altitude  $z$ .

(i) The sum of probabilities of system state  $j$  over all possible  $j$ -states equals one,

$$[F2a] \quad \sum_j p_{\phi j} = 1.$$

(ii) Average energy of a molecule having random, thermal motions  $u, v, w - V_z$  and systematic motion  $V_z$  is

$$[F2b] \quad \sum_j p_{\phi j} \epsilon_{\phi j} = \langle \epsilon_{\phi z} \rangle = 3kT_z/2 - m_{\phi} \{ \langle w_{\phi z} \rangle V_{\phi z} - V_{\phi z}^2 \}.$$

Another constraint, constant total *number flux* of gas particles in the  $\gamma_T$  (or  $z$ ) direction

$$[F2c] \quad j_{z \text{ total}} = n_z \sum_{\phi} \zeta_{\phi z} \{ \sum_j p_{\phi j} w_{\phi j} - V_{\phi z} \} = n_z \sum_{\phi} \{ \zeta_{\phi z} \langle w_{\phi z} \rangle - V_{\phi z} \} = C,$$

is imposed later. Local number density of all gas species combined is  $n_z$  and local *number fraction* of species- $\phi$  molecules at  $z$  is  $\zeta_{\phi z}$  (Greek “zeta” sub “phi”  $z$ ). [F2c] prevents local accumulation of molecules. In closed, isobaric systems constant  $C = 0$ .

In [F2a-c], summation over  $\mu$ -space-system-state-index  $j$  represents summation over all quantum states or integration over all  $u$ - $v$ - $w$ - (or  $\mu$ )-velocity space.<sup>15</sup>

The following derivation considers a one-component, isobaric gas in a closed system. Its concepts apply for each component of a multi-species mixture.<sup>15</sup> We seek the *most probable quantum-state distribution*  $\mathbf{p}$ , where  $\mathbf{p} = \{p_1, p_2, p_3, \dots\}$  with  $p_1$  the probability of gas-molecule energy-state  $\epsilon_1$ ,  $p_2$  the probability of gas-molecule-energy state  $\epsilon_2$ , etc. We identify this set  $\{p_1, p_2, p_3, \dots\}$  in  $p_j$  hyperspace with maximum system information entropy subject to required constraints [F2a-b].<sup>16</sup> By Lagrange’s method we seek distribution  $\mathbf{p}$  in the  $\mu$ -space-ensemble system that maximizes  $\Lambda$  with

$$\Lambda = -k \sum_j p_j \log_e(p_j) + \lambda_1 (\sum_j p_j - 1) + \lambda_2 (\sum_j p_j \epsilon_{\phi j} - \langle \epsilon_{\phi z} \rangle).$$

Maximum information entropy of the system subject to constraints [F2a-b] occurs if

$$\partial \Lambda / \partial p_j = 0 \quad \text{for } j = 1, 2, 3, 4, 5, 6, \dots \quad \text{and} \quad \partial \Lambda / \partial \lambda_i = 0 \quad \text{for } i = 1, 2.$$

Redefining the “constants,” with subscript  $z$  indicating possible  $z$  dependence,

$$[F3] \quad p_{\phi j} = \exp\{-\alpha_z - \beta_z \epsilon_{\phi j}\},$$

$$[F3a] \quad \sum_j p_{\phi j} = \exp(-\alpha_z) \sum_j \exp\{-\beta_z \epsilon_{\phi j}\} = 1,$$

$$[F3b] \quad \sum_j p_{\phi j} \epsilon_{\phi j} = \exp(-\alpha_z) \sum_j \epsilon_{\phi j} \exp\{-\beta_z \epsilon_{\phi j}\} = 3kT_z/2 - m_{\phi} \{ \langle w_{\phi z} \rangle V_{\phi z} - V_{\phi z}^2 \},$$

with  $V_{\phi z}$  a possible systematic velocity due to  $\gamma_T$  or other cause(s).

To determine  $\alpha_z$  and  $\beta_z$  we transform from quantized to continuous energy  $\epsilon_{\phi z} = m_{\phi} \{ u^2 + v^2 + w^2 - 2V_{\phi z} w + 2V_{\phi z}^2 \} / 2$  and use  $p_{\phi}(u, v, w; V) = p_{\phi}(u, v, w; 0) + V(\partial p_{\phi} / \partial V)_{V=0}$ , known both theoretically and experimentally to be accurate when  $V \lesssim \langle c_z \rangle / 3$ .<sup>17</sup> In cases we consider,  $V_{\phi z} / \langle c_z \rangle \ll 1$ . This approximation of [F3] with energy  $\epsilon_{\phi z}$  gives

$$p_{\phi}(u, v, w; V_{\phi z}) = \exp(-\alpha_z) \{ 1 + \beta_z m_{\phi} V_{\phi z} w \} \exp(-\beta_z m_{\phi} (u^2 + v^2 + w^2) / 2).$$

To motivate derivation of the correct result we temporarily transform from  $p_{\phi}(u, v, w; T, \gamma_T)$  to  $n_{\phi}(u, v, w; T, \gamma_T)$ , the latter being the former multiplied by  $n_z \zeta_{\phi z}$ .

Distribution  $n_\phi$  must contain another property beyond those already deduced, namely, molecules at  $z$  are, on average, “last equilibrated” at  $z \pm \lambda_{\phi z}$ , with  $\lambda_{\phi z}$  (Greek “lambda” sub  $\phi z$  [Greek “phi”  $z$ ]) a mean-free-path length at  $z$  of species- $\phi$  molecules, the top (plus) sign corresponding to  $w < 0$ , and the bottom (minus) sign to  $w > 0$ . Then, as in the above approximation,  $n_\phi(u, v, w; z \pm \lambda_{\phi z}, \gamma_T) = n_\phi(u, v, w; z, \gamma_T) \pm \lambda_{\phi z} (\partial n_\phi / \partial z)_z$  and<sup>18</sup>

$$n_\phi(u, v, w; z, \gamma_T) = n_z \zeta_{\phi z} \exp(-\alpha_z) \{ 1 \pm q_{\zeta\phi} \mp 5q_{T\phi}/2 + \beta_z m_\phi V_{\phi z} w \pm q_{T\phi} \beta_z \epsilon_\phi \} \exp(-\beta_z \epsilon_\phi).$$

Where upper and lower signs occur, the upper sign applies for  $w < 0$  and the lower for  $w > 0$ ;  $q_{T\phi} = \lambda_{\phi z} \gamma_T / T_z$ ,  $\gamma_T = (\partial T_z / \partial z)_z$ ,  $q_{\zeta\phi} = \lambda_{\phi z} \gamma_{\zeta\phi} / \zeta_{\phi z}$ ,  $\gamma_{\zeta\phi} = (\partial \zeta_{\phi z} / \partial z)_z$ ,  $\zeta_{\phi z}$  is number fraction of species  $\phi$  at  $z$ , and  $\epsilon_\phi = m_\phi (u^2 + v^2 + w^2) / 2$ . The average  $z$  at “last equilibration” may be fixed or variable.<sup>19</sup> For simplicity we use a fixed one at  $z \pm \lambda_{\phi z}$ .

By  $\partial \Lambda / \partial \lambda_i = 0$  for  $i = 1$  and  $2$ ,  $\exp(-\alpha_z) = (\beta_z m_\phi / 2\pi)^{3/2}$  and  $\beta_z = 1/kT_z$ . The velocity distribution in the lab frame fully consistent with all its known properties is<sup>20</sup>

$$\begin{aligned} \text{[F4]} \quad p_\phi(u, v, w; T, \gamma_T) &= n_\phi(u, v, w; T, \gamma_T) / n_z \zeta_{\phi z} \\ &= (\beta_z m_\phi / 2\pi)^{3/2} \{ 1 \pm q_{\zeta\phi} \mp 5q_{T\phi}/2 + \beta_z m_\phi V_{\phi z} w \pm q_{T\phi} \beta_z \epsilon_\phi \} \exp(-\beta_z \epsilon_\phi). \end{aligned}$$

Where upper and lower signs occur, the upper applies for  $w < 0$  and the lower for  $w > 0$ .

Distribution [F4] is quasi-stationary when  $V_{\phi z}$  is transient, changing while the gas relaxes to its stationary state. But we suppose probability density  $p_\phi(u, v, w; T, \gamma_T)$  approximates well a sharply peaked (over the 3-dimensional-velocity-distribution-hyperspace baseplane) most-probable distribution for even a quasi-stationary, nonequilibrium state. At  $q_{T\phi} = q_{\zeta\phi} = V_{\phi z} = 0$ , [F4] reduces to the Maxwell distribution, written directly from [F1]. For both Maxwell’s distribution and [F4],  $p_\phi(u, v, w; T, \gamma_T) \times du dv dw$  is the fraction of species- $\phi$  gas molecules having velocity components between  $u$  and  $u+du$ , between  $v$  and  $v+dv$ , and between  $w$  and  $w+dw$ .

*Number flux* is molecules passing unit area of an imaginary *control surface* in unit time. *Z-direction molecular effusion* components in the laboratory frame are

$$\text{[F5]} \quad j_{\phi z \pm} = n_z \zeta_{\phi z} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{0(-\infty)}^{\infty(0)} dw p_\phi w = n_z \zeta_{\phi z} \langle c_{\phi z} \rangle \{ \pm 1 - q_{\zeta\phi} + q_{T\phi}/2 + 2V_{\phi z} / \langle c_{\phi z} \rangle \} / 4.$$

In comparison, Maxwell’s distribution  $p_{\phi \text{Max}}$ , valid when  $\gamma_T = \gamma_{\zeta\phi} = 0$ , gives

$$\text{[F6]} \quad j_{\phi z \pm} = n_z \zeta_{\phi z} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{0(-\infty)}^{\infty(0)} dw p_{\phi \text{Max}} w = n_z \zeta_{\phi z} \langle c_{\phi z} \rangle \{ \pm 1 + 2V_{\phi z} / \langle c_{\phi z} \rangle \} / 4.$$

A crucial property of [F5] and [F6] is that in the laboratory frame  $j_{\phi z \text{net}} = j_{\phi z+} + j_{\phi z-}$  summed over all species gives  $j_{z \text{total}} = 0$ , i.e., [F2c]. Since no net force acts on any element of gas in isobaric systems, another crucial property is zero net-momentum flux across any plane in the (isobaric) system. Both Maxwell’s distribution and [F4] give  $\pm z$ -direction momentum flux  $= \pm n_z \sum_\phi \zeta_{\phi z} m_\phi \langle w^2 \rangle = \pm n_z / \beta_z = \pm P_z$ , a constant.<sup>20</sup>

Species- $\phi$  *diffusion coefficient* or *diffusivity* at  $z$  (by simple mean-free-path theory which ignores all details of collisions) is  $D_{\phi z} = \langle c_{\phi z} \rangle \lambda_{\phi z} / 2$  with  $\lambda_{\phi z}$  a mean-free-path length of species- $\phi$  gas molecules at  $z$ .<sup>21</sup> Net number flux of species  $\phi$  in the laboratory coordinate frame by [F5], viz.,  $j_{\phi z \text{net}} = j_{\phi z+} + j_{\phi z-}$ , is<sup>22</sup>

$$[F7] \quad j_{\phi z \text{ net}} = n_z \zeta_{\phi z} \langle w \rangle = n_z \zeta_{\phi z} D_{\phi z} \{-\gamma_{\zeta \phi} / \zeta_{\phi z} + \gamma_T / 2T_z\} + n_z \zeta_{\phi z} V_{\phi z}.$$

The first term in [F7] is *molecular diffusion*, the second is *thermal diffusion*, and the third is convection. Summing  $j_{\phi z \text{ net}}$  over all  $\phi$  gives zero total flux, by [F2c], so that

$$[F7a] \quad V_z = \langle V_z \rangle = \sum_{\phi} \zeta_{\phi z} V_{\phi z} = \sum_{\phi} D_{\phi z} \{\gamma_{\zeta \phi} - \zeta_{\phi z} \gamma_T / 2T_z\}.$$

Because  $V_z$  balances to zero the total net flow due to molecular and thermal diffusions, we call  $V_z$  the balancing *counterflow velocity*. In even a stationary one-component system,  $\zeta_{1z} = 1$ ,  $\gamma_{\zeta 1} = 0$ , and  $V_z = -D_{1z} \gamma_T / 2T_z$ . In a two-component system,  $\zeta_{1z} + \zeta_{2z} = 1$ ,  $\gamma_{\zeta 1} + \gamma_{\zeta 2} = 0$ , and  $V_z = (D_{1z} - D_{2z}) \gamma_{\zeta 1} - (\zeta_{1z} D_{1z} + \zeta_{2z} D_{2z}) \gamma_T / 2T_z$ .

Maxwell's expression [F6] and the "last equilibration" concept together with  $n_{z \pm \lambda} = n_z (1 \mp q_{T\phi})$ ,  $\zeta_{\phi z \pm \lambda} = \zeta_{\phi z} (1 \pm q_{\zeta \phi})$ , and  $\langle c_{\phi z \pm \lambda} \rangle = \langle c_{\phi z} \rangle (1 \pm q_{T\phi} / 2)$  give [F5] and [F7]. Because of this robustness of Maxwell's expression, Dahneke<sup>23</sup> used it to obtain a universal boundary condition for molecular adsorption (e.g., condensation) and particle deposition (e.g., coagulation).

We now illustrate simple, mean-free-path (mfp) kinetic theory with a few applications of distribution [F4].

## 7. Simple Kinetic Theory of Gas Transport Processes

We determine the *transport coefficients* in gases, namely, (a) thermal conductivity  $\kappa$  (Greek "kappa") that characterizes heat or energy transfer flux, (b) viscosity  $\eta$  (Greek "eta") that characterizes momentum transfer flux, and (c) diffusivity  $D$  (script D) and thermal-diffusion diffusivity  $D^T$  ( $D$  superscript T) that characterize particle number (or mass) transfer flux. By 1917 thermal diffusion was theoretically predicted and experimentally verified<sup>24</sup> but no mechanism or theory, simple or elaborate, has provided a clear vision of how it occurs.<sup>25</sup> Using [F4] we shall provide one.

Net  $z$ -direction heat-, momentum-, and number-flux are denoted  $q_{z \text{ net}}$ ,  $\tau_{zx \text{ net}}$ , and  $j_{z \text{ net}}$ . In calculating fluxes (transport per unit area per unit time) of molecular number (or mass), momentum, or energy (or heat) at  $z$  we use gas properties at their "last equilibration" (on average at  $z \pm \lambda$ ) before reaching plane  $z$ .

(a) *Energy transfer rate* or *heat flux*  $q_z$  due to translational energy of molecules in an isobaric gas contains for each species the sum of opposing fluxes

$$q_{\phi z \text{ net}} = n_z \zeta_{\phi z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} p_{\phi}(u, v, w; T, \gamma_{Tz}) w m_{\phi} (u^2 + v^2 + w^2 - 2V_z w + 2V_z^2) / 2 \\ + n_z \zeta_{\phi z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^0 p_{\phi}(u, v, w; T, \gamma_{Tz}) w m_{\phi} (u^2 + v^2 + w^2 - 2V_z w + 2V_z^2) / 2$$

$$q_{\phi z \text{ net}} = - \{n_z \zeta_{\phi z} \langle c_{\phi z} \rangle \lambda_{\phi z} k / 2\} \{\gamma_{Tz} + T_z \gamma_{\zeta \phi} / 2\zeta_{\phi z}\} = - \kappa_{\phi z} \{\gamma_{Tz} + T_z \gamma_{\zeta \phi} / 2\zeta_{\phi z}\}.$$

Note that  $\gamma_{\zeta \phi}$  is coupled to  $\gamma_{Tz}$ , called the Dufour or diffusion-thermo effect, wherein heat transfer is augmented by diffusion. We shall further address such coupling later.

For a gas mixture ( $\phi = 1, 2, \dots$ ),  $\sum_{\phi} \zeta_{\phi z} = 1$ , and  $\sum_{\phi} \gamma_{\zeta \phi} = 0$  and

$$[\text{F8}] \quad \mathbf{q}_{z\text{total}} = -n_z \sum_{\phi} \{ (\zeta_{\phi z} \langle c_{\phi z} \rangle \lambda_{\phi z} k/2) (1 + \gamma_{\zeta\phi} / 2 \zeta_{\phi z} \gamma_T) \} \gamma_{Tz} = -\kappa_z \gamma_{Tz}.$$

The *thermal conductivity* or *heat-transfer coefficient* of the mixture is

$$[\text{F8a}] \quad \kappa_z = n_z \sum_{\phi} \{ (\zeta_{\phi z} \langle c_{\phi z} \rangle \lambda_{\phi z} k/2) (1 + \gamma_{\zeta\phi} / 2 \zeta_{\phi z} \gamma_T) \} \quad \text{and} \quad \lambda_{\phi z} = 2\kappa_{\phi z} / (n_z \langle c_{\phi z} \rangle k).$$

Except in a pure species or mixtures with all species having equal  $D_{\phi z} = \langle c_{\phi z} \rangle \lambda_{\phi z} / 2$ ,  $\kappa_z$  depends on the  $\zeta_{\phi z}$ . Diffusivity  $D_{\phi z}$  appears in  $\kappa_z$  and will appear in expressions for viscosity, diffusivity, and thermal-diffusion diffusivity. Accuracy in predictions of  $\kappa_z$ ,  $\eta_z$ ,  $D_z$ , and  $D_z^T$  may sometimes be considerably improved using better values of  $D_{\phi z}$ . The simple theory is, in any case, invaluable in providing mechanistic insight.

Heat flux via gas molecules (as opposed to atoms) that carry internal energies of vibration and rotation and via sufficiently hot atoms and molecules to be electronically excited exceeds that predicted by [F8]. To make [F4] general, internal energy must be added to translational energy  $\epsilon$ , as on page 573. Noble-gas atoms carry neither vibrational nor rotational energy and below 10,000 K are predominantly in their ground electronic state so that  $\langle \epsilon_z \rangle = 3kT_z/2$  due to  $u, v, w - V_z$  kinetic energy alone. Internal energy of molecules may be incorporated in  $\kappa$  by use of quasi-equilibrium, equipartition of energy, or the correction due to A. Eucken<sup>26</sup> who wrote for thermal conductivity of a polyatomic gas,  $\kappa_z = (c_v + 9k/4)\eta_z$ . For diatomic gases ( $c_p = 7k/2$ ,  $c_v = 5k/2$ ) theoretical and measured Prandtl numbers  $\eta_c/\kappa$  are 0.74 and 0.71.

(b) *X-direction shear stress* at a plane normal to the  $z$  axis, denoted  $\tau_{zx}$  (Greek “tau” sub  $zx$ ), is  $x$ -direction force per unit area due to net  $x$ -direction-momentum flux carried across the plane at  $z$  by random  $z$ -direction gas-molecule motions whenever shear rate at  $z$  is not zero, i.e., shear rate is  $\gamma_{Uz} = (dU/dz)_z \neq 0$ . We consider *laminar flow*, i.e., local,  $x$ -direction velocity is  $U_{z\pm\lambda} = U_z \{1 \pm \lambda \gamma_{Uz} / U_z\}$ . We retain a temperature gradient to determine its effect, if any. Net  $z$ -direction transfer rate of  $x$ -direction momentum across unit area perpendicular to  $z$  is

$$\begin{aligned} \tau_{zx\text{net}} &= n_z \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} du dv dw p_{\phi}(u, v, w; T, \gamma_T) w m_{\phi} U_z (1 - \lambda_z \gamma_{Uz} / U_z) \\ &\quad + n_z \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^0 du dv dw p_{\phi}(u, v, w; T, \gamma_T) w m_{\phi} U_z (1 + \lambda_z \gamma_{Uz} / U_z) \end{aligned}$$

$$[\text{F9}] \quad \tau_{zx\text{net}} = - \{ n_z \sum_{\phi} \zeta_{\phi z} m_{\phi} \langle c_{\phi z} \rangle \lambda_{\phi z} / 2 \} \gamma_{Uz} = -\eta_z \gamma_{Uz}.$$

Gas viscosity  $\eta_z$  (Greek “eta” sub  $z$ ) for a mixture or a pure gas is given by

$$[\text{F9a}] \quad \eta_z = n_z \sum_{\phi} \zeta_{\phi z} m_{\phi} \langle c_{\phi z} \rangle \lambda_{\phi z} / 2 \quad \text{and} \quad \lambda_{\phi z} = 2\eta_{\phi z} / \{ n_z m_{\phi} \langle c_{\phi z} \rangle \lambda_{\phi z} \}.$$

This result agrees with the “exact rigid-sphere approximation”  $\eta_z = 0.499 n_z m \langle c_z \rangle \lambda_z$  (see endnote 21 and citations in endnote 14 for details on the rigid-sphere model, especially 8.3a of HCB). Laminar flow result [F9] applies for *Newtonian fluids*, defined as fluids consistent with [F9], which all gases are. Surprisingly, because  $\eta_z$  depends on  $T_z$  and  $\zeta_{\phi z}$ ,  $\eta_z$  is independent of both  $\gamma_T$  and  $\gamma_{\zeta}$  with terms containing  $\gamma_T$  and  $\gamma_{\zeta}$  canceling exactly. However, this independence disappears in applications.

For example,  $T_z$  and  $\zeta_{\phi z}$  are needed to evaluate a rectangular cooling duct of width  $W$  and height  $H$ , with  $W \gg H$ , heated on top and cooled on bottom. After stationary gas flow is established, the volumetric flow  $Q_f$  and velocity profile  $U(z)$  are

$$Q_f = W \int_0^H dz U(z) \quad \text{where} \quad U(z) = \Delta P/L \left\{ (z/H) \int_0^H dz (z/\eta_z) - \int_0^z dz (z/\eta_z) \right\}$$

with  $\Delta P$  the pressure drop over length  $L$  in the stationary flow. For gas mixtures, like air,  $U(z)$  and  $Q_f$  depend on the temperature and composition distributions.

(c) *Diffusion and thermal diffusion* are our final gas-transport topics. While [F4] characterizes well both thermal conductivity and viscosity, providing novel insight into the former quantity, its greatest transport-theory value is in describing diffusion, thermal diffusion, *thermophoresis*, and *diffusiophoresis* of particles in gases.

Transient components of  $V_{\phi z}$  occur initially as a system relaxes to its stationary-state  $T_z$  and  $\zeta_{\phi z}$  distributions. We assume an all-species counterflow velocity  $V_{\phi z} = V_z$  because of intimate mixing of the species, slow motion, and velocity  $V_z$  being driven essentially by (to prevent) a pressure difference. In a closed, isobaric system all transport is coupled by constraint [F2c].

The “cause” of *diffusion and thermal diffusion* in a gas is already apparent from our analysis. It is the universal evolution toward maximum system information entropy subject to required physical constraints. This “cause” of diffusion and of all transport in gases and other systems has not previously been widely realized.

We write expressions for coupled transport of species in a *binary mixture*, a two-component gas containing both concentration and temperature gradients.

Binary-system counterflow  $V_z$  in the laboratory frame in a closed, isobaric system ( $\zeta_{1z} + \zeta_{2z} = 1$ ,  $\gamma_{\zeta 1} + \gamma_{\zeta 2} = 0$ ) is given – as before, following [F7a] – by [F7a]

$$[F10] \quad V_z = (D_{1z} - D_{2z}) \gamma_{\zeta 1} - (\zeta_{1z} D_{1z} + \zeta_{2z} D_{2z}) \gamma_T / 2T_z$$

where  $D_{\phi z} = \langle c_{\phi z} \rangle \lambda_{\phi z} / 2$ . [F2c] must be satisfied during transient relaxation of the system and in its final, stationary state (in the stationary state each  $j_{\phi z, \text{net}} = 0$ ). By [F7],

$$[F11a] \quad j_{1z, \text{net}} = -n_z [\zeta_{2z} D_{1z} + \zeta_{1z} D_{2z}] \gamma_{\zeta 1} + n_z \zeta_{1z} \zeta_{2z} [D_{1z} - D_{2z}] \gamma_T / 2T_z$$

$$[F11b] \quad j_{2z, \text{net}} = -n_z [\zeta_{2z} D_{1z} + \zeta_{1z} D_{2z}] \gamma_{\zeta 2} - n_z \zeta_{1z} \zeta_{2z} [D_{1z} - D_{2z}] \gamma_T / 2T_z.$$

[F11] impose  $j_{z, \text{total}} = 0$  but allow  $j_{\phi z, \text{net}} \neq 0$  so that relaxation to equilibrium can occur. Coefficients in [F11] were previously unknown (texts cited in endnotes 14 and 27 may be consulted on this point). The need for equal magnitudes of corresponding coefficients was recognized but its use was hobbled by incomplete concepts.<sup>25,27</sup> We use  $D_{1z} = [\zeta_{1z} D_{11z} + \zeta_{2z} D_{12z}]$  and  $D_{2z} = [\zeta_{1z} D_{21z} + \zeta_{2z} D_{22z}]$  with  $D_{11}$  the diffusivity of a species-1 molecule in pure species-1 gas and  $D_{12}$  its diffusivity in pure species-2 gas. In dilute gases, 3-body collisions are negligible and these expressions are accurate.

Our analysis is fully consistent with all known requirements and contains three advantages over past analyses. (a) Writing local concentration of species  $\phi$  as  $n_z \zeta_{\phi z}$  provides the important advantage that total temperature dependence is contained in  $n_z$  and total concentration dependence in  $\zeta_{\phi z}$ . Using  $n_z \zeta_{\phi z}$ , temperature and concentration gradients are simply and exactly written, avoiding a problem that has

plagued thermal-diffusion theory from its beginnings.<sup>25,27</sup> (b) Velocity  $V_z$  included in distribution [F4] provides fluxes in the laboratory coordinate frame and provides equations [F11] with completely defined coefficients for both molecular and thermal diffusion. (c) The underlying “cause” of diffusion and thermal diffusion and of thermophoresis and diffusiphoresis is revealed in our microscopic-level, nonequilibrium-statistical-mechanics theory to be the universal evolution of all systems toward maximum information entropy subject to required constraints.

The *stationary state* of a closed, binary system satisfies  $j_{1z\text{net}} = j_{2z\text{net}} = 0$  (as well as  $j_{1z\text{net}} + j_{2z\text{net}} = 0$ ) and [F11a-b] take their stationary forms

$$[F12] \quad \gamma_{\zeta_1} - \mu_z \gamma_T / T_z = \gamma_{\zeta_2} + \mu_z \gamma_T / T_z = 0$$

where  $\mu_z$  (Greek “mu” sub z) =  $\zeta_{1z} \zeta_{2z} [D_{1z} - D_{2z}] / [2\zeta_{2z} D_{1z} + 2\zeta_{1z} D_{2z}]$ ; [F12] are *stationary or steady-state equations* valid for any pair of stable, nonreacting gas species.

By integration of the first of Equations [F12] we obtain  $T_z = T_z(\zeta_{1z})$ , viz.,

$$[F13] \quad T_z = \{\zeta_{1z} / \zeta_{10}\}^{c_1} \{(1 - \zeta_{1z}) / (1 - \zeta_{10})\}^{c_2} \{(c_0 + \zeta_{1z}) / (c_0 + \zeta_{10})\}^{c_3} T_0.$$

Integrating [F13] we assumed  $D_{jz} = (\zeta_{jz} D_{jz} + \zeta_{kz} D_{jkz})$ . Constants<sup>28</sup>  $c_0, c_1, c_2, c_3$ , containing ratios of  $D$ s, are independent of temperature in mfp theory but not quite in the rigorous theory. Given a value of  $\zeta_{10} = 1 - \zeta_{20}$ ,  $T_n - \zeta_{1n}$  pairs are related by

$$[F14a] \quad T_n = \{(\zeta_{10} + n\Delta\zeta_1) / \zeta_{10}\}^{c_1} \{(1 - \zeta_{10} - n\Delta\zeta_1) / (1 - \zeta_{10})\}^{c_2} \\ \times \{(c_0 + \zeta_{10} + n\Delta\zeta_1) / (c_0 + \zeta_{10})\}^{c_3} T_0 \quad \text{with } n = 0, 1, 2, 3, 4, \dots$$

where  $\Delta\zeta_1$  is a suitably-small, selected increment in  $\zeta_1$ ;  $\zeta_2 = 1 - \zeta_1$ . Corresponding values of  $z_n$  are obtained from the stationary-state requirement  $-q = \kappa_n \gamma_T = \kappa_0 \gamma_{T_0}$  from which  $\gamma_{T_n} = (\kappa_0 / \kappa_n) \gamma_{T_0}$  so that (in a simple one of many possible algorithms)

$$[F14b] \quad z_n = \sum_{n=1}^n \Delta z_n / \delta \quad \text{where } \Delta z_n = \{\kappa_n (T_n - T_{n-1}) / \kappa_0 (T_1 - T_0)\} \Delta z_1 \quad \text{and } \delta = \sum_{n=1}^N \Delta z_n / z_1.$$

In [F14b],  $N$  is the value of  $n$  at which  $T_n$  reaches  $T_1$  in [F14a];  $\Delta z_1$  is arbitrary. Values of  $\kappa_n$  and  $\kappa_0$  are approximated by  $\kappa_n = \zeta_{1n} (\kappa_{10} + \gamma_{\kappa 1} \Delta T_n) + \zeta_{2n} (\kappa_{20} + \gamma_{\kappa 2} \Delta T_n)$  with  $\Delta T_n = (T_n - T_0)$  with fitted constants  $\kappa_{\phi 0}$  and  $\gamma_{\kappa \phi}$  shown with data for a few gases in Figure F1.

Figure F2 shows stationary  $\zeta_{1z} / \zeta_{10}$  for a few  $\zeta_{10}$  in binary Nitrogen-Argon mixtures with  $T_0 = 273.2$  K and  $\Delta T_1 = 300$  K. Nitrogen is the species-1 gas.

*Thermal diffusion ratio*  $k_T^{25,27,29(a)}$  is an historically important measure of thermal diffusion based on stationary result  $\gamma_{\zeta_2} = -\gamma_{\zeta_1} = k_{T2} \gamma_T / T_z$ , with  $k_{T2}$  assumed equal to  $-D_2^T / D_2$ . This equation ([F12]) is used to characterize the *two-bulb experiment*<sup>28</sup> wherein one of two connected bulbs is held at temperature  $T_0$  and the other at  $T_z$ . After equilibration, measured bulb-number-fraction differences  $\Delta\zeta_2 = \zeta_{2z} - \zeta_{20}$  gives  $k_{T2} = \Delta\zeta_2 / \log_e(T_z / T_0)$ . It is supposed that  $D_{2z}^T = -k_{T2} D_{2z}$  at some intermediate temperature. But, by [F12],  $\gamma_{\zeta_2} = -\mu_z \gamma_T / T_z$  which provides  $k_{T2} = -\zeta_{1z} \zeta_{2z} [D_{1z} - D_{2z}] / [2\zeta_{2z} D_{1z} + 2\zeta_{1z} D_{2z}] = -k_{T1}$  giving general insight, as does  $D_{iz}^T / D_{iz} = 1/2$ , with  $i = 1$  or  $2$ .

That [F11] and [F12] are novel is manifest by their differences from accepted theory. Hirschfelder, Curtiss, and Bird (HCB)<sup>27</sup> followed by Bird, Stewart, and Lightfoot (BSL)<sup>27</sup> assume  $j_{1z} = -j_{2z}$ ,  $D_{1z} = D_{2z}$ , and  $D_1^T = -D_2^T$ . However, it is not  $D_{1z} = D_{2z}$  and  $D_1^T = -D_2^T$  that control diffusion and thermal diffusion in the binary system but

$\zeta_{2z}D_{1z} + \zeta_{1z}D_{2z}$  and  $\zeta_{1z}\zeta_{2z}[D_{1z} - D_{2z}]/2$ . Consequently, the assumptions of HCB and BSL lead directly to problems. In their treatment of binary diffusion BSL wrote

$$D_{12} = 0.0018583 \sqrt{[T^3(1/M_1 + 1/M_2)] / (P \sigma_{12}^2 \Omega_{12}^{(1,1)*})}$$

with  $D_{12}$  (assumed =  $D_{21}$ ) in cm<sup>2</sup>/sec, T the absolute temperature in K, P the pressure in atmospheres,  $M_i$  the molecular weight of species i in gram-moles,  $\Omega_{12}^{(1,1)*}$  the collision integral of HCB<sup>30</sup> at dimensionless temperature  $kT/\epsilon_{12}$ ,  $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ , and  $\epsilon_{12}$

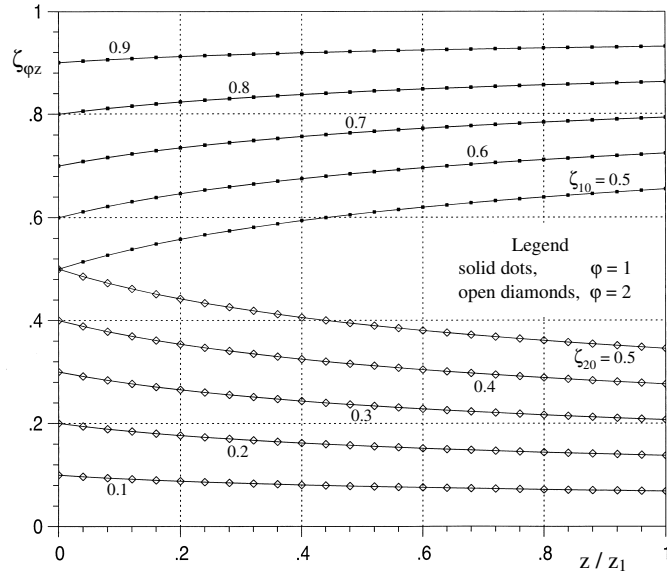
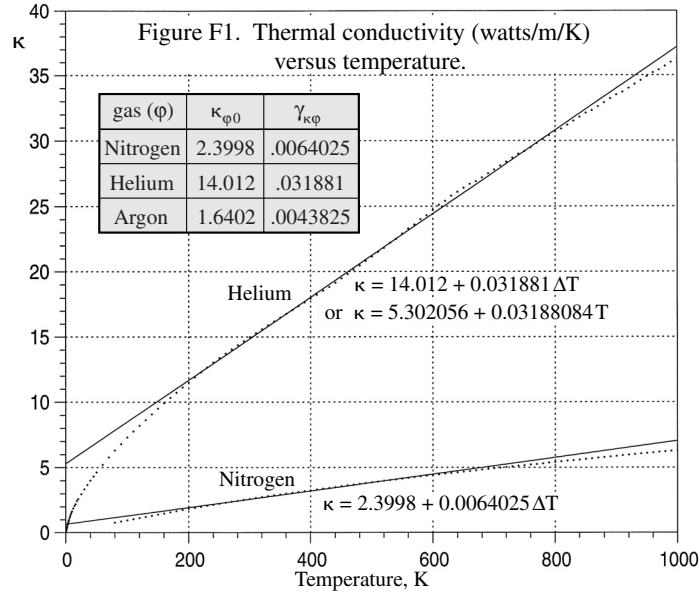


Figure F2. Number fraction versus altitude  $z/z_1$ .

$= \sqrt{(\epsilon_1 \epsilon_2)}$ . The last two quantities are used in the Lennard-Jones potential between species- $i$  and - $j$  molecules separated by  $r$ , with  $i = 1$  or  $2$  and  $j = 1$  or  $2$ . This potential, used to calculate collision dynamics and collision integrals (deflection angles), is

$$\phi_{ij}(r) = 4\epsilon_{ij} [(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6].$$

A curious feature of this result for  $D_{12}$  is lack of concentration dependence of  $D_{12}$  even though HCB and BSL include tables of measured data showing significant concentration dependence of  $D_{12}$ . The single coefficient of the present theory to be used in [F12] in place of the HCB-BSL  $\{k_T\}$  is  $\{\mu = \zeta_1 \zeta_2 [D_1 - D_2] / [2\zeta_2 D_1 + 2\zeta_1 D_2]\}$  which depends on concentration mainly through the factor  $\zeta_1 \zeta_2$ . Composition dependence is absent in HCB and BSL diffusivity due to their assumptions  $j_1 + j_2 = 0$ ,  $D_{12} = D_{21}$ , and  $D_1^T + D_2^T = 0$ , but their treatments of viscosity and thermal conductivity are not so misled by earlier work.

Diffusivities of mfp theory differ functionally from those of rigorous theory. By mfp theory,<sup>31</sup>  $D_{12} = \langle c \rangle / [2n_z \pi \sum_k \zeta_k (d_1 + d_k)^2 \sqrt{(1 + m_1/m_k)}]$  so that  $D_{12} \neq D_{21}$  contrary to the rigorous theory. Between mfp and rigorous theory we expect different dependencies on  $T_z$  and on  $m_1$  and  $m_2$  since all these quantities influence collisions. Or perhaps assumption  $D_{12} = D_{21}$  is motivated by a nonrigorous simplification of rigorous theory, as in concentration dependence.

HCB<sup>27</sup> obtained a thermal diffusion ratio too complex to write here, but we quote some of their summary of it. "The thermal diffusion ratio is a very complex function of temperature, concentration, and the molecular weights, ... The primary concentration dependence is given by the factor  $[\zeta_{1z} \zeta_{2z} - \text{in agreement with } \mu_z]$  and to lesser extent on ... [in qualitative agreement with  $\mu_z$ ]. ... The thermal diffusion ratio can be positive or negative. A positive value of  $[k_T]_1$  signifies that component 1 tends to move into the cooler region and 2 towards the warmer region." While the HCB  $k_T$  significantly differs from  $\mu_z$ , the properties of the two are at least qualitatively similar;  $\mu_z$  is, however, much simpler to derive, write, understand, and use.

These problems in long-accepted and widely-used theory indicate (a) complexity of the subject, (b) error or incompleteness in inherited concepts, and (c) lack of fundamental understanding of these processes.

Error and confusion in diffusion and thermal diffusion have indeed propagated from early investigations of Chapman-Enskog theory. These processes are the worst-predicted of the theory. We have corrected some errors in past analyses<sup>25,27,29(a)</sup> by using quantities  $n_z$  and  $\zeta_{\phi z}$  as the variables in equations for  $j_{\phi z, \text{net}}$ , by including transient and stationary counterflow velocity  $V_z$  necessary for correct characterization of all transport, and by basing the theory on an apparently reliable foundation: maximization of information entropy with required physical constraints. Experimental data are now needed to judge these corrections and guide future work.

## 8. Thermophoresis and Diffusiophoresis

We address *thermophoresis* and *diffusiophoresis* of particles suspended in gas (i.e., an aerosol). Thermophoresis is the systematic migration of gasborne particles (or molecules) due to a temperature gradient. Diffusiophoresis is the same effect

due to a concentration gradient in the suspending gas. We start with thermophoresis.

Like diffusion and thermal diffusion, thermophoresis is poorly understood despite many studies of it, both theoretical and experimental.<sup>23, 25, 27, 29, 32-34</sup>

Suspended-particle number concentration  $n_{pz}$  is generally much smaller than suspending-gas-molecule number concentration, i.e.,  $n_{pz} \ll n_{gz}$ . Essentially,  $\zeta_{gz} = 1$ ,  $\zeta_{pz} = 0$ ,  $\gamma_{gz} = \gamma_{pz} = 0$ . Stationary, suspending-gas counterflow is  $V_{gz} = -D_{gz}\gamma_T/2T_z$ . By [F7], a pure suspending gas is motionless in the laboratory frame.

To understand thermophoresis we derive the *thermophoretic velocity of a particle*  $\langle W_p \rangle = W_p$  in gradient  $\gamma_T$  in a pure, stagnant gas. Rather than molecular diffusion we contemplate migration of a *single, individual particle*. For an individual particle in a pure gas we replace  $(1 \pm q_{cp} \mp 5q_{Tp}/2)$  in [F4], from derivation of  $n_\phi = n_z \zeta_{\phi z} p_\phi$ , with  $(1 \mp 3q_{Tp}/2)$ , from direct derivation of  $p_\phi$  for an individual particle.

For small suspended particles, *Knudsen number*  $Kn = \lambda/a$  can be large, with  $a$  the spherical-particle radius (or characteristic half-length for another shape<sup>17</sup>) and  $\lambda$  the mfp length of the suspending-gas molecules. Flow about particles at  $Kn \gg 1$  is called *free-molecule flow*. Waldmann<sup>33</sup> investigated sphere motion in such flows. Jacobsen and Brock,<sup>34</sup> and others,<sup>32, 33</sup> considered  $W_p$  for  $0 \leq Kn \leq 1$ .

We write the beginning equation and the final result, the first being

$$[F15] \quad W_p = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^0 p_{pz} w + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} p_{pz} w,$$

where  $p_{pz}$  is [F4] modified as described above. The final result, with particle-fluid friction coefficient  $f_{pz}$  (defined on page 160) and  $k$  the Boltzmann constant, is

$$[F16] \quad W_p = -D_{pz} \gamma_T / 2T_z = -k\gamma_T / 2f_{pz}.$$

In [F16] we ignore influence of a particle on local temperature gradient; but the possibility exists and data of Waldmann and Schmitt<sup>33</sup> indicate that local  $\gamma_{Tz}$  can be strongly influenced by a particle. At  $Kn = 0$ , Carslaw and Jaeger<sup>35</sup> found temperature gradient  $\gamma_{Tz}$  across a sphere of thermal conductivity  $\kappa_p$  in a medium of thermal conductivity  $\kappa_g$  and temperature gradient  $\gamma_{T\infty}$  (at  $z$  but far from the sphere) to be

$$[F17] \quad \gamma_{Tz} / \gamma_{T\infty} = 1 + C_\kappa(Kn_\kappa) \{ (1 - \kappa_p / \kappa_g) / (2 + \kappa_p / \kappa_g) \},$$

where  $C_\kappa(Kn_\kappa)$  (added here to the Carslaw-Jaeger result) is 1 at  $Kn_\kappa = 0$ . Dahneke<sup>23</sup> wrote correction factor  $C_\kappa(Kn_\kappa)$  by analogy. For a sphere of radius  $a$  and  $Kn_\kappa = \lambda_\kappa / a$ ,

$$[F18] \quad C_\kappa(Kn_\kappa) = (Kn_\kappa + 1) / [2Kn_\kappa(Kn_\kappa + 1) / \alpha + 1]$$

with  $\lambda_\kappa$  given by equations [F8],<sup>21</sup> and *thermal accommodation coefficient*  $\alpha \approx 1$ , with  $\alpha$  the average fraction of thermal-energy difference transferred per molecular collision. At large  $Kn_\kappa$ ,  $C_\kappa(Kn_\kappa) = \alpha / (2Kn_\kappa) \rightarrow 0$  and  $W_p$  is independent of  $\kappa_p / \kappa_g$ .

Combining results [F16]-[F18] gives the desired expression

$$[F19] \quad W_p = - \{ 1 + C_\kappa(Kn_\kappa) (1 - \kappa_p / \kappa_g) / (2 + \kappa_p / \kappa_g) \} D_{pz} \gamma_T / 2T_z = -D_{pz} F(\kappa_p, Kn_\kappa, \alpha) \gamma_T / 2T_z.$$

While the jury is still out, comparison of [F16] and [F19] with limited data seems to indicate that the predicted  $W_p$  is too small by a factor of 1/2.

Finally, we consider diffusiophoresis. Because a concentration gradient is required in diffusiophoresis, the suspending gas must be a mixture of two or more components. We consider a binary suspending gas containing, in addition to the two gases, suspended particles or molecules as a low-concentration solute species.

Ignoring the solute particles or molecules because their concentration is small, the gas counterflow velocity is given by [F10]. Thus, in addition to the thermophoretic velocity [F16] a particle also moves in the laboratory frame due to a nonzero counterflow velocity. The total particle migration velocity in this frame is

$$[F20] \quad W_p = (D_{1z} - D_{2z})\gamma_{\zeta_1} - (D_{pz} F(\kappa_p, \mathbf{K}n, \alpha) + \zeta_{1z} D_{1z} + \zeta_{2z} D_{2z})\gamma_T/2T_z.$$

When  $\gamma_T = 0$  particle velocity  $W_p = (D_{1z} - D_{2z})\gamma_{\zeta_1}$  is due to  $\gamma_{\zeta_1}$  alone, i.e., due to pure diffusiophoresis. *In the stationary state*,  $\gamma_{\zeta_1} = \mu_z \gamma_T/T_z$  by [F12]. Then, total thermophoretic and diffusiophoretic velocity (or phoretic velocity) of the particle is

$$[F21] \quad W_p = -\{D_{pz} F(\kappa_p, \mathbf{K}n, \alpha) + \zeta_{1z} D_{1z} + \zeta_{2z} D_{2z} - \zeta_{1z} \zeta_{2z} (D_{1z} - D_{2z})^2 / (\zeta_{2z} D_{1z} + \zeta_{1z} D_{2z})\} \gamma_T / 2T_z.$$

We conclude with two observations. It has often been asked, Can thermophoretic velocity sometimes be positive? The answer by [F16] and [F19] is no. But [F21] represents a stationary *apparent thermophoretic velocity* which can be positive as well as negative. So,  $W_p$  can *appear* to be a positive thermophoresis.

For clarity of interpretation, thermophoretic velocity should be measured in a pure gas as well as mixtures (like air). Then some results will be pure thermophoresis that provide reliable data for testing [F16], [F19], and [F20].

### Notes and References for Appendix F.

<sup>1</sup> For a superior treatment see Fletcher, E. A., "Introducing thermodynamics to undergraduates - The first and second laws," *International J. of Mech. Eng. Education* **11**, 29-36, 1983.

<sup>2</sup> How the second-law-predicted heat death of the universe will eventually occur has been described by Fred Adams and Greg Laughlin in their popular-level book *The Five Ages of the Universe* (The Free Press, New York, 1999). However, one should not lose sleep over the eventual demise of the universe. Our sun's brightness will not begin to diminish perceptively for another six billion years. Events described in Book III will precede and supercede that event, are more urgent, and imminent.

<sup>3</sup> Boltzmann's original H-theorem expression is modernized here using quantum theory concepts. For a description of the *logarithm function*, see endnote 27 of Chapter 8.

<sup>4</sup> The number of distinct quantum states of a system containing N identical atoms contains  $N! / \prod_j n_j!$  indistinguishable exchanges of the  $N = \sum_j n_j$  atoms divided into distinguishable groups of  $n_j$  atoms at energy levels  $E_j$ , with  $j = 1, 2, 3, \dots$ , where symbols  $\prod_j$  and  $\sum_j$  (upper case Greek "pi" sub j and "sigma" sub j) indicate, respectively, the product and sum over all j values and "n factorial" =  $n! = n \times (n-1) \times \dots \times 2 \times 1$  with  $0! = 1$ . This number of possible states of a system is usually much larger than its number of atoms; only when all or most atoms have one energy  $E_j$  are the two numbers comparable. But even when all or most atoms have identical energy  $E_j$ , differences in atom locations give a similarly high number of different, distinguishable states all having essentially identical  $E_j$ . (For further details see Tolman, Richard C., *The Principles of Statistical Mechanics*, Oxford University Press, Oxford, England, 1938, Chapter 13 and Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird (denoted HCB), *Molecular Theory of Gases and Liquids*, John Wiley, New York, 1954, Chapter 2.)

<sup>5</sup> Gibbs, J. Willard, *Elementary Principles in Statistical Mechanics*, Yale University Press, New Haven, CT, 1902; reprinted by Dover Publications, Inc., New York, 1960.

<sup>6</sup> See Jaynes, E. T., "Gibbs' vs Boltzmann's Entropies," *American Journal of Physics* **33**, 1965, 391-398. This same author is quoted pertinently in endnote 11 of Chapter 2. The former paper is found with other salient articles in *E. T. Jaynes: Papers on Probability, Statistics and Statistical Physics*, R. D. Rosenkrantz (editor), Kluwer Academic Publishers, Dordrecht, The Netherlands, 1983. All Jaynes' papers are available at <http://bayes@wustl.edu/etj/node1.html>.

<sup>7</sup> We demonstrate entropy decrease in slow crystallization in a closed system by use of the characteristic property for such systems (Helmholtz free energy  $F = E - TS$ , Section 3), which is minimum at equilibrium. Then for slow, quasi-equilibrium crystallization,  $\Delta F = \{E_2 - TS_2\} - \{E_1 - TS_1\} = \Delta E - T\Delta S = 0$ . It follows that for slow, quasi-equilibrium crystallization,  $\Delta E = T\Delta S$ .

In crystal formation from solute atoms, each molecule added to the crystal gives up a *latent heat of crystallization*  $q$ . Without work extraction from a closed system the first law of thermodynamics is  $Q = \Delta E$ , where  $\Delta E$  is increase in system energy and heat  $Q$  is heat transferred to the system. (Positive or negative  $\Delta E$  and  $Q$  represent energy and heat received by or released from the system.) Thus, crystallization of  $N$  molecules gives  $\Delta E = Q = -Nq$  so that  $\Delta S = Q/T = -Nq/T < 0$ . That is, as  $N$  molecules slowly crystallize they slowly release into the system latent energy of crystallization  $Nq$  which is subsequently released to the environment. The net effect is system energy decrease in the form of heat released from the system. Since system-boundary temperature  $T_b$  is slightly lower than internal system temperature  $T$ , *increase* in entropy of the environment (universe)  $\Delta S_e = Q/T_b$  slightly exceeds system entropy *decrease*  $\Delta S = Q/T$ .

<sup>8</sup> See, for example, Shannon, Claude E., *A Mathematical Theory of Communication*, University of Illinois Press, Urbana, IL, 1949.

<sup>9</sup> System type and its traditional designation in statistical mechanics are given in the first two columns of the Table on page 570. The third column indicates properties of the system regarded as fixed, known, or required for specification of system state, with  $N$ ,  $V$ ,  $E$ ,  $T$ ,  $\mu$ , and  $P$  being, respectively, number of system molecules, system volume, system energy, absolute temperature, *chemical potential*, and pressure. The *partition function*  $Z$  is shown in column 4 for each system type and column 5 shows the *characteristic property* that characterizes system state, i.e., the property minimized at equilibrium. Isolated systems evolve spontaneously toward minimum negative entropy or maximum  $S$ . Closed systems evolve spontaneously toward minimum *Helmholtz free energy*  $F = E - TS$ . Open systems evolve toward either minimum  $-PV$  or minimum *Gibbs free energy*  $G = E + PV - TS$ , depending on the type of open system. Like entropy for the isolated system, each of these properties characterizes system state for the indicated system type. The chemical potential is defined as  $\mu = G/N$  so that specifying either one of  $\mu$  or  $G$  also specifies the other if  $N$  is known. Spontaneous evolution of system types are characterized by  $d(-S)/dt \leq 0$ ,  $dF/dt \leq 0$ ,  $d(-PV)/dt \leq 0$ , and  $dG/dt \leq 0$ , with the equilibrium state defined by the minimum condition at which the characteristic property is constant. A useful concept for all system types is that minimum characteristic property  $-S$ ,  $F$ ,  $-PV$ , or  $G$  defines maximum system entropy or level of ignorance in specification of the system's microscopic state given its known macroscopic properties, i.e., everything actually known about the system. The *Maxent principle* derives from the work of Boltzmann, Gibbs, R. T. Cox, Claude Shannon, and, especially, E. T. Jaynes (loc. cit.).

<sup>10</sup> This table is adapted from Lloyd L. Lee (*Molecular Thermodynamics of Nonideal Fluids*, Butterworths, Boston, 1988, 34) who provides several examples of the Maxent method.

<sup>11</sup> Why an ensemble average? Two *equivalent* ensembles may be used. The first is many replications of a prototype system. The second is a single prototype system observed at many times. The latter corresponds to an actual system evolving in time. The most-probable state in the ensemble of macroscopically identical systems is the most probable state of the single system evolving in time. When probability of a particular or set of microstates dominates, it dominates both averages.

<sup>12</sup> See, e.g., Taylor, Angus E., *Advanced Calculus*, Ginn and Company, Boston, 1955, 198-201.

<sup>13</sup> One process that illustrates the capability we are describing is clustering of molecules and onset or nucleation of a new phase. This process has been treated by a number of authors, mostly in

journal articles rather than books. Predictions of the theory are qualitatively correct but their remain considerable discrepancies in predictions of exactly what nucleation rate should obtain.

Dahneke (in *Theory of Dispersed Multiphase Flow*, Richard E. Meyer (editor), Academic Press, New York, 1983, 97-133) provides expressions for droplet growth rates in gases and vapors.

Chemical kinetics illustrations are given by Eyring, H., and E. M. Eyring, *Modern Chemical Kinetics*, Reinhold, New York, 1963.

<sup>14</sup> (a) Hirschfelder, J. O., *et al*, loc. cit., 455. (b) Chapman, Sydney, and T. G. Cowling (denoted CC), *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, 1960, 37. (c) Reed, Thomas M., and Keith E. Gubbins, *Applied Statistical Mechanics*, Butterworth-Heinemann Reprint, Boston, 1973, 354. (d) Jeans, Sir James, *An Introduction to the Kinetic Theory of Gases*, Cambridge University Press, Cambridge, 1962, 28.

<sup>15</sup> Hill, Terrell L., *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960. We ignore entropy of mixing in which case  $S = \sum_i \sum_j p_i p_j \log_e(p_i p_j) = \sum_i p_i \log_e(p_i) + \sum_j p_j \log_e(p_j)$ .

<sup>16</sup> Maximizing information entropy (Maxent principle) subject to macroscopic constraints imposes on a system only what is *actually known* about the system. It leads directly to characteristic properties for equilibrium systems of various sorts. Macroscopic constraints and Maxent together with known equilibrium-thermodynamic relations define a characteristic thermodynamic property for each type of system. For nonequilibrium systems, thermodynamics does not apply so that (1) the Lagrange multipliers cannot be determined by use of thermodynamics and (2) no characteristic thermodynamic property of a nonequilibrium system emerges from the analysis. Otherwise Maxent treatments of equilibrium and steady-state, nonequilibrium systems are identical.

<sup>17</sup> Dahneke, B., *Aerosol Science* **4**, 1973, 147-161. Mean molecule speed =  $\langle c_z \rangle = \sqrt{(8kT_z/\pi m)}$ .

<sup>18</sup> We dodge circular logic by simply finding a fully-consistent result. The problem is that in order to determine constants  $\exp(-\alpha_z)$  and  $\beta_z$  we need the z-dependence of  $p_\phi(u, v, w; T, \gamma_T)$  and *vice versa*.

<sup>19</sup> Jeans (loc. cit., 104) derives a formula for fraction F of molecules or particles that travel distance  $\delta$  or more before their motion is "randomized" by one or more collisions. The fraction is  $F(\delta) = \exp(-\delta/\lambda)$ , with  $\lambda$  the molecule or particle mean-free-path length. Probability a particle starting between  $\delta$  and  $\delta+d\delta$  will pass plane  $\delta = 0$  before being re-randomized is  $\{[F(\delta) - F(\delta+d\delta)]/d\delta\}d\delta = -(dF/d\delta)d\delta$ , with  $\delta/\lambda = \Delta z/(\lambda \cos \theta) = \sqrt{(u^2 + v^2 + w^2)}\Delta z/(w\lambda) \equiv \omega\Delta z/(w\lambda) = \eta$  and  $\omega = \sqrt{(3kT_z/m)}$ ,  $\epsilon = m(u^2 + v^2 + w^2)/2$ , and  $\beta_z = 1/kT_z$ . The resulting probability that a molecule or suspended particle passes plane  $z_0$  from plane  $\Delta z = (z - z_0)$  is  $\exp(-\eta) p(u, v, w; T, \gamma_T) d\eta du dv dw$  wherein  $z$  in  $p(u, v, w; T, \gamma_T)$  is transformed to  $\eta$  before integration over  $\eta$ . Since  $\eta$  contains  $\Delta z/w$  it is always negative for molecules passing plane  $\Delta z = 0$ ; to pass plane  $\Delta z = 0$ , when  $\Delta z > 0$ ,  $w < 0$  and when  $\Delta z < 0$ ,  $w > 0$ .

<sup>20</sup> A term omitted in [F4] contains  $(\partial(\beta_z V_z)/\partial z)_z$  where  $V_z$  is given by [F7a]. We equate this term to zero for two reasons. (i) Since  $\beta_z = n_z/P$  and  $P$  is constant, the z dependence of  $\beta_z V_z$  is the same as that of  $n_z V_z$ . But by the continuity equation (conservation of mass) of fluid mechanics  $n_z V_z$  must be constant. (ii) If  $(\partial(\beta_z V_z)/\partial z)_z$  is retained in the derivation of [F4] and z-direction momentum flux is calculated, linear momentum is conserved if and only if  $(\partial(\beta_z V_z)/\partial z)_z$  is zero.

<sup>21</sup> We have used a *mean-free-path length*  $\lambda_{\phi z}$  as a characteristic length. In rigid-sphere, mean-free-path theory, average frequency of collisions of a species- $\phi$  molecule of diameter  $d_\phi$  is  $\nu_\phi = n_z \pi \sum_k \zeta_{kz} (d_k + d_\phi)^2 \langle c_{\phi z} \rangle \sqrt{(1 + m_\phi/m_k)}$ , where index  $k$  includes all species. Average or mean-free-path length between collisions is  $\lambda_{\phi z} = \langle c_{\phi z} \rangle / \nu_\phi = 1 / \{ n_z \pi \sum_k \zeta_{kz} (d_k + d_\phi)^2 \sqrt{(1 + m_\phi/m_k)} \}$ . But simple, rigid-sphere theory introduces error because it ignores complexity in molecular collisions such as dependence of collision cross section on relative velocity and collision path. Error is circumvented in the end by using  $D_{\phi z}$  or viscosity  $\eta_z$  in place of its mean-free-path-theory equivalent. Dynamic viscosity at  $z$ ,  $\eta_z$  (Greek "eta" sub  $z$ ), of a gas of rigid-sphere molecules provides the frequently-used  $\lambda_{\eta z} = \eta_z / (0.499 \rho_z \langle c_z \rangle)$ , with gas-molecule *mass density*  $\rho_z$  (= Greek "rho" sub  $z$ ) =  $n_z m$  and arithmetic-mean speed of mass- $m_\phi$  molecule  $\langle c_{\phi z} \rangle = \sqrt{(8kT_z/\pi m_\phi)}$  in gas at temperature  $T_z$ . A superior exp-

ression for molecule or *particle* mfp length is  $D_{pz} = \langle c_{pz} \rangle \lambda_{pz} / 2 = kT_z / f_{pz}$  or  $\lambda_{pz} = 2kT_z / (\langle c_{pz} \rangle f_{pz})$ .

<sup>22</sup> Let  $q_{T\phi}$  or  $q_{c\phi}$  be generically denoted  $q$  and let  $q \ll 1$  as it normally is. Quantity  $q$  remains small even when  $\lambda$  is large because the temperature and concentration “jumps” imposed as (artificial) boundary conditions to retain continuum transport expressions cause  $\gamma_T$  and  $\gamma_c$  to be greatly reduced when  $\lambda$  is large. The following strategy thus applies. In a sum of terms each with some factor  $q^N$ , with  $N = 0, 1, 2, 3, \dots$  the *order* of the  $q^N$  term, we retain only terms of the lowest order because higher-order terms are negligible in comparison. However, an important exception to this rule occurs when a difference is taken. Calculating net flux [F7] from [F5] involves taking a difference with the remaining terms in [F7] both being negligible in [F5] but the dominant ones in [F7].

<sup>23</sup> Dahneke, 1983, loc. cit., in endnote 12.

<sup>24</sup> Chapman, S., and F. W. Dootson, *Philosophical Magazine* **33**, 1917, 248

<sup>25</sup> Chapman, Sydney, and T. G. Cowling (denoted CC), loc.cit., 142-144, 252ff, 399-404.

<sup>26</sup> Eucken, A., *Physik. Zeitschrift* **14**, 1913, 324-332; see also CC, 237ff; HCB, 498-501; BSL, 257.

<sup>27</sup>  $D_{1z} = D_{2z}$  and  $D_{1z}^T = -D_{2z}^T$  are standard results but the value of neither is known (see HCB, loc. cit., 518ff, 584-585; Bird, R. B., W. E. Stewart, and E. N. Lightfoot (denoted BSL), *Transport Phenomena*, Wiley, New York, 1960, 502, 510ff, 568-569) and concentration dependence is ignored. Moreover, error occurs in use of  $\gamma_\phi = \partial n_\phi / \partial z \neq dn_\phi / dz = \gamma_\phi + (\partial n_\phi / \partial T) \gamma_T$ . This error is avoided using  $n_\phi = n_z \zeta_{\phi z}$  in which  $n_z$  contains the full temperature dependence and  $\zeta_{\phi z}$  the full composition dependence giving the simple, exact result for small  $\delta$ :  $n_{z+\delta} \zeta_{\phi z+\delta} = n_z \zeta_{\phi z} (1 + \delta \gamma_\phi / \zeta_{\phi z} - \delta \gamma_T / T_z)$ .

<sup>28</sup> In the binary system we take  $D_{1z} = \zeta_{1z} D_{11z} + \zeta_{2z} D_{12z}$  and  $D_{2z} = \zeta_{1z} D_{21z} + \zeta_{2z} D_{22z}$ . Solution of [F12] containing these expressions gives [F13] with constants  $c_1 = 2D_{12} / (D_{12} - D_{22})$ ,  $c_2 = -2D_{21} / (D_{11} - D_{21})$ . To define  $c_3$  we first define temporary variables  $\omega_1 = (D_{11} - D_{12})$ ,  $\omega_2 = (D_{12} - D_{22})$ ,  $\omega_3 = (D_{11} - D_{21})$ ,  $\omega_4 = (D_{11} - D_{12} - D_{21} + D_{22})$ ,  $\omega_5 = (D_{11} D_{22} - D_{12} D_{21})$  and  $c_3 = 2\{\omega_1 \omega_2 \omega_3 - D_{12} \omega_3 \omega_4 + \omega_2 \omega_5\} / \{\omega_2 \omega_3 \omega_4\}$ . Constant  $c_0$  in [F13] is  $c_0 = \omega_2 / \omega_1$ . Partial fractions were used in integrating [F12].

In a pure gas the temperature field is  $T_z / T_0 = (\sqrt{(1 + Bz/z_1) + C}) / (1 + C)$  where  $A = \kappa_0 / \gamma_k \Delta T_1$ ,  $B = (2A + 1) / A^2$ , and  $C = T_0 / A \Delta T_1 - 1$ .

<sup>29</sup> (a) Grew, K. E., and T. L. Ibbs, *Thermal Diffusion in Gases*, Cambridge University Press, 1952.

(b) Bird, R. B., *et al*, loc. cit., 568, 574-575.

<sup>30</sup> The collision integral  $\Omega^{(1,1)*}$  as defined by HCB is the ratio of actual to rigid-sphere collision cross-section. HCB, loc. cit., 484ff, 523.

<sup>31</sup> Modification of  $\lambda$  is required as given by Chapman, *et al*, loc. cit., 91 and by Jeans, loc. cit., 137.

<sup>32</sup> Talbot, L., *Rarefied Gas Dynamics*, Sam S. Fisher (editor), AIAA, New York, 1980, 467-488.

<sup>33</sup> Waldmann, L., *Zeitschrift für Naturforschung* **14a**, 1959, 376. See also Waldmann, L., and K. H. Schmitt, in *Aerosol Science*, C. N. Davies (editor), Academic Press, New York, 1966, 137-162.

<sup>34</sup> Jacobsen, S., and J. Brock, *Journal of Colloid and Interface Science* **20**, 1965, 544.

<sup>35</sup> Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, 1959, 426.