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*Thermal ramifications  
of*

## **INDISTINGUISHABILITY**

**Introduction.** We have, on page 95 and many times subsequently, had occasion to refer casually to objects (“tokens,” “particles,”...) that are identical but indistinguishable. One might argue—as, indeed, we *will* argue—that objects that are *truly* identical *cannot* be distinguished,<sup>121</sup> but our intention was too commonsensical to support such a quibble: we had in mind things like little “billiard balls of identical mass and radius” on which we had written identifying marks. “Distinguishability” has been a non-trivial attribute of the objects of past interest to us, for it has entered—as at (94)—into the *way we count* the number of ways that this or that can happen. “Indistinguishability” will be consequential for that identical reason . . . and, in the quantum realm, for other reasons as well.

We commonly keep track of similar objects by “marking” them, like the butterflies in a collection. As physicists, we “stamp numbers on things” in ways deemed irrelevant to the physics of those things. But to “stamp a number” on a thing is to manipulate (in a distinctive way) its internal degrees of freedom.

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<sup>121</sup> At one celebrated point it served Richard Feynman’s purpose to argue—as had Leibniz before him—that objects that are identical in all respects must be the *same* object. A similar idea (pertaining to the identity of gravitational and inertial mass) led Einstein to the invention of general relativity. We, however, would get into trouble if we were to adopt such a radical position.

Electrons, helium atoms, etc.—the objects of most typical interest to us as thermodynamicists—are, however, too simple, too impoverished of internal degrees of freedom . . . to support such identifying marks! We will be concerned here with the ramifications of that fact so far as it becomes manifest in the physics of thermalized many-body systems.

In real-world applications of quantum mechanics the consequences of indistinguishability are all-pervasive, dominant even in the physics of few-body systems that are far from thermal equilibrium: the design of the periodic table is, for example, attributable in large part to the indistinguishability of electrons.<sup>122</sup> In classical mechanics the effects of indistinguishability are much less conspicuous.<sup>123</sup> But it was a classical thermalized many-body system that first alerted physicists to the importance of the distinguishable/indistinguishable distinction:

**1. Gibbs' paradox.** Let  $\mathfrak{S}_A$  refer to an ideal gas sample containing  $N_A$  molecules of type A, and let  $\mathfrak{S}_B$  refer to an ideal gas sample containing  $N_B$  molecules of type B. We assume B-molecules to be distinguishable from A-molecules (perhaps because they have a different mass:  $m_B \neq m_A$ ). Assume  $\mathfrak{S}_A$  and  $\mathfrak{S}_B$  to be share the space within a thermally insulated cylinder, but to be separated by a freely-moveable diathermal partition (Figure 59). The two gases will then have equal pressures and temperatures

$$pV_A = N_A kT \quad \text{and} \quad pV_B = N_B kT$$

from which it follows that

$$V_A/N_A = V_B/N_B \tag{212}$$

The entropy of the composite system is given, according to (28), by

$$\begin{aligned} S_{\text{before}} &= S_A + S_B \\ &= N_A k \log V_A + N_B k \log V_B + \text{some inconsequential terms} \end{aligned}$$

Now remove the partition. The gases interdiffuse, each expanding freely into the other's domain. We learned from Joule that the free expansion of an ideal gas is an isothermal process. So after thermalization is complete we will have

$$\begin{aligned} S_{\text{after}} &= N_A k \log(V_A + V_B) + N_B k \log(V_A + V_B) \\ &\quad + \text{the same inconsequential terms} \end{aligned}$$

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<sup>122</sup> There is no *classical* theory of the periodic table, though Mendeleev's discovery (1869) did inspire many quaint attempts—some by major figures—to construct such a theory. Somebody should write an account of this dead history.

<sup>123</sup> The word “indistinguishable” is indexed in every quantum text (see, for example, Chapter 5 in Griffiths' *Introduction to Quantum Mechanics* (1995)) but, so far as I have been able to discover, in no classical mechanics text.

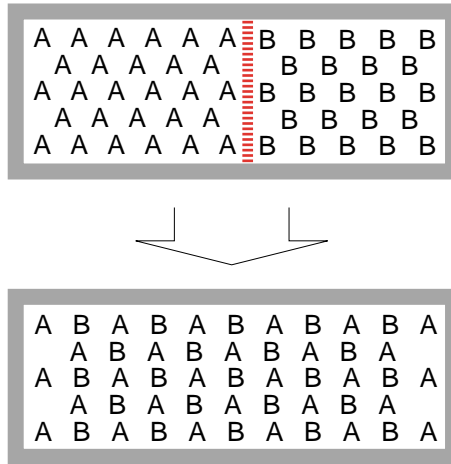


FIGURE 59: Above: thermally isolated samples of A-gas and B-gas are separated by a free-sliding diathermal partition, so have the same initial pressure and temperature. Below: the partition is removed, and the gases intermix. The pressure of each drops

$$p \longrightarrow \begin{cases} p_A = pV_A/(V_A + V_B) & : \text{ final partial pressure of A-gas} \\ p_B = pV_B/(V_A + V_B) & : \text{ final partial pressure of B-gas} \end{cases}$$

but  $p_A + p_B = p_{\text{initial}}$ .

The **entropy of mixing** has therefore the value

$$\begin{aligned} \Delta S &\equiv S_{\text{after}} - S_{\text{before}} \\ &= (N_A + N_B)k \log(V_A + V_B) - N_A k \log V_A - N_B k \log V_B \end{aligned} \tag{213.1}$$

$$\begin{aligned} &= -(N_A + N_B)k \left\{ \frac{N_A}{N_A + N_B} \log \frac{V_A}{V_A + V_B} + \frac{N_B}{N_A + N_B} \log \frac{V_B}{V_A + V_B} \right\} \\ &= -(N_A + N_B)k \{ C_A \log C_A + C_B \log C_B \} \end{aligned} \tag{213.2}$$

where

$$C_A \equiv \frac{N_A}{N_A + N_B} = \frac{V_A}{V_A + V_B}$$

and

$$C_B \equiv \frac{N_B}{N_A + N_B} = \frac{V_B}{V_A + V_B} = 1 - C_A$$

describe the **concentrations** of the A and B molecules in the final mixture.

NOTE that  $0 \leq C_A, C_B \leq 1$  so  $\Delta S \geq 0$ , the minus sign notwithstanding: relaxing the constraint and allowing mixing to proceed to thermalized completion has served to increase the entropy of the system.

Equations (213) hold *no matter how slight might be the feature that distinguishes A-molecules from B-molecules*, and they would appear to hold even in the absence of any such feature ... except that if A-molecules and B-molecules are identical then the presence or absence of the partition should be thermodynamically irrelevant: we expect to have

$$\Delta S \begin{cases} \geq 0 & \text{if } A \text{ and } B \text{ molecules are distinguishable} \\ = 0 & \text{if } A \text{ and } B \text{ molecules are indistinguishable} \end{cases}$$

That our expectation is unfulfilled is the upshot of ‘‘Gibbs paradox.’’

Gibbs observed that if, in our original entropy formula, we were to replace

$$\text{volume} \longmapsto \text{volume per molecule}$$

then in the case  $A \neq B$  we in place of (213.1) would have

$$\begin{aligned} \Delta S &= N_A k \log \frac{V_A + V_B}{N_A} + N_B k \log \frac{V_A + V_B}{N_B} - N_A k \log \frac{V_A}{N_A} - N_B k \log \frac{V_B}{N_B} \\ &= \text{same expression as before, after cancellations} \end{aligned}$$

while in the case  $A = B$  we get

$$\begin{aligned} \Delta S &= (N_A + N_B) k \log \frac{V_A + V_B}{N_A + N_B} - N_A k \log \frac{V_A}{N_A} - N_B k \log \frac{V_B}{N_B} \\ &= (N_A + N_B) k \log \left[ \frac{V_A + V_B}{N_A + N_B} \cdot \frac{N_A}{V_A} \right] \quad \text{by (212)} \\ &= (N_A + N_B) k \log \left[ \frac{1 + V_B/V_A}{1 + N_B/N_A} \right] \\ &= (N_A + N_B) k \log 1 \quad \text{by (212) again} \\ &= 0 \end{aligned}$$

It’s fairly clear why Gibbs’ trick works: removal of the partition increases the volume per molecule if  $A \neq B$ , but does not do so if  $A = B$ . Note, however, that the trick entails a *modification of the formula that describes the entropy of an ideal gas*:

$$S \longmapsto S_{\text{indistinguishable}} = S - Nk \log N \sim S - k \log N!$$

And that entails an adjustment in the way we count the states of given energy: (124) becomes

$$S_{\text{indistinguishable}} = k \log \frac{g(U, N, \dots)}{N!} \quad (214)$$

The implication, by (140), is that if we work in the macrocanonical formalism then we must modify the construction of the partition function

$$Z \longmapsto Z_{\text{indistinguishable}} = \frac{1}{N!} Z \quad (215)$$

The preceding discussion derives historically from the concluding pages of Gibbs' monograph<sup>124</sup> and is, it should be noted, entirely classical: no  $\hbar$ 's intrude. It serves to alert us to the fact that

- i*) indistinguishability entails adjustment of the way we count
- ii*) adjusted counting alters the description of the entropy of a system
- iii*) altered entropy changes—sometimes profoundly—the thermodynamic properties of the system.

It would, on this evidence, be incorrect to allege (as is often done) that the physical ramifications of indistinguishability are intrinsically and exclusively quantum mechanical. But it is the case, as will emerge, that in quantum mechanics the subject acquires a depth and variety for which classical mechanics does not prepare us.

**2. Classical vs. quantum mechanical embodiments of indistinguishability.** We look first to the classical side of the coin. Think of a system (for sake of conceptual concreteness let it be a *bulk* system—a gas, let us say) composed of  $N$  physically similar point-particles. To describe such a system a kinetic theorist would sprinkle  $N$  points onto 6-dimensional phase space and watch (as Maxwell and Boltzmann did) the motion of a function  $f(\mathbf{x}, \mathbf{p}, t)$  that (in some course-grained sense) describes the local density of such points. We, however, are statistical mechanics in the tradition of Gibbs: we work in  $6N$ -dimensional phase space  $\Gamma$ , where a single point  $\{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N\}$  describes the momentary state of the entire system, and when we “sprinkle points onto  $\Gamma$ ” it is to describe an *ensemble* of systems. We write

$$\begin{aligned} P(p, x; 0) &\equiv P(p_1, p_2, \dots, p_{3N}, x_1, x_2, \dots, x_{3N}; 0) \\ &\equiv P(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N; 0) \end{aligned}$$

to describe the initial distribution of ensemble points, and  $P(p, x; t)$  to describe the result of its dynamical evolution. Liouville's theorem<sup>125</sup> asserts that an observer who drifts with the dynamical phase flow

$$\{p_0, x_0\} \xrightarrow{H} \{p(p_0, x_0; t), x(p_0, x_0; t)\}$$

will see the local point density to be constant

$$\frac{dP}{dt} = \sum_i \left\{ \frac{\partial P}{\partial p_i} \dot{p}_i + \frac{\partial P}{\partial x_i} \dot{x}_i \right\} + \frac{\partial P}{\partial t} = 0$$

from which we obtain “Liouville's equation”

$$\begin{aligned} \sum_i \left\{ \frac{\partial H}{\partial x_i} \frac{\partial P}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial P}{\partial x_i} \right\} - \frac{\partial P}{\partial t} &= 0 \\ &\downarrow \\ \frac{\partial P}{\partial t} &= [H, P] \end{aligned} \quad (216)$$

<sup>124</sup> *Elementary Principles of Statistical Mechanics* (1902).

<sup>125</sup> See, for example, H. Goldstein, *Classical Mechanics* (2<sup>nd</sup> edition 1980), Section 9–8.

Liouville's equation describes how point populations move, and can in particular be used to recover the canonical motion of individual points, thought of as "1-point populations."<sup>126</sup> But ...

In statistical mechanical applications we have interest only in populations that are *steady* in the sense that

$$\frac{\partial P}{\partial t} = 0$$

For this reason: t-independence is the most conspicuous feature of *thermalized* populations. Such populations are fairly easy to construct. If  $G(p, x)$  were a constant of the motion

$$[H, G] = 0$$

then any  $f(G)$  would serve. But constants of many-body motion are in short supply! We note, however, that  $H$  is itself—trivially/universally—a constant of the motion, so every

$$P(p, x) = \frac{1}{Z} f(H(p, x))$$

is steady. And, in particular, Gibbs'

$$P(p, x) = \frac{1}{Z} e^{-H(p, x)/kT}$$

is steady.<sup>127</sup>

To declare our classical interest in a gas made of identical mass points we might write something like

$$H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{2m} \sum_i \{\mathbf{p}_i \cdot \mathbf{p}_i + U_{\text{wall}}(\mathbf{x}_i)\} + \sum_{i,j}' U_{\text{intermolecular}}(r_{ij})$$

with  $r_{ij} \equiv |\mathbf{x}_i - \mathbf{x}_j|$ . The associated macrocanonical distribution function

$$P(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{Z} e^{-H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)/kT} \quad (217.1)$$

$$Z = \int g(E, N) e^{-E/kT} dE \quad (217.1)$$

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<sup>126</sup> Write  $P(x, p, t) = \delta(p - p(p_0, x_0; t))\delta(x - x(p_0, x_0; t))$  and from Liouville's equation obtain

$$\begin{aligned} \frac{\partial H}{\partial x} \delta'(p \dots) \delta(x \dots) - \frac{\partial H}{\partial p} \delta(p \dots) \delta'(x \dots) \\ = \delta'(p \dots) \delta(x \dots) (-\dot{p}) + \delta(p \dots) \delta'(x \dots) (-\dot{x}) \end{aligned}$$

Argue that therefore

$$\frac{\partial H}{\partial x} = -\dot{p} \quad \text{and} \quad \frac{\partial H}{\partial p} = +\dot{x}$$

The multi-dimensional generalization is straightforward.

<sup>127</sup> Evidently *other* considerations must serve to assign the macrocanonical distribution a distinguished place among its siblings.

is *symmetric*—in the sense invariant under all subscript permutations

$$\wp \equiv \begin{pmatrix} 1 & 2 & \dots & N \\ i_1 & i_2 & \dots & i_N \end{pmatrix}$$

—for the simple reason that  $H$  is. But at this point we are brought into confrontation with a delicate issue which, so far as I am aware, is not addressed in the literature, and which it is entirely possible I am about to misrepresent:

Though it is not feasible to assemble structured objects—objects endowed with a distinctive shape—from gas, it is certainly possible to construct such objects from “identical tinker toys” (think, for example, of a lump of gold, or of a cut diamond) and to “do thermodynamics” on such assemblies. The shape of the object must be written into the design of the Hamiltonian, which we may take to have the form

$$H = \frac{1}{2m} \sum_i \mathbf{p}_i \cdot \mathbf{p}_i + \underbrace{U(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)}_{\text{—lack of symmetry reflects “structure”}}$$

If the particles are considered to be *identical but distinguishable* then equations (217) serve quite well, but if the particles are *indistinguishable* then the permutational asymmetry of  $P(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)$ —inherited at (217.1) from that of the Hamiltonian—becomes intolerable. We are obligated (i) to *extract the symmetric part* of the distribution

$$P_{\text{sym}}(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) \equiv \frac{1}{N!} \sum_{\text{permutations}} P(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)$$

and (ii) to conflate statepoints that (like  $\{\mathbf{p}_1, \mathbf{p}_2, \mathbf{x}_1, \mathbf{x}_2\}$  and  $\{\mathbf{p}_2, \mathbf{p}_1, \mathbf{x}_2, \mathbf{x}_1\}$ ) are permutational siblings of one another. The normalization condition then reads

$$\begin{aligned} & \int \dots \int_{\text{all permutationally inequivalent phasepoints}} P_{\text{sym}}(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) \left( \frac{d^3 p d^3 x}{h^3} \right)^N \\ &= \frac{1}{N!} \int \dots \int_{\text{all of phase space}} P_{\text{sym}}(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) \left( \frac{d^3 p d^3 x}{h^3} \right)^N = 1 \end{aligned}$$

Noting that all permutational siblings of the Hamiltonian give rise—whether or not the Hamiltonian happens to be symmetric—to the *same* density-of-states function  $g(E, N)$ , we conclude that for structured systems of indistinguishable particles the macrocanonical distribution formulæ (217) should be written

$$\begin{aligned} P_{\text{sym}}(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N) &= \frac{1}{Z} \left\{ \frac{1}{N!} \sum_{\text{permutations}} e^{-H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)/kT} \right\} \\ Z &= \int g_{\text{distinct}}(E, N) e^{-E/kT} dE \end{aligned}$$

where

$$\begin{aligned} g_{\text{distinct}}(E, N) &\equiv \text{density of the } \textit{distinct/distinguishable} \text{ states} \\ &\quad \text{of the indistinguishable particle system} \\ &= \frac{1}{N!} \cdot \begin{cases} \text{what would have been the density of states} \\ \text{if the particles were distinguishable} \end{cases} \end{aligned}$$

“Onion integration” has become integration over a *wedge* of onion (of which all the other  $N! - 1$  wedges are redundant copies).

The main points to emerge from the preceding (classical) discussion are that

- symmetry is forced upon  $P(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)$  by the indistinguishability of the particles
- all but  $1/N!$ <sup>th</sup> of phase space is rendered redundant by indistinguishability.

The gross shape/structure of the system poses a conceptual problem (breaks the permutational symmetry of the Hamiltonian) but, it would seem, a problem of only slight physical consequence ... for we can expect shape effects to scale like surface effects (which is to say: like  $N^{2/3}/N = N^{-1/3}$ ): we can expect the thermodynamics of a lump of gold to be, by every practical measure, shape-independent, and the theory of bulk systems to pertain.

Turning now to quantum mechanics (often claimed to be the *exclusive* playground of indistinguishability) ... if  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$  is taken to describe the quantum state of an  $N$ -body system then—so runs the standard argument<sup>128</sup>—indistinguishability entails the symmetry of

$$P(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \equiv |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2$$

which in turn entails (after some argument) that the wave function is either **totally symmetric**

$$\Psi(\mathbf{x}_{i_1}, \mathbf{x}_{i_2}, \dots, \mathbf{x}_{i_N}) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad : \text{ all permutations } \wp$$

or **totally antisymmetric**

$$\begin{aligned} \Psi(\mathbf{x}_{i_1}, \mathbf{x}_{i_2}, \dots, \mathbf{x}_{i_N}) &= (-)^{\wp} \cdot \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad : \text{ all permutations } \wp \\ (-)^{\wp} &= \begin{cases} +1 & : \wp \text{ even} \\ -1 & : \wp \text{ odd} \end{cases} \end{aligned}$$

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<sup>128</sup> Much could be said in favor of an approach to quantum indistinguishability that operates at the level of abstraction introduced into quantum theory by Dirac. Textbook authors find it “simpler,” however, to work closer to the familiar ground: it is *by convention* that they work “in the  $\mathbf{x}$ -representation,” and I am content on this occasion to follow their lead.



Experimental discoveries and theoretical advances over a span of fifteen years<sup>129</sup> led to the realization that

- elementary particles can be expected to possess (in addition to their other endowments, like electric charge) **mass** (possibly zero) and intrinsic angular momentum or **spin**
- spin (in units of  $\hbar$ ) is necessarily either **integral** or **half-integral**
- the wavefunction of a collection of identical bosons (particles with integral spin) is necessarily symmetric; the wavefunction of a collection of identical fermions (particles with half-integral spin) is necessarily antisymmetric
- the bosons/fermions in question need not be “elementary particles” but can be composite structures (hydrogen atoms/molecules, helium atoms, *etc.*)

The connection (established by Pauli) between “spin” and “statistics” is really a connection of the form

$$\text{integral/half-integral spin} \longleftrightarrow \text{wavefunction symmetry/antisymmetry}$$

“Statistics” enters the picture because—as will be shown in the next section—*symmetry/antisymmetry exerts direct control upon the energy spectrum and state density* (whence upon the statistical mechanics and thermodynamics) of a many-body system.

To render more explicit the upshot of the preceding remarks, let  $\mathfrak{S}$  be assembled from  $N$  non-interactive 1-dimensional quantum mechanical elements. Let

$$\mathbf{h}\psi_n(x) = \epsilon_n\psi_n(x)$$

be the time-independent Schrödinger equation of an individual element, and assume the  $\epsilon$ -spectrum to be non-degenerate (this guarantees the orthogonality of the normalized eigenstates). Finally—as an expository convenience—let us set  $N = 2$ . The Hamiltonian of  $\mathfrak{S}$  can, by our assumptions, be described

$$\mathbf{H} = \mathbf{h}_1 + \mathbf{h}_2$$

DISTINGUISHABLE ELEMENTS

 Immediately

$$\mathbf{H}\psi_a(x_1)\psi_b(x_2) = (\epsilon_a + \epsilon_b)\psi_a(x_1)\psi_b(x_2)$$

which we might notate  $\mathbf{H}\Psi_{ab}(x_1, x_2) = E_{ab}\Psi_{ab}(x_1, x_2)$ . We note that the system eigenvalue  $E_{ab}$  is (if  $a \neq b$ ) at least 2-fold degenerate, for  $\Psi_{ab}(x_1, x_2)$

<sup>129</sup> I am thinking here of Pauli’s formulation of the **exclusion principle** (1925), the discover of spin (Uhlenbeck & Gaudsmit, 1925), the invention of the Dirac equation (1928), Wigner’s classification of the irreducible unitary representations of the Lorentz group (1937), Pauli’s demonstration that the principles of relativistic quantum field theory imply a necessary connection between spin and statistics (1940). For historical details see Chapter 3 in Max Jammer, *The Conceptual Development of Quantum Mechanics* (1966) and Ian Duck & E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem* (1997).

and  $\Psi_{ba}(x_1, x_2)$  share that eigenvalue. Higher degeneracy would arise if the  $\epsilon$ -spectrum permitted one to write  $\epsilon_a + \epsilon_b = \epsilon_c + \epsilon_d$ .

**INDISTINGUISHABLE BOSONS** We agree to omit reference to the spin of the elements (alternatively: to assume them to be spinless). The Hamiltonian remains as it was, but (unless  $a = b$ ) the eigenfunctions  $\Psi_{ab}(x_1, x_2)$  must be *symmetrized*

$$\begin{aligned} \Psi_{ab}(x_1, x_2) \longmapsto \Psi_{ab}^{\text{sym}}(x_1, x_2) &\equiv \frac{\Psi_{ab}(x_1, x_2) + \Psi_{ab}(x_2, x_1)}{\sqrt{2}} \\ &= \frac{1}{\sqrt{2}} \left\{ \psi_a(x_1)\psi_b(x_2) + \psi_a(x_2)\psi_b(x_1) \right\} \\ &= \Psi_{ab}^{\text{sym}}(x_2, x_1) \\ &= \Psi_{ba}^{\text{sym}}(x_1, x_2) \end{aligned}$$

before they become admissible as descriptors of the bosonic system. Note that  $E_{ab}$  has lost its former 2-fold degeneracy (though degeneracy of the other—“accidental”—type may persist).<sup>130</sup>

**INDISTINGUISHABLE FERMIONS** The spin variables that we agree to omit are now *necessarily* present ... but for present purposes irrelevant. Again, the Hamiltonian remains as it was, but the eigenfunctions  $\Psi_{ab}(x_1, x_2)$  must now be *antisymmetrized*

$$\begin{aligned} \Psi_{ab}(x_1, x_2) \longmapsto \Psi_{ab}^{\text{antisym}}(x_1, x_2) &\equiv \frac{\Psi_{ab}(x_1, x_2) - \Psi_{ab}(x_2, x_1)}{\sqrt{2}} \\ &= \frac{1}{\sqrt{2}} \left\{ \psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1) \right\} \\ &= -\Psi_{ab}^{\text{antisym}}(x_2, x_1) \\ &= -\Psi_{ba}^{\text{antisym}}(x_1, x_2) \end{aligned}$$

before they become admissible as descriptors of the fermionic system. Notice that

$$\Psi_{ab}(x_1, x_2) = 0 \quad \text{at} \quad x_1 = x_2$$

and that  $\Psi_{aa}(x_1, x_2)$  vanishes everywhere, so describes no state at all. Again,  $E_{ab}$  has lost its former 2-fold degeneracy (though degeneracy of the other—accidental—type may persist). Moreover,  $E_{aa}$  has *disappeared* from the energy

<sup>130</sup> For  $N > 2$  one proceeds similarly, writing

$$\Psi_{ab\dots q}^{\text{sym}}(x_1, x_2, \dots, x_N) \equiv \text{perm} \begin{pmatrix} \psi_a(x_1) & \psi_a(x_2) & \dots & \psi_a(x_N) \\ \psi_b(x_1) & \psi_b(x_2) & \dots & \psi_b(x_N) \\ \vdots & \vdots & & \vdots \\ \psi_q(x_1) & \psi_q(x_2) & \dots & \psi_q(x_N) \end{pmatrix}$$

where “perm” refers to the “permanent,” which is defined like the determinant, but with the minus signs omitted (see H. Minc, *Permanents* (1978)).

spectrum of the 2-body system, this being the upshot of Pauli’s “exclusion principle.”<sup>131</sup>

I digress now to pick up another thread that—though seldom remarked—winds through this story. In classical mechanics we write

$$\langle A \rangle = \iint A(p, x) P(p, x) dp dx \quad (218.1)$$

(or its obvious higher-dimensional analog) to describe the expected value of the “observable”  $A(p, x)$  with respect to the distribution  $P(p, x)$ . In quantum mechanics the function  $A(p, x)$  is (by a certain rule) replaced by an operator  $\mathbf{A}$  and one writes

$$\langle \mathbf{A} \rangle = \int \psi^*(x) \mathbf{A} \psi(x) dx$$

to describe the expected outcome of  $A$ -measurements if the system is in the quantum state described by  $\psi(x)$ . In 1932 E. P. Wigner drew attention<sup>132</sup> to the fact that this last equation can be rendered

$$\langle \mathbf{A} \rangle = \iint A(p, x) P_\psi(p, x) dp dx \quad (218.2)$$

provided one defines

$$P_\psi(p, x) \equiv \frac{2}{h} \int \psi^*(x + \xi) e^{\frac{2i}{h} p \xi} \psi(x - \xi) d\xi \quad (219)$$

Thus was planted the seed that by the early 1950’s, owing largely to the work of J. E. Moyal,<sup>133</sup> had grown into a full-blown “phase space formulation of quantum mechanics.”<sup>134</sup> But Wigner’s initial motivation and intent were more limited: he proposed to construct

$$P(p, x) \equiv \sum_n e^{-E_n/kT} P_{\psi_n}(p, x) = \text{power series in } \hbar$$

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<sup>131</sup> For  $N > 2$  one proceeds similarly, writing

$$\Psi_{ab\dots q}^{\text{antisym}}(x_1, x_2, \dots, x_N) \equiv \det \begin{pmatrix} \psi_a(x_1) & \psi_a(x_2) & \dots & \psi_a(x_N) \\ \psi_b(x_1) & \psi_b(x_2) & \dots & \psi_b(x_N) \\ \vdots & \vdots & & \vdots \\ \psi_q(x_1) & \psi_q(x_2) & \dots & \psi_q(x_N) \end{pmatrix}$$

Such “determinantal wavefunctions” appeared first in the work of Dirac (1926), but are usually called “Slater determinants” after their appearance in a paper by J. C. Slater (1929).

<sup>132</sup> “On the quantum correction for thermodynamic equilibrium,” *Phys. Rev.* **40**, 749 (1932).

<sup>133</sup> “Quantum mechanics as a statistical theory,” *Proc. Camb. Phil. Soc.* **45**, 92 (1949).

<sup>134</sup> For a fairly elaborate account of that theory, see Chapter 2 in my *ADVANCED QUANTUM TOPICS* (2000).

and—by exploiting the fact that (218.1) and (218.2) are structurally identical—thus to expose the successive quantum corrections to the statements of classical statistical mechanics.

My own objective, at the moment, is to describe the symmetry properties that the Wigner distribution inherits from those of the  $N$ -particle wave function, and that might serve to distinguish it from the simple permutational symmetry that is universal within the classical theory of indistinguishable particles.<sup>135</sup> Looking to the evaluation of  $P_{\Psi_{ab}}(p_1, p_2, x_1, x_2)$  in the bosonic/fermionic cases, we find

$$\begin{aligned}
& \left(\frac{2}{\hbar}\right)^2 \frac{1}{2} \iint \left\{ \psi_a^*(x_1 + \xi_1) \psi_b^*(x_2 + \xi_2) \pm \psi_b^*(x_1 + \xi_1) \psi_a^*(x_2 + \xi_2) \right\} \\
& \quad \cdot e^{2\frac{i}{\hbar}(p_1 \xi_1 + p_2 \xi_2)} \\
& \quad \cdot \left\{ \psi_a(x_1 - \xi_1) \psi_b(x_2 - \xi_2) \pm \psi_b(x_1 - \xi_1) \psi_a(x_2 - \xi_2) \right\} d\xi_1 d\xi_2 \\
& = \frac{1}{2} \left\{ \frac{2}{\hbar} \int \psi_a^*(x_1 + \xi_1) e^{2\frac{i}{\hbar} p_1 \xi_1} \psi_a(x_1 - \xi_1) d\xi_1 \right\} \\
& \quad \cdot \left\{ \frac{2}{\hbar} \int \psi_b^*(x_2 + \xi_2) e^{2\frac{i}{\hbar} p_2 \xi_2} \psi_b(x_2 - \xi_2) d\xi_2 \right\} \\
& + \frac{1}{2} \left\{ \frac{2}{\hbar} \int \psi_b^*(x_1 + \xi_1) e^{2\frac{i}{\hbar} p_1 \xi_1} \psi_b(x_1 - \xi_1) d\xi_1 \right\} \\
& \quad \cdot \left\{ \frac{2}{\hbar} \int \psi_a^*(x_2 + \xi_2) e^{2\frac{i}{\hbar} p_2 \xi_2} \psi_a(x_2 - \xi_2) d\xi_2 \right\} \\
& \pm \frac{1}{2} \left\{ \frac{2}{\hbar} \int \psi_a^*(x_1 + \xi_1) e^{2\frac{i}{\hbar} p_1 \xi_1} \psi_b(x_1 - \xi_1) d\xi_1 \right\} \\
& \quad \cdot \left\{ \frac{2}{\hbar} \int \psi_b^*(x_2 + \xi_2) e^{2\frac{i}{\hbar} p_2 \xi_2} \psi_a(x_2 - \xi_2) d\xi_2 \right\} \\
& \pm \frac{1}{2} \left\{ \frac{2}{\hbar} \int \psi_b^*(x_1 + \xi_1) e^{2\frac{i}{\hbar} p_1 \xi_1} \psi_a(x_1 - \xi_1) d\xi_1 \right\} \\
& \quad \cdot \left\{ \frac{2}{\hbar} \int \psi_a^*(x_2 + \xi_2) e^{2\frac{i}{\hbar} p_2 \xi_2} \psi_b(x_2 - \xi_2) d\xi_2 \right\} \\
& \equiv \frac{1}{2} P_{aa}(p_1, x_1) P_{bb}(p_2, x_2) + \frac{1}{2} P_{bb}(p_1, x_1) P_{aa}(p_2, x_2) \\
& \quad \pm \frac{1}{2} P_{ab}(p_1, x_1) P_{ba}(p_2, x_2) \pm \frac{1}{2} P_{ba}(p_1, x_1) P_{ab}(p_2, x_2)
\end{aligned} \tag{220}$$

which is (in both the bosonic and the fermionic cases) manifestly *symmetric* under  $(p_1, x_1) \rightleftharpoons (p_2, x_2)$  exchange, and in the fermionic case clearly *vanishes*

<sup>135</sup> We note, in this connection, that (219) is readily shown to supply the “marginal distribution”

$$\int P_{\Psi}(p_1, p_2, \dots, p_N, x_1, x_2, \dots, x_N) dp_1 dp_2 \cdots dp_N = |\Psi(x_1, x_2, \dots, x_N)|^2$$

and that the expression on the right is symmetric for *both* bosons and fermions.

everywhere if  $a = b$ . If  $(p_1, x_1)$  and  $(p_2, x_2)$  refer to the *same* phase point—call it  $(p, x)$ —then the expression (220) becomes

$$P_{aa}(p, x)P_{bb}(p, x) \pm P_{ab}(p, x)P_{ba}(p, x) \quad : \quad \begin{cases} \text{bosonic case} \\ \text{fermionic case} \end{cases}$$

If, on the other hand, the identical particles were *distinguishable* then for the distinct unsymmetrized states  $\Psi_{ab}(x_1, x_2)$  and  $\Psi_{ba}(x_1, x_2)$  the Wigner process gives

$$\begin{aligned} \Psi_{ab}(x_1, x_2) &\mapsto P_{aa}(p_1, x_1)P_{bb}(p_2, x_2) \\ \Psi_{ba}(x_1, x_2) &\mapsto P_{bb}(p_1, x_1)P_{aa}(p_2, x_2) \end{aligned}$$

both of which become

$$P_{aa}(p, x)P_{bb}(p, x)$$

at coincident phase points. Evidently

- bosonic symmetry increases the likelihood of coincidence;
- fermionic antisymmetry decreases the likelihood of coincidence.

The same point will emerge in a different way from the discussion to which we now turn.<sup>136</sup>

**3. Distinguishable states of a system of indistinguishable particles.** If we would describe the thermodynamics of a system  $\mathfrak{S}$  of “particles,” and if we elect to work within the macrocanonical formalism . . . then we have first to determine the number  $g(E, N)$  of distinct ways that the system can possess energy  $E$  (and then—as a separate activity—to use that information to compute the partition function  $Z$ ). It is in this connection that the *indistinguishability* of the particles—and, more particularly, whether they are bosons or fermions—becomes relevant, for it bears directly upon the questions

- what system-states can be constructed?
- how are they to be counted?

A simple example serves to illustrate the points at issue:

Let  $\mathfrak{S}$  be a 2-particle system. Let  $\epsilon_1, \epsilon_2$  and  $\epsilon_3$  be the energies available to each *individual* particle, which we assume to be identical and non-interactive. The system-energy is (by the latter assumption) the sum of the particle energies. Proceeding initially on the assumption that the particles—though identical—are *distinguishable*, let A and B be their names. The possible configurations of the system, and their associated energies, are shown in Table 1. The partition function of our toy system is

$$Z = e^{-\beta(2\epsilon_1)} + e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + 2e^{-\beta(\epsilon_1+\epsilon_2)} + 2e^{-\beta(\epsilon_1+\epsilon_3)} + 2e^{-\beta(\epsilon_2+\epsilon_3)}$$

If the particles are in fact *not* distinguishable then Gibbs would have us divide

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<sup>136</sup> Since  $P(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{x}_1, \dots, \mathbf{x}_N)$  is permutationally symmetric in *all* cases, it becomes a challenge to extract from the Wigner formalism a statement equivalent to the familiar requirement that  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  must be either symmetric or antisymmetric.

| ENERGY                    | CONFIGURATION |              |              |
|---------------------------|---------------|--------------|--------------|
|                           | $\epsilon_1$  | $\epsilon_2$ | $\epsilon_3$ |
| $2\epsilon_1$             | AB            |              |              |
| $2\epsilon_2$             |               | AB           |              |
| $2\epsilon_3$             |               |              | AB           |
| $\epsilon_1 + \epsilon_2$ | A             | B            |              |
| $\epsilon_1 + \epsilon_2$ | B             | A            |              |
| $\epsilon_1 + \epsilon_3$ | A             |              | B            |
| $\epsilon_1 + \epsilon_3$ | B             |              | A            |
| $\epsilon_2 + \epsilon_3$ |               | A            | B            |

TABLE 1: Configurations and energies available to a 2-particle system of identical but distinguishable particles, each of which has a 3-energy spectrum. If the particles are in fact indistinguishable then Gibbs recommends an adjustment

$$g(E, 2) \mapsto \frac{1}{2!}g(E, 2)$$

that results in what—for historical reasons unknown to me—is conventionally called **Boltzmann statistics**. The adjustment deals effectively with the bottom six states, but overcompensates in the top three cases.

by 2!, writing

$$Z_{\text{Boltzmann}} = \frac{1}{2}e^{-\beta(2\epsilon_1)} + \frac{1}{2}e^{-\beta(2\epsilon_2)} + \frac{1}{2}e^{-\beta(2\epsilon_3)} + e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)} \quad (221)$$

If, on the other hand, we assume the particles to be (quantum mechanical) bosons then we obtain the data shown in Table 2, which gives

$$Z_{\text{Bose-Einstein}} = e^{-\beta(2\epsilon_1)} + e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)} \quad (222)$$

in which the first three terms on the right (the “diagonal” terms) are enhanced relative to their occurrence in the classical construct  $Z_{\text{Boltzmann}}$ .

If, finally, we assume the particles to be (quantum mechanical) fermions then we obtain the data shown in Table 3, which gives

$$Z_{\text{Fermi-Dirac}} = e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)} \quad (223)$$

in which the “diagonal” terms have been extinguished.

| ENERGY                    | CONFIGURATION |              |              |
|---------------------------|---------------|--------------|--------------|
|                           | $\epsilon_1$  | $\epsilon_2$ | $\epsilon_3$ |
| $2\epsilon_1$             | XX            |              |              |
| $2\epsilon_2$             |               | XX           |              |
| $2\epsilon_3$             |               |              | XX           |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |

TABLE 2: States available to a 2-particle system of 3-state bosons. Such systems obey **Bose-Einstein statistics**.

| ENERGY                    | CONFIGURATION |              |              |
|---------------------------|---------------|--------------|--------------|
|                           | $\epsilon_1$  | $\epsilon_2$ | $\epsilon_3$ |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |

TABLE 3: States available to a 2-particle system of 3-state fermions. Such systems obey **Fermi-Dirac statistics**.

It should, however, be borne in mind that fermions possess spin  $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$  and so possess  $2s + 1 = 2, 4, 6, \dots$  internal degrees of freedom. Electrons, for example, come in “two flavors:” “**spin up**” and “**spin down**.” This circumstance expands the options, alters the state-counting details. If we allow ourselves to assume—unrealistically—that the energetics of a fermionic system are flavor-insensitive then Table 3 expands to assume the form of Table 4.

The tabulated data, though it refers to a toy system, does lend support to the informal proposition (page 185) that—relative to Gibbs’ classical theory of indistinguishability (Boltzmann statistics)—*particles subject to Bose-Einstein statistics love to cohabit states, while particles subject to Fermi-Dirac statistics refuse to*.

“State-counting by tabulation” becomes unworkable in physically realistic situations (*i.e.*, as the number of energy levels  $\epsilon_i$  grows to infinity and the number  $N$  of particles becomes thermodynamically large). More powerful methods are required, but before we become lost in the details it is well to recognize them for what they are: counting procedures.

| ENERGY                    | CONFIGURATION |              |              |
|---------------------------|---------------|--------------|--------------|
|                           | $\epsilon_1$  | $\epsilon_2$ | $\epsilon_3$ |
| $2\epsilon_1$             | XX            |              |              |
| $2\epsilon_2$             |               | XX           |              |
| $2\epsilon_3$             |               |              | XX           |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_2$ | X             | X            |              |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_1 + \epsilon_3$ | X             |              | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |
| $\epsilon_2 + \epsilon_3$ |               | X            | X            |

TABLE 4: States available to a 2-particle system of 3-state fermions if each fermion comes in two flavors.

**4. State counting by a generating function technique.** Let us persist (compare page 181) in our “quantum mechanical ideal gas”-like assumption, to wit: that  $\mathfrak{S}$  is assembled from non-interactive identical particles (not, for the moment, assumed to be indistinguishable), each of which is described

$$h\psi_\alpha = \epsilon_\alpha \psi_\alpha \quad : \quad \epsilon_\alpha \text{ is } g_\alpha\text{-fold degenerate}$$

The state of  $\mathfrak{S}$  is described most conveniently by the set  $\{n_1, n_2, \dots, n_\alpha, \dots\}$  of **occupation numbers**:

$$n_\alpha \equiv \text{number of particles in state } \psi_\alpha$$

Necessarily  $n_\alpha \geq 0$  (all  $\alpha$ ) and

$$N = \sum_{\alpha} n_{\alpha} \tag{224}$$

If the particles are *distinguishable* then (by a simple combinatoric argument) system-states of energy

$$E = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}$$

can be constructed in a total of



$$G(E, N) = \frac{N!}{n_1! n_2! \dots} g_1^{n_1} g_2^{n_2} \dots \quad (225)$$

distinct ways, so the partition function becomes

$$\begin{aligned} Z &= \int G(E) e^{-\beta E} dE = \sum'_{\{\mathbf{n}\}} \frac{N!}{n_1! n_2! \dots} g_1^{n_1} g_2^{n_2} \dots e^{-\beta \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}} \\ &= \sum'_{\{\mathbf{n}\}} \frac{N!}{n_1! n_2! \dots} \left( g_1 e^{-\beta \epsilon_1} \right)^{n_1} \left( g_2 e^{-\beta \epsilon_2} \right)^{n_2} \dots \end{aligned}$$

where (as henceforth) the prime on  $\sum'$  signifies that the summation is to be carried out subject to the constraint  $\sum_{\alpha} n_{\alpha} = N$ . From the multinomial theorem it follows that the preceding result can be expressed

$$\begin{aligned} &= \left( g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2} + \dots \right)^N \\ &= \mathcal{Z}^N \end{aligned} \quad (226)$$

$$\mathcal{Z} \equiv \sum_{\alpha} g_{\alpha} e^{-\beta \epsilon_{\alpha}} \quad (227)$$

Now bring into play the assumption that the particles are *indistinguishable*, first in the weak (classical) sense “undistinguished.” Gibbs/Boltzmann respond by after-the-fact adjustment

$$Z \longmapsto Z_{\text{Boltzman}} \equiv \frac{1}{N!} \mathcal{Z}^N \quad (228)$$

But—as we have seen—in a quantum mechanical context “undistinguished” becomes “indistinguishable in principle,” and more serious tailoring is required. In the bosonic case ( $\Psi$  symmetric) the occupation numbers can assume any values, but the combinatorial considerations that gave rise to the multinomial coefficients in (225) lose their force. In the fermionic case ( $\Psi$  antisymmetric) the exclusion principle entails that one can place

- 1 particle in the  $\alpha^{\text{th}}$  state in  $g_{\alpha}$  ways
- 2 particles in the  $\alpha^{\text{th}}$  state in  $g_{\alpha}(g_{\alpha} - 1)/2!$  ways
- 3 particles in the  $\alpha^{\text{th}}$  state in  $g_{\alpha}(g_{\alpha} - 1)(g_{\alpha} - 2)/3!$  ways
- $\vdots$
- $g_{\alpha}$  particles in the  $\alpha^{\text{th}}$  state in only one way

and cannot squeeze more than  $g_{\alpha}$  particles into that state. So we have

$$G(E, N) = \begin{cases} g_1^{n_1} g_2^{n_2} \dots & : \text{BOSE-EINSTEIN} \\ \binom{g_1}{n_1} \binom{g_2}{n_2} \dots & : \text{FERMI-DIRAC} \end{cases}$$

In developing the characteristic implications of those two statements we will find it convenient to assume—recognizing that in the fermionic case this does not make much physical sense—that  $g_\alpha = 1$  (all  $\alpha$ ): then in both cases we have  $G(E, N) = 1$  for all allowed sets  $\{\mathbf{n}\}$ , giving

$$\begin{aligned} Z &= \sum'_{\{\mathbf{n}\}} e^{-\beta \sum_\alpha n_\alpha \epsilon_\alpha} \\ &= \sum'_{\{\mathbf{n}\}} \left( e^{-\beta \epsilon_1} \right)^{n_1} \left( e^{-\beta \epsilon_2} \right)^{n_2} \dots \quad : \quad \text{BOTH CASES} \end{aligned} \quad (229)$$

The difference between the cases resides now in the circumstance that

- each  $n_\alpha$  ranges on  $\{0, 1, 2, 3, \dots\}$  in the Bose-Einstein case
- each  $n_\alpha$  ranges on  $\{0, 1\}$  in the Fermi-Dirac case.

The evaluation of  $Z_{\text{Bose-Einstein}}$  and  $Z_{\text{Fermi-Dirac}}$  acquires its difficulty (such as it is) from the circumstance that the summation is subject to a constraint. If it were permissible to *ignore* the constraint then it would follow at once from (229) that

$$Z_{\text{Bose-Einstein}} = \prod_\alpha \frac{1}{1 - e^{-\beta \epsilon_\alpha}} \quad (230.1)$$

$$Z_{\text{Fermi-Dirac}} = \prod_\alpha (1 + e^{-\beta \epsilon_\alpha}) \quad (230.2)$$

Our problem is to figure out some way to take the constraint (224) into account. Diverse approaches to the problem have been described in the literature. They come in richly assorted degrees of difficulty and conceptual clarity, and can be classified under three broad heads:

- **combinatorial methods**
- the **method of the grand canonical ensemble**, wherein  $N$ —which is never known with precision anyway—is considered to be *variable*, and governed by a distribution function of the form  $e^{-\mu N}$
- **generating function methods**.

It is one of the latter that I proceed now to describe.<sup>137</sup>

Defining functions

$$\begin{aligned} f_{\text{E-B}}(z) &\equiv \prod_\alpha (1 - ze^{-\beta \epsilon_\alpha})^{-1} \\ f_{\text{F-D}}(z) &\equiv \prod_\alpha (1 + ze^{-\beta \epsilon_\alpha})^{+1} \end{aligned}$$

we propose to extract the terms that are homogeneous of degree  $N$  in  $z$ ; i.e., to look to the coefficient of  $z^N$  in the Maclaurin expansion of  $f(z)$ :

$$Z_N = \frac{1}{N!} f^{(N)}(z) \Big|_{z=0}$$

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<sup>137</sup> My argument has been adapted from E. Schrödinger,<sup>4</sup> page 45 *et seq.*

REMARK: Here and below it will be my practice to omit  $E-B$  and  $F-D$  subscripts from expressions and equations that pertain identically to both cases. I will, as here, use the subscript  $N$  to identify results that pertain to  $N$ -particle systems.

Evidently it is in quite a standard sense

$$f(z) = \sum_N \frac{1}{N!} Z_N z^N$$

in that the functions  $f(z)$  serve to “generate”—for all  $N$ 's at once—the partition functions  $Z_N$ . Direct evaluation of the derivative (which might be of order  $\approx 10^{23}$ !) being quite out of the question, we resort at this point to some celebrated two-step trickery devised by C. G. Darwin & R. H. Fowler in 1922.<sup>138</sup> First, we employ this corollary

$$\frac{d^n}{da^n} f(a) = \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{f(z)}{(z-a)^{n+1}} dz$$

of the Cauchy integral theorem

$$f(a) = \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{f(z)}{z-a} dz$$

to write

$$Z_N = \frac{1}{2\pi i} \oint_{\mathcal{C}} \frac{f(z)}{z^{N+1}} dz$$

where the contour  $\mathcal{C}$  is subject only to the restrictions (i) that it encircles the origin and (ii) that it envelops no pole except the pole at the origin. With the observation that the preceding equation can be written

$$= \frac{1}{2\pi i} \oint_{\mathcal{C}} e^{Ng(z)} dz \tag{231}$$

$$Ng(z) \equiv -(N+1) \log z + \log f(z) \tag{232}$$

we find ourselves positioned to orchestrate the second part of the trick, which is to use standard asymptotic methods to approximate the integral in the limit that  $N$  becomes very (which is to say: thermodynamically) large.

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<sup>138</sup> C. G. Darwin (1887–1962) was a grandson of Charles Darwin, and was a young researcher at Cambridge when he collaborated with Fowler in an effort to place statistical mechanics on a new computational base. In 1927 he devised a theory of electrons that anticipated some aspects of Dirac's theory. Soon thereafter he became Master of Christ's College, and devoted the rest of his life to administrative and statesmanly work. R. H. Fowler (1887–1962) came late to physics, from pure mathematics. In addition to his life-long interest in statistical mechanics and its applications he was influential as one of the first British physicists to cultivate an interest in quantum mechanics. It was a Heisenberg preprint that he passed on to a student that inspired the student (Dirac!) to become active in the field.

We have, by way of preparation, to describe a certain function-theoretic property that we can expect to pertain generally to the functions  $g(z)$ . To that end . . . let the truncated product

$$f_{\text{eb}}(z) \equiv \frac{1}{(1-z)(1-\frac{1}{2}z)(1-\frac{1}{3}z)(1-\frac{1}{4}z)}$$

play the role of a typical Bose-Einstein generator  $f_{\text{E-B}}(z)$ , and let

$$f_{\text{fd}}(z) \equiv (1+z)(1+\frac{1}{2}z)(1+\frac{1}{3}z)(1+\frac{1}{4}z)\cdots(1+\frac{1}{10}z)$$

relate similarly to the Fermi-Dirac generators  $f_{\text{F-D}}(z)$ .<sup>139</sup> In imitation of (232), define

$$g_{\text{be}}(z; N) \equiv \frac{\log f_{\text{be}}(z) - (N-1) \log z}{N}$$

$$g_{\text{fd}}(z; N) \equiv \frac{\log f_{\text{fd}}(z) - (N-1) \log z}{N}$$

and look to the graphs (Figures 60–63) of the values assumed by those functions on the real axis. We find that in *both* cases

- $g(z; N)$  has a pole at the origin;
- $g(z; N)$  has a saddlepoint at a point  $x_0$  on the real axis somewhere to the right of the origin.

The saddlepoint resides, more particularly, at the leading zero of

$$g'(x; N) = \frac{1}{N} \frac{f'(x)}{f(x)} - \frac{N+1}{N} \frac{1}{x} \quad (233)$$

Now, the *asymptotic evaluation of integrals* is a lovely subject about which (in view of its many important physical applications) physicists tend to know less than they should. The basic ideas go back to Laplace, and were extended in various directions during the course of the 19<sup>th</sup> and early 20<sup>th</sup> Centuries: “Laplace’s method” gave rise to the “method of stationary phase” (Stokes and Kelvin) and to the “method of steepest descent” (Riemann and Debye), which is also known as the “saddlepoint method.” I have reviewed the bare essentials of the subject on several previous occasions,<sup>140</sup> and must be content on the present occasion simply to quote the result I need . . . which is that

$$Z_N = \frac{1}{2\pi i} \oint_{\mathcal{C}} e^{Ng(z)} dz \sim e^{Ng(x_0)} \frac{1}{\sqrt{2\pi N g''(x_0)}}$$

<sup>139</sup> It is only for diagrammatic convenience that I have set  $\beta\epsilon_n = \log n$ .

<sup>140</sup> See, for example, MATHEMATICAL THERMODYNAMICS (1967), pages 99–102. See also A. Erdélyi, *Asymptotic Expansions* (1956), Chapter 2. The topic is indexed in R. Courant & D. Hilbert, *Methods of Mathematical Physics* (1967) and in many of the more recent “mathematical methods” texts. It is treated at length in Chapters 3 & 4 of F. W. J. Olver’s *Asymptotics and Special Functions* (1997).

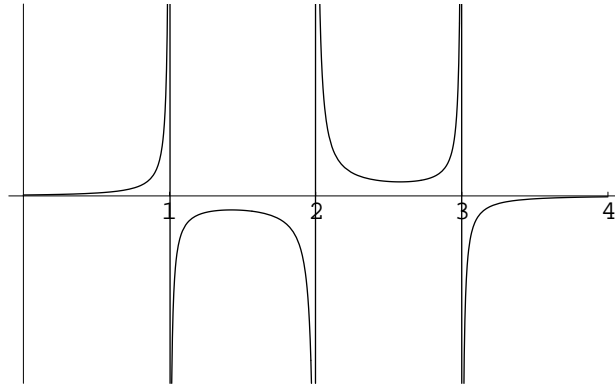


FIGURE 60: Graph of  $f_{eb}(x)$ . That it is alternately positive and negative is entirely characteristic of the general case. The function has unit value at the  $x = 0$  (a fact not evident in figure, where the plotted values of  $f_{eb}$  range from  $-130$  to  $+150$ ) and on the negative  $x$ -axis drops rapidly/smoothly to zero

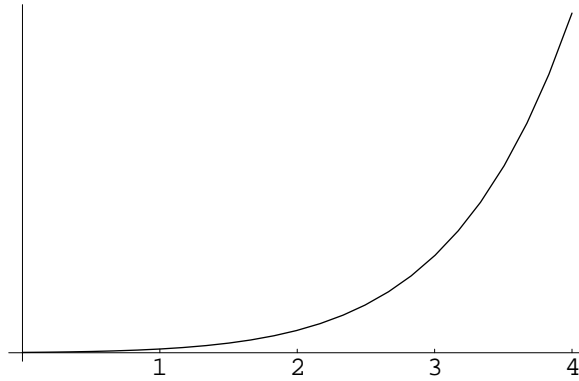


FIGURE 61: Graph of  $f_{id}(x)$ . The function again has unit value at the origin, and on the negative  $x$ -axis would be seen to oscillate with decreasing amplitude.

whence

$$\log Z_N \sim Ng(x_0) - \frac{1}{2} \log \{2\pi Ng''(x_0)\}$$

The second term on the right is, for  $N$  sufficiently large, dominated by the leading term, and will henceforth be neglected: thus do we obtain

$$\begin{aligned} \log Z_N &\sim -(N + 1) \log x_0 + \log f(x_0) \\ &= -(N + 1) \log x_0 \mp \sum_{\alpha} \log \{1 \mp x_0 e^{-\beta \epsilon_{\alpha}}\} \end{aligned} \quad (234)$$

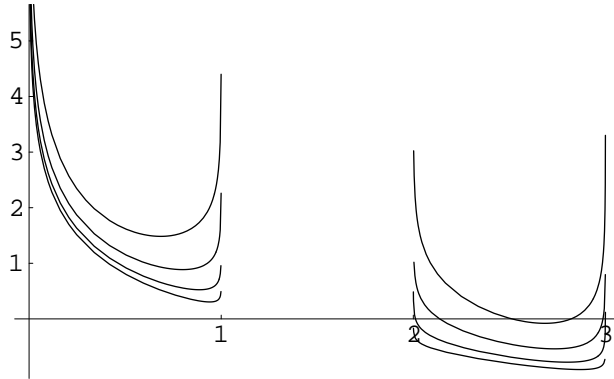


FIGURE 62: Graphs of  $g_{\text{eb}}(x; N)$  become progressively lower as  $N$  assumes the values 2, 4, 8, 16. The gaps arise because the logarithm of a negative number (see again FIGURE 60) is imaginary. The point of interest is that  $g_{\text{eb}}(x; N)$  is minimal at a point  $x_0$  that, as it happens, approaches ever closer to  $e^{\beta\epsilon_1} = e^{\log 1} = 1$  as  $N$  gets larger. The point  $z_0 = x_0 + i0$  marks a saddlepoint of the complex valued function  $g_{\text{eb}}(z; N)$ .

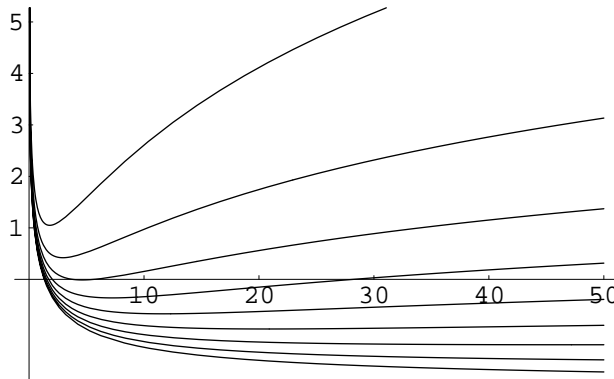


FIGURE 63: Graphs of  $g_{\text{fd}}(x; N)$  also become progressively lower as  $N$  ranges on 2, 3, 4, 5, 6, 7, 8, 9, 10. Such curves display minima so long as  $N$  is less than the value at which the infinite product was truncated, but it is in this case not easy to make statements about the location  $x_0$  of the minimum. Again,  $x_0$  marks the location of a saddlepoint of the complex-valued function  $g_{\text{fd}}(z; N)$ .

The very great combinational difficulties implicit in (229) are—by these elegant analytical devices (and in the limit of large  $N$ )—deposited in a single parameter:  $x_0$ . The question now is this: What is the *value* of  $x_0$ , and what (if any) is its physical significance? The answer to these questions is at least partially clarified by the following observations:

From (233) it follows (in the approximation that  $\frac{N+1}{N} \approx 1$ ) that

$$N = x_0 \frac{f'(x_0)}{f(x_0)}$$

But

$$\begin{aligned} x \frac{f'(x)}{f(x)} &= x \frac{d}{dx} \log \prod_{\alpha} (1 \mp x e^{-\beta \epsilon_{\alpha}})^{\mp 1} \\ &= \mp x \sum_{\alpha} \frac{e^{-\beta \epsilon_{\alpha}}}{1 \mp e^{-\beta \epsilon_{\alpha}}} \\ &= \sum_{\alpha} \frac{1}{\frac{1}{x} e^{\beta \epsilon_{\alpha}} \mp 1} \end{aligned}$$

so we have

$$N = \sum_{\alpha} \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_{\alpha}} \mp 1} \quad (235)$$

which presents a single occurrence of  $x_0$ , and that in a fairly promising place.<sup>141</sup> It is interesting in this connection to observe that

$$\frac{\partial}{\partial \epsilon_{\alpha}} \log Z_N = \mp \frac{\pm \beta x_0 e^{-\beta \epsilon_{\alpha}}}{1 \mp x_0 e^{-\beta \epsilon_{\alpha}}} + \frac{\partial x_0}{\partial \epsilon_{\alpha}} \frac{\partial}{\partial x_0} \log Z_N$$

But on page 193 we had  $\log Z_N \sim Ng(x_0)$  so  $\partial \log Z_N / \partial x_0 = Ng'(x_0)$  vanishes by the definition of  $x_0$ , and (after elementary simplifications) we obtain

$$= -\beta \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_{\alpha}} \mp 1} \quad (236.1)$$

On the other hand, we can use (229) to write

$$\begin{aligned} \frac{\partial}{\partial \epsilon_{\alpha}} \log Z_N &= \frac{1}{Z_N} \frac{\partial}{\partial \epsilon_{\alpha}} Z_N \\ &= \frac{\sum'_{\{\mathbf{n}\}} (-\beta n_{\alpha}) e^{-\beta \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}}}{\sum'_{\{\mathbf{n}\}} e^{-\beta \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}}} = -\beta \langle n_{\alpha} \rangle \end{aligned} \quad (236.2)$$

<sup>141</sup> In the Bose-Einstein case this result is consistent with the trend evident in Figure 62, for if we set  $x_0 = e^{\beta \epsilon_0}$  (here  $\epsilon_0$  refers to the ground state, previously denoted  $\epsilon_1$ ) we obtain

$$N = \frac{1}{1-1} + \sum_{\alpha > 0} \frac{1}{e^{\beta(\epsilon_{\alpha} - \epsilon_0)} - 1} = \infty$$

in the limit  $N \uparrow \infty$ .

Using these two results in combination, we obtain

$$\langle n_\alpha \rangle = \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_\alpha} \mp 1} \quad (237.1)$$

from which it follows by (235) that—not at all to our surprise—

$$N = \sum_\alpha \langle n_\alpha \rangle \quad (237.2)$$

and also that<sup>142</sup>

$$U = \langle E \rangle = \sum_\alpha \epsilon_\alpha \langle n_\alpha \rangle = \sum_\alpha \frac{\epsilon_\alpha}{\frac{1}{x_0} e^{\beta \epsilon_\alpha} \mp 1} \quad (238)$$

Equations (237) and (238) are interesting so far as they go, for they do serve to relate  $x_0$  in simple ways to quantities of direct thermodynamic importance. Sharper results can, however, be obtained if we particularize the molecular energy spectrum  $\{\epsilon_1, \epsilon_2, \dots\}$ .

Suppose, therefore, we revert to the example (pages 139–144) of “particles in a 1-box.” Then

$$\epsilon_\alpha = \epsilon_0 \alpha^2 \quad : \quad \alpha = 1, 2, 3, \dots$$

with  $\epsilon_0 \equiv h^2/8m\ell^2$ . Equation (237) assumes the form

$$\begin{aligned} N &= \sum_\alpha \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_0 \alpha^2} \mp 1} \approx \int_0^\infty \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_0 \alpha^2} \mp 1} d\alpha \\ &= (\ell/h) \sqrt{8mkT} \cdot \int_0^\infty \frac{1}{\frac{1}{x_0} e^{u^2} \mp 1} du \quad (239) \end{aligned}$$

while (238) becomes

$$\begin{aligned} U &= \frac{1}{\beta} \sum_\alpha \frac{\beta \epsilon_0 \alpha^2}{\frac{1}{x_0} e^{\beta \epsilon_0 \alpha^2} \mp 1} \approx \frac{1}{\beta} \int_0^\infty \frac{\beta \epsilon_0 \alpha^2}{\frac{1}{x_0} e^{\beta \epsilon_0 \alpha^2} \mp 1} d\alpha \\ &= kT(\ell/h) \sqrt{8mkT} \cdot \int_0^\infty \frac{u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du \quad (240) \end{aligned}$$

—these in the approximation that the sums can be replaced by integrals.

<sup>142</sup> I present the following description of  $U$  as though it were “obvious” (which, indeed, it is), but it can be derived by introducing (234) into (138):

$$U = -\frac{\partial}{\partial \beta} \log Z$$



Equation (239) provides a description—if only an *implicit* description—of  $x_0$  as a function of  $\ell T^{\frac{1}{2}}/N$ . From (234) we read

$$\log Z_N = -N \log x_0 \mp (\ell/h)\sqrt{8mkT} \int_0^\infty \log [1 \mp x_0 e^{-u^2}] du \quad (241)$$

in which connection it is often useful to notice that

$$\frac{\partial \log Z_N}{\partial x_0} = \frac{1}{x_0} \underbrace{\left\{ -N + x_0(\ell/h)\sqrt{8mkT} \int_0^\infty \frac{e^{-u^2}}{1 \mp x_0 e^{-u^2}} du \right\}}_{\text{vanishes by (239)}} = 0$$

The 1-box is, however, an artificial plaything: results that are in some analytical respects more interesting—and that in all respects have a more immediate claim to physical interest—are obtained if we suppose our non-interactive bosons/fermions to be confined within a 3-box. For a particle in an  $\ell_1 \times \ell_2 \times \ell_3$  *rectangular* 3-box the spectral energies are identified by a *triple* of integers

$$\epsilon_{\alpha_1 \alpha_2 \alpha_3} = (h^2/8m) \left\{ (\alpha_1/\ell_1)^2 + (\alpha_2/\ell_2)^2 + (\alpha_3/\ell_3)^2 \right\}$$

and in the instance of a cubic box ( $\ell_1 = \ell_2 = \ell_3 = \ell = V^{\frac{1}{3}}$ ) become

$$= (h^2/8m\ell^2) \left\{ \alpha_1^2 + \alpha_2^2 + \alpha_3^2 \right\}$$

In place of (239) we have

$$\begin{aligned} N &= \sum_{\alpha_1, \alpha_2, \alpha_3} \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_0 (\alpha_1^2 + \alpha_2^2 + \alpha_3^2)} \mp 1} \\ &\approx \iiint_0^\infty \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_0 (\alpha_1^2 + \alpha_2^2 + \alpha_3^2)} \mp 1} d\alpha_1 d\alpha_2 d\alpha_3 \\ &= [(\ell/h)\sqrt{8mkT}]^3 \cdot \iiint_0^\infty \frac{1}{\frac{1}{x_0} e^{u_1^2 + u_2^2 + u_3^2} \mp 1} du_1 du_2 du_3 \end{aligned}$$

which in spherical coordinates becomes

$$= (V/h^3)(8mkT)^{\frac{3}{2}} \cdot \frac{1}{8} \int_0^\infty \frac{4\pi u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du \quad (242)$$

where the factor  $\frac{1}{8} = 4^{-\frac{3}{2}}$  reflects that fact that we want to sum only on lattice points within the positive octant of the sphere: this equation serves—implicitly—to describe  $x_0$  as a function of  $VT^{\frac{3}{2}}/N$ . Similarly, (240) and (241) become

$$U = kT(V/h^3)(2mkT)^{\frac{3}{2}} \int_0^\infty \frac{4\pi u^4}{\frac{1}{x_0} e^{u^2} \mp 1} du \quad (243)$$

$$\log Z_N = -N \log x_0 \mp (V/h^3)(2mkT)^{\frac{3}{2}} \int_0^\infty 4\pi u^2 \log [1 \mp x_0 e^{-u^2}] du \quad (244.1)$$

But upon integrating by parts we have

$$\int_0^\infty u^2 \log [1 \mp x_0 e^{-u^2}] du = \underbrace{\frac{1}{3} u^3 \log [1 \mp x_0 e^{-u^2}]_0^\infty}_0 \mp \frac{2}{3} \int_0^\infty \frac{u^4}{\frac{1}{x_0} e^{u^2} \mp 1} du$$

which we can use in (244.1) to obtain

$$\log Z_N = -N \log x_0 + \frac{2}{3} (V/h^3) (2mkT)^{\frac{3}{2}} \int_0^\infty \frac{4\pi u^4}{\frac{1}{x_0} e^{u^2} \mp 1} du \quad (244.2)$$

From (244.1) and (242) it follows readily that, as before,

$$\frac{\partial \log Z_N}{\partial x_0} = 0 \quad (245)$$

while from (244.2) we therefore have

$$\begin{aligned} U &= kT^2 \left\{ \frac{\partial \log Z_N}{\partial T} + \frac{\partial \log Z_N}{\partial x_0} \frac{\partial x_0}{\partial T} \right\} \\ &= kT^2 \frac{\partial \log Z_N}{\partial T} \quad \text{by (245)} \end{aligned}$$

which promptly gives back (243). Which is gratifying.

But there is, Schrödinger reminds us, more to be said concerning the thermodynamic status of the parameter  $x_0$ . We have (see again (141.2))

$$F = -kT \log Z$$

and (according to (56·F) on page 59)

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = kT \left( \frac{\partial \log Z_N}{\partial V} \right)_{T,N}$$

from which by (244.4) we learn, on comparison with (243), that

$$pV = \frac{2}{3} U \quad \text{for both } \begin{cases} \text{boxed non-interactive } \mathbf{bosons} \text{ and} \\ \text{boxed non-interactive } \mathbf{fermions} \dots \text{ and also for} \\ \mathbf{classical ideal gas:} \text{ see pages 42 and 43} \end{cases}$$

Notice finally that multiplication of  $kT$  into (244.2) yields an equation that can be written

$$\begin{aligned} NkT \log x_0 &= \frac{2}{3} U - kT \log Z_N \\ &= pV + F \\ &= U - TS + pV \quad : \quad \text{see page 62} \end{aligned}$$

and gives

$$x_0 = e^{(u - Ts + pv)/kT} \quad (246)$$

where  $u \equiv U/N$ ,  $s \equiv S/N$  and  $v \equiv V/N$  define the “specific” internal energy, entropy and volume. The parameter  $x_0$ , which came to us on page 194 as a fairly arcane mathematical artifact, is seen thus to be related in simple ways to quantities of direct thermodynamic importance.

Our equations (242) and (243) appear—differently notated—as equations (5.107) and (5.108) in §5.4 of Griffiths’ *Introduction to Quantum Mechanics* (1995), where they are obtained by other (more standard) means. Where we write  $x_0$  Griffiths writes  $e^{\mu/kT}$ , and he calls  $\mu$  the “chemical potential” . . . as so, indeed, would we: for bulk systems we (at (58·U) on page 58) had a relation which, upon division by  $N$ , becomes

$$\mu = u - Ts + pv$$

and which when brought to (246) gives precisely

$$x_0 = e^{\mu/kT}$$

**5. Recovery of and departures from ideal gas behavior.** For a classical ideal gas confined to a 3-dimensional enclosure one has the familiar equation of state

$$\frac{pV}{NkT} = 1$$

On the other hand, we established on the preceding page that for both bosonic and fermionic gases we can write

$$\frac{pV}{NkT} = \frac{\frac{2}{3}U}{NkT}$$

which by (242) and (243) becomes

$$\begin{aligned} & \int_0^\infty \frac{u^4}{\frac{1}{x_0}e^{u^2} \mp 1} du \\ &= \frac{2}{3} \int_0^\infty \frac{u^2}{\frac{1}{x_0}e^{u^2} \mp 1} du \equiv \mathcal{F}_\mp(x_0) \end{aligned} \quad (247)$$

after cancellation of the shared factor  $4\pi(V/h^3)(2mkT)^{\frac{3}{2}}$ . The long bosonic/fermionic song and dance, at least as it relates to thermalized gas-like systems, appears to have reduced, in the last analysis, to the ratio of a pair of awkward integrals!

Let (242) be written

$$\frac{4\pi(2mk)^{\frac{3}{2}}}{h^3} \left( \frac{VT^{\frac{3}{2}}}{N} \right) \int_0^\infty \frac{u^2}{\frac{1}{x_0}e^{u^2} \mp 1} du = 1 \quad (248)$$

Clearly, if  $VT^{\frac{3}{2}}/N$  is very large then  $x_0$  must be very small. But if  $x_0 \ll 1$  then  $\frac{1}{x_0} \exp u^2 \gg 1$  for all  $u$ , so the  $\mp 1$ ’s on the right side of (247) can be abandoned:

in that high-temperature/high specific volume/low-density approximation we have

$$\begin{aligned}\mathcal{F}_{\mp} &\approx \frac{2}{3} \frac{\int_0^{\infty} e^{-u^2} u^4 du}{\int_0^{\infty} e^{-u^2} u^2 du} \quad : \quad x_0 \ll 1 \\ &= \frac{2}{3} \frac{\frac{3}{8}\sqrt{\pi}}{\frac{1}{4}\sqrt{\pi}} \\ &= 1\end{aligned}$$

The implication is that bosonic and fermionic gases *both behave like classical ideal gases at high temperatures/low densities*: they exhibit their distinctive properties—the features that distinguish them from ideal gases and from one another—only at

- low temperatures or at
- high densities

or when those two conditions are suitably combined.

The integrals that enter into the definitions (247) of  $\mathcal{F}_{\mp}(x_0)$  are readily described in terms of a class of functions that were known already to Euler and that enter into a variety of physical calculations, especially in particle physics. I refer to the “polylogarithm” functions, of which

$$\text{Li}_{\nu}(z) \equiv \sum_{k=1}^{\infty} \frac{z^k}{k^{\nu}} \equiv \frac{z}{\Gamma(\nu)} \int_0^{\infty} \frac{t^{\nu-1}}{e^t - z} dz$$

provide a couple of the standard definitions.<sup>143</sup> *Mathematica* is much more familiar with these functions (which it calls `PolyLog[ $\nu$ ,  $z$ ]`) than most physicists can claim to be, and supplies

$$\begin{aligned}\int_0^{\infty} \frac{u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du &= \pm \frac{1}{4} \sqrt{\pi} \text{PolyLog}\left[\frac{3}{2}, \pm x_0\right] \\ \int_0^{\infty} \frac{u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du &= \pm \frac{3}{8} \sqrt{\pi} \text{PolyLog}\left[\frac{5}{2}, \pm x_0\right]\end{aligned}$$

whence

$$\mathcal{F}_{\mp}(x_0) = \frac{\text{PolyLog}\left[\frac{5}{2}, \pm x_0\right]}{\text{PolyLog}\left[\frac{3}{2}, \pm x_0\right]} \quad (249)$$

Notable simplifications occur at  $x_0 = 1$  where, according to *Mathematica*,

$$\mathcal{F}_{-}(1) = \frac{\text{Zeta}\left[\frac{5}{2}\right]}{\text{Zeta}\left[\frac{3}{2}\right]} = 0.51351$$

and

$$\mathcal{F}_{+}(1) = \frac{(\sqrt{2} - 4) \text{Zeta}\left[\frac{5}{2}\right]}{(\sqrt{8} - 4) \text{Zeta}\left[\frac{3}{2}\right]} = 1.13338$$

<sup>143</sup> See A. P. Prudnikov, Yu. A. Brychkov & O. I. Marichev, *Integrals & Series* (1986), Volume 3, page 795.

In the preceding equations `Zeta[z]` refers to the Riemann zeta function

$$\zeta(z) \equiv \frac{1}{\Gamma(z)} \int_0^\infty \frac{t^{z-1}}{e^t - 1} dt \equiv \sum_{k=1}^\infty \frac{1}{k^z}$$

When asked to plot the functions  $\mathcal{F}_\mp(x_0)$  *Mathematica* produces the following figure, but it refuses to extend the lower (Bose-Einstein) branch beyond  $x_0 = 1$

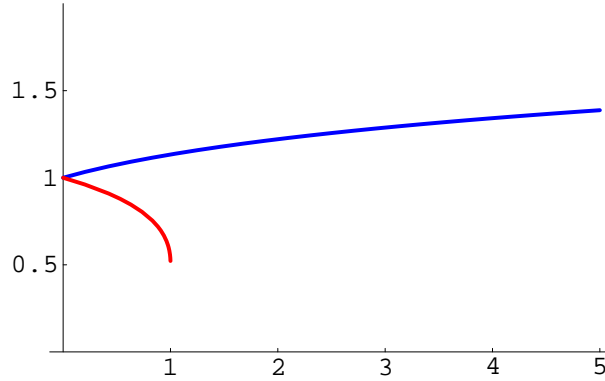


FIGURE 64: Graphs showing the  $x_0$ -dependence of the Fermi-Dirac function  $\mathcal{F}_+$  (upper blue curve) and of the Bose-Einstein function  $\mathcal{F}_-$  (lower red curve). The lower curve ends abruptly at  $x_0 = 1$  for reasons explained in the text.

—this for the reason that  $\mathcal{F}_-(x_0)$  is complex for  $x_0 > 1$ .<sup>144</sup> For example, we have

$$\begin{aligned} \mathcal{F}_-(1.0001 - 0.0001 i) &= 0.516717 + 0.00762155 i \\ \mathcal{F}_-(1.0001) &= 0.513547 + 0.00696797 i \\ \mathcal{F}_-(1.0001 + 0.0001 i) &= 0.516717 - 0.00762155 i \end{aligned}$$

For  $x_0 \approx 0$  (which is to say: at high temperatures/low densities) we are led from (249) to Maclaurin series that can be written

$$\left. \begin{aligned} \mathcal{F}_-(x_0) &= 1 - 0.1767 x_0 - 0.0658 x_0^2 - 0.0365 x_0^3 - \dots \\ \mathcal{F}_+(x_0) &= 1 + 0.1767 x_0 + 0.0658 x_0^2 + 0.0365 x_0^3 + \dots \end{aligned} \right\} \quad (250)$$

where the numerics arise by evaluation of  $\frac{1}{4\sqrt{2}}$ ,  $\frac{27-32\sqrt{3}}{432}$  and expressions of rapidly increasing complexity. More informative, however, would be series that proceed in powers of a variable of direct thermodynamic significance ... which

<sup>144</sup> We are informed by *Mathematica*'s "Index of Mathematical Functions" that "`PolyLog[n,z]` has a branch cut discontinuity in the complex  $z$  plane running from 1 to  $\infty$ ."

can be produced as follows: let (248) be written

$$\begin{aligned}\vartheta &\equiv \left[ \frac{4\pi(2mk)^{\frac{3}{2}}}{h^3} \left( \frac{VT^{\frac{3}{2}}}{N} \right) \right]^{-1} = \int_0^\infty \frac{u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du \\ &= \pm \frac{\sqrt{\pi}}{4} \text{PolyLog} \left[ \frac{3}{2}, \pm x_0 \right] \\ &= \frac{\sqrt{\pi}}{4} \left\{ x_0 \pm \frac{1}{2\sqrt{2}} x_0^2 + \frac{1}{3\sqrt{3}} x_0^3 \pm \frac{1}{4\sqrt{4}} x_0^4 + \dots \right\}\end{aligned}$$

and use *Mathematica's* `InverseSeries` command to obtain

$$x_0 = \frac{4}{\sqrt{\pi}} \left\{ \vartheta + 0.7978 \vartheta^2 + 0.2931 \vartheta^3 + 0.0662 \vartheta^4 + \dots \right\}$$

in—remarkably—both cases. Insertion into (250) gives

$$\left. \begin{aligned}\mathcal{F}_-(\vartheta) &= 1 - 0.1767 \vartheta - 0.0752 \vartheta^2 - \dots \\ \mathcal{F}_+(\vartheta) &= 1 + 0.1767 \vartheta + 0.0268 \vartheta^2 + \dots\end{aligned} \right\} \quad (250.1)$$

where again

$$\vartheta \equiv 0.02813 \frac{Nh^3}{V(mkT)^{\frac{3}{2}}} \quad (250.2)$$

Returning with this information to (247) we obtain explicit descriptions

$$\begin{aligned}pV &= NkT \left\{ 1 - 0.1767 \vartheta - 0.0752 \vartheta^2 - \dots \right\} : \text{BOSE-EINSTEIN} \\ pV &= NkT \left\{ 1 + 0.1767 \vartheta + 0.0268 \vartheta^2 - \dots \right\} : \text{FERMI-DIRAC}\end{aligned}$$

of how bosonic/fermionic gases begin to depart from the ideal gas law as

- the temperature  $T$  becomes small, and/or
- the particle density  $N/V$  becomes large, and/or
- the particle mass  $m$  is made small, and/or
- “ $h$  becomes large,” which is the way the theory reminds us that we are dealing here with a specifically *quantum mechanical effect*.

The preceding equations very much resemble the “virial expansion”<sup>145</sup>

$$pV = NkT \left\{ 1 + \frac{B(T, N)}{V} + \frac{C(T, N)}{V^2} + \dots \right\}$$

that in the classical theory of real gases is used to describe the departure from ideal behavior that results from particle interactions. But in the present theory it is *not interaction but indistinguishability* that is responsible for that departure.

It is well to remind ourselves that the equation of state  $pV = NkT$  captures only one prominent aspect of the thermodynamics of ideal gases, for (as was

<sup>145</sup> See again (209) on page 166.

remarked already on page 43) “ideal gas” refers to a  $c$ -parameterized *family* of systems, all of which share that same equation of state. That equation of state is insensitive also to whether or not we bring into play the “Gibbs-Boltzmann indistinguishability mechanism” of page 176. To distinguish one ideal gas from another we must dig deeper than the equation of state ... to the descriptions of  $U$  and of  $S$ .

Looking first to the former: for  $x_0 \ll 1$  it follows from (243)

$$U = \frac{kTV(2mkT)^{\frac{3}{2}}}{h^3} \frac{3}{2} \pi^{\frac{3}{2}} x_0 \left\{ 1 \pm 2^{-\frac{3}{2}} x_0 + \dots \right\}$$

where, as was established on the preceding page,

$$x_0 = \frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}} \left\{ 1 + 0.7978 \vartheta + \dots \right\}$$

so in leading order we recover—in both the bosonic and fermionic cases—the classical result

$$U = \frac{3}{2} NkT$$

appropriate to structureless point particles (no internal degrees of freedom).

The entropy of the bosonic/fermionic system can be computed from the general relation<sup>146</sup>

$$S = \left( 1 + T \frac{\partial}{\partial T} \right) k \log Z$$

It was established on page 198 that

$$\begin{aligned} k \log Z &= \frac{\frac{2}{3}U}{T} - Nk \log x_0 \\ &= Nk(1 - \log x_0) \end{aligned}$$

so

$$S = Nk(1 - \log x_0) - Nk \cdot T \frac{1}{x_0} \frac{\partial x_0}{\partial T}$$

which in the high-temperature limit becomes

$$\begin{aligned} &= Nk \left( 1 - \log \frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}} \right) + Nk \cdot \frac{3}{2} \\ &= k \left\{ N \log \frac{V(2\pi mkT)^{\frac{3}{2}}}{h^3} + \frac{3}{2} N \right\} - k \left\{ N \log N - N \right\} \quad (251) \end{aligned}$$

But the classical argument that at (170) gave

$$S_{\text{distinguishable}} = k \left\{ N \log \frac{\ell (2\pi mkT)^{\frac{1}{2}}}{h} + \frac{1}{2} N \right\} \quad \text{for particles in a 1-box}$$

gives

$$S_{\text{distinguishable}} = k \left\{ N \log \frac{V(2\pi mkT)^{\frac{3}{2}}}{h^3} + \frac{3}{2} N \right\} \quad \text{for particles in a 3-box}$$

<sup>146</sup> See again (140) on page 127.

while in Stirling approximation (page 106)  $N \log N - N \sim \log N!$ . Returning with this information to (251), we conclude that

$$\begin{aligned} S_{\text{hot Bose-Einstein gas}} &= S_{\text{hot Fermi-Dirac gas}} \\ &= S_{\text{distinguishable}} - k \log N! \end{aligned}$$

... the interesting point being that

$$\left. \begin{array}{l} \text{boson indistinguishability} \\ \text{fermion indistinguishability} \end{array} \right\} \mapsto \text{Gibbs-Boltzmann indistinguishability}$$

as the temperature becomes high and/or the density becomes low:  $x_0 \ll 1$ .

But if Bose-Einstein and Fermi-Dirac gases become thermodynamically identical in the regime just studied, they differ profoundly in the opposite limit  $x_0 \gg 1$ . We look first to the latter:

**6. Degenerate Fermi-Dirac gas.** The theory of dense/cold Fermi-Dirac gases proceeds straightforwardly from the mathematical circumstance illustrated in the following figure:

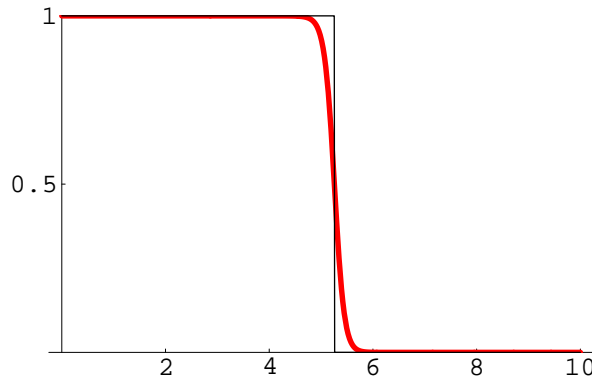


FIGURE 65: Graph (shown in **red**) of the function  $(\frac{1}{x_0}e^{u^2} + 1)^{-1}$  with  $x_0$  set equal to  $10^{12}$ . The knee gets sharper and sharper as  $x_0$  is made progressively larger, and can be considered to reside at the point  $u_0$  where

$$\begin{aligned} \left(\frac{1}{x_0}e^{u^2} + 1\right)^{-1} = \frac{1}{2} &: \text{ gives } u_0 = \sqrt{\log x_0} \\ &= 5.25652 \text{ in the case illustrated} \end{aligned}$$

In leading approximation the function in question can be replaced by the step function shown in **black**:

$$\left(\frac{1}{x_0}e^{u^2} + 1\right)^{-1} \approx \begin{cases} 1 & : 0 \leq u \leq u_0 \\ 0 & : u > u_0 \end{cases}$$



The integrals that appear recurrently in equations subsequent to (247) therefore simplify greatly: in leading approximation we have

$$\int_0^\infty \frac{u^2}{\frac{1}{x_0} e^{u^2} \mp 1} du = \int_0^{\sqrt{\log x_0}} u^2 du = \frac{1}{3} (\log x_0)^{\frac{3}{2}}$$

$$\int_0^\infty \frac{u^4}{\frac{1}{x_0} e^{u^2} \mp 1} du = \int_0^{\sqrt{\log x_0}} u^4 du = \frac{1}{5} (\log x_0)^{\frac{5}{2}}$$

so (247) becomes

$$\frac{pV}{NkT} = \frac{2}{3} \frac{\frac{1}{5} (\log x_0)^{\frac{5}{2}}}{\frac{1}{3} (\log x_0)^{\frac{3}{2}}} = \frac{2}{5} \log x_0 = \frac{2}{5} u_0^2$$

The equation at the top of page 202 gives  $\vartheta = \frac{1}{3} (\log x_0)^{\frac{3}{2}}$  so we have

$$= \frac{2}{5} (3\vartheta)^{\frac{2}{3}} = \frac{2}{5} \cdot \frac{h^2}{2m} \left( \frac{3N}{4\pi V} \right)^{\frac{2}{3}} \frac{1}{kT} \quad (252)$$

giving

$$p \left( \frac{V}{N} \right)^{\frac{5}{3}} = \frac{2}{5} \left( \frac{3}{4\pi} \right)^{\frac{2}{3}} \frac{h^2}{2m} : \text{constant} \quad (253)$$

This resembles the  $pV^\gamma$  that in classical theory serves (at any temperature) to describe isentropic curves inscribed on the  $pV$ -plane (adiabats), but has now the status of a *low temperature equation of state from which  $T$  has disappeared*: (253) describes a limiting situation in which the degenerate Fermi-Dirac gas behaves (in Schrödinger's phrase) "like a pure mechanism." The pressure

$$p = \frac{2}{5} \left( \frac{3}{4\pi} \right)^{\frac{2}{3}} \frac{h^2}{2m} \left( \frac{N}{V} \right)^{\frac{5}{3}}$$

—though an artifact not of particle motion but of particle indistinguishability—can be enormous: for the conduction electrons in a metal one has  $N/V \approx 10^{24} \text{ cm}^{-3}$  and  $m \approx 10^{-27} \text{ g}$ , and finds<sup>147</sup>

$$p \approx 10^6 \text{ atmospheres}$$

According to Figure 65, the occupation numbers are—as a direct expression of the Pauli exclusion principle—unity for  $u \leq u_0$  and zero for  $u > u_0$ . Pursuing this thought ... it was, in effect, established just above that

$$V \cdot \frac{\frac{4}{3}\pi(\sqrt{2mkT} u_0)^3}{8} = Nh^3$$

= minimal phase volume required  
to accommodate  $N$  states

<sup>147</sup> I have taken this example from ter Haar,<sup>108</sup> page 92.

But (see again page 197)  $\epsilon_0 \alpha^2 \equiv kTu^2$  informs us that  $\sqrt{2mkT}u = p_0\alpha$  where  $p_0 \equiv \sqrt{2m\epsilon_0}$  refers to the *momentum* of a particle in its ground state. In excited states one has

$$\mathbf{p} = p_0 \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} \quad \text{and total momentum} \quad p = p_0 \sqrt{\alpha_1^2 + \alpha_2^2 + \alpha_3^2} = p_0 \alpha$$

So we have

$$Nh^3 = V \cdot \frac{\text{volume of a sphere of radius } p_F \text{ in momentum space}}{8}$$

where  $p_F$  is the ‘‘Fermi momentum’’ and  $\epsilon_F \equiv p_F^2/2m$  is the associated ‘‘Fermi energy.’’

In leading approximation the internal energy of an ideal fermi-Dirac gas becomes

$$\begin{aligned} U &= 4\pi kT(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{1}{5}(\log x_0)^{\frac{5}{2}} && \text{by (243)} \\ &= 4\pi kT(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{1}{5}\left(\frac{5}{2}pV/NkT\right)^{\frac{5}{2}} \\ &= N^{-\frac{5}{2}}V^{\frac{7}{2}}(kT)^0 p^{\frac{5}{2}} \cdot 4\pi(2m)^{\frac{3}{2}}h^{-3}\frac{1}{5}\left(\frac{5}{2}\right)^{\frac{5}{2}} \\ &\quad p^{\frac{5}{2}} = \left(\frac{2}{5}\right)^{\frac{5}{2}}\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\left(\frac{h^2}{2m}\right)^{\frac{5}{2}}\left(\frac{N}{V}\right)^{\frac{25}{6}} \text{ by (253)} \\ &= \frac{3}{5}\frac{h^2}{2m}N\left(\frac{3N}{4\pi V}\right)^{\frac{2}{3}} && (254) \end{aligned}$$

This equation<sup>148</sup> describes the so-called ‘‘zero-point energy’’ of such a gas.

Looking finally to the entropy of a fully degenerate Fermi-Dirac gas, we by (244.2) have

$$\begin{aligned} \log Z &= -N \log x_0 + \frac{2}{5}(V/h^3)(2mkT)^{\frac{3}{2}} \cdot 4\pi\frac{1}{5}(\log x_0)^{\frac{5}{2}} \\ &= -N \log x_0 + \frac{2}{3}U/kT \\ &= -N \log x_0 + \frac{2}{5}\frac{h^2}{2m}N\left(\frac{3N}{4\pi V}\right)^{\frac{2}{3}}\frac{1}{kT} \\ &= -\frac{3}{5}\frac{h^2}{2m}N\left(\frac{3N}{4\pi V}\right)^{\frac{2}{3}}\frac{1}{kT} \text{ by the description (252) of } \log x_0 && (255) \end{aligned}$$

from which it follows that

$$S = \left(1 + T \frac{\partial}{\partial T}\right) k \log Z = 0 \quad (256)$$

But this—by

$$S = k \log \left\{ \begin{array}{l} \text{number of distinct ways the} \\ \text{expected state can be achieved} \end{array} \right\} \quad (152)$$

<sup>148</sup> Compare ter Haar,<sup>108</sup> page 91, where an identical result is obtained by other means.

—amounts simply to the statement that the ground state of a Fermi-Dirac gas is non-degenerate (can be achieved in only one way), which was evident at the outset.

We have been working in the approximation (see again Figure 65 and last line of its caption) that

$$\frac{1}{\frac{1}{x_0}e^{u^2} + 1} \approx 1 - \int_{-\infty}^u \delta(y - u_0) dy \quad : \quad x_0 \gg 1 \quad (257.1)$$

To obtain results appropriate to situations in which  $T$  is somewhat greater than zero we must improve upon that approximation. The standard procedure<sup>149</sup> was devised by Sommerfeld (1928). I propose an alternative: in place of (257.1) write

$$\frac{1}{\frac{1}{x_0}e^{u^2} + 1} \approx 1 - \int_{-\infty}^u \underbrace{\frac{1}{a\sqrt{\pi}}e^{-\left(\frac{y-u_0}{a}\right)^2}}_{\text{Gaussian}} dy \quad (257.21)$$

and tune the value of  $a$  so that at the “half-value point”  $u = u_0 = \sqrt{\log x_0}$  the expressions on left and right have the same slope. This is readily seen to entail

$$a = \frac{2}{\sqrt{\pi} u_0} = \frac{2}{\sqrt{\pi \log x_0}} \quad (257.22)$$

and gives rise to figures such as the one shown below.

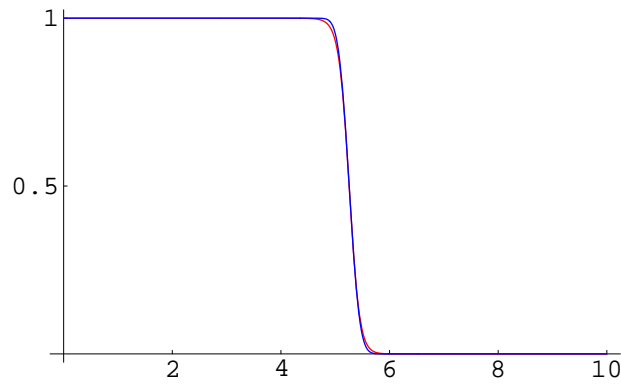


FIGURE 66: Comparison of the functions at appear on the **left** and **right** sides of (257.2) in the case  $x_0 = 10^{12}$ , which entails  $u_0 = 5.25$  and  $a = 0.215$ .

We now write (see Figure 67)

$$1 - \int_{-\infty}^u \frac{1}{a\sqrt{\pi}}e^{-\left(\frac{y-u_0}{a}\right)^2} dy = \text{downstep function} + \text{correction} \quad (258)$$

downstep function  $\equiv 1 - \text{UnitStep}[u - u_0]$

<sup>149</sup> See Schrödinger,<sup>4</sup> pages 74–75 or ter Haar,<sup>108</sup> pages 92–93.

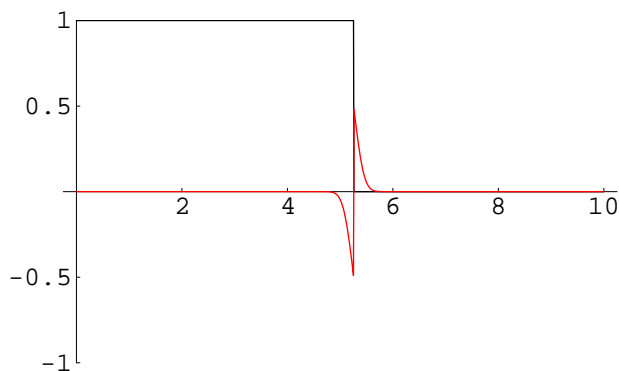


FIGURE 67: Graphic representation of (258). The red “correction function”  $w(u)$  can evidently be described

$$w(u; x_0) = \text{UnitStep}[u - u_0] - \int_{-\infty}^u \frac{1}{a\sqrt{\pi}} e^{-\left(\frac{y-u_0}{a}\right)^2} dy$$

$$= \begin{cases} -\frac{1}{2} [1 - \text{erf}(\frac{u_0 - u}{a})] & : u < u_0 \\ +\frac{1}{2} [1 - \text{erf}(\frac{u - u_0}{a})] & : u > u_0 \end{cases}$$

where  $\text{erf}(z)$  denotes the “error function.”

The idea would be to write (compare pages 200 & 205)

$$\int_0^{\infty} \frac{u^2}{\frac{1}{x_0} e^{u^2} + 1} du \approx \frac{1}{3} (\log x_0)^{\frac{3}{2}} + \int_0^{\infty} u^2 w(u; x_0) du$$

$$\int_0^{\infty} \frac{u^4}{\frac{1}{x_0} e^{u^2} + 1} du \approx \frac{1}{5} (\log x_0)^{\frac{5}{2}} + \int_0^{\infty} u^4 w(u; x_0) du$$

but here I must, for the moment, be content to let the subject drop.

**7. Degenerate Bose-Einstein gas.** Recall, by way of orientation, that at (237) we obtained equations that for systems of non-interactive bosons read

$$N = \sum_{\alpha} \langle n_{\alpha} \rangle \quad (259.1)$$

$$\langle n_{\alpha} \rangle = \frac{1}{\frac{1}{x_0} e^{\beta \epsilon_{\alpha}} - 1} \quad (259.2)$$

On the natural assumption that  $0 < \beta \epsilon_1 < \beta \epsilon_2 < \beta \epsilon_3 < \dots$  we have

$$0 < e^{\beta \epsilon_1} < e^{\beta \epsilon_2} < e^{\beta \epsilon_3} < \dots$$

If  $x_0$  were to advance  $0 \rightarrow \infty$  along the positive real line we would first see

- $\langle n_1 \rangle$  blow up (and turn unphysically negative) at  $x_0 = e^{\beta\epsilon_1}$ , then see
- $\langle n_2 \rangle$  blow up (and turn negative) at  $x_0 = e^{\beta\epsilon_2}$ , then see
- $\langle n_3 \rangle$  blow up (and turn negative) at  $x_0 = e^{\beta\epsilon_3}$ , then see ...

but those particular absurdities—those catastrophic consequences (see again Figure 60) of “the bosonic minus sign”—need not concern us, for (see again page 192 and Figure 62) the parameter  $x_0$  came to us as the *address of the saddlepoint most proximate to the origin*, and lies therefore necessarily on the interval

$$0 < x_0 < e^{\beta\epsilon_1} \tag{260}$$

It follows from preceding observations that the expected occupation numbers  $\langle n_\alpha \rangle$  stand in ordered sequence

$$N \geq \langle n_1 \rangle > \langle n_2 \rangle > \langle n_3 \rangle > \dots > 0$$

and they are, of course, subject to the constraint (259.1). Look to the limiting case  $\langle n_1 \rangle = N$ : a little algebra supplies

$$x_0 = \frac{N}{N+1} e^{\beta\epsilon_1} \approx (1 - N^{-1}) e^{\beta\epsilon_1} \tag{261}$$

which—consistently with the evidence of Figure 62—shows  $x_0$  to have squeezed exquisitely close to the upper limit of its allowed range (260). Too close ... for the  $\langle n_\alpha \rangle$  with  $\alpha \geq 2$  have not obligingly died: we find ourselves in violation of the constraint.

Turning now from generic generalities to the particulars of bosonic gases ... we might expect, as an expression of (259) and as anticipated already at (242), to write

$$N = 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \int_0^\infty \frac{u^2}{\frac{1}{x_0} e^{u^2} - 1} du \tag{262}$$

But if we are to avoid catastrophes of precisely the sort discussed above we must impose the stipulation that  $\frac{1}{x_0} \geq 1$ ; *i.e.*, that  $0 < x_0 \leq 1$ . Were we to set  $x_0 = 1$  we would have (according to *Mathematica*)

$$N = 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{\sqrt{\pi}}{4} \zeta\left(\frac{3}{2}\right) \\ \frac{\sqrt{\pi}}{4} \zeta\left(\frac{3}{2}\right) = 1.15758$$

Elsewhere on the allowed interval we have

$$= 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{\sqrt{\pi}}{4} \text{PolyLog}\left[\frac{3}{2}, x_0\right]$$

A glance at the graph of  $\frac{\sqrt{\pi}}{4} \text{PolyLog}\left[\frac{3}{2}, x_0\right]$  (Figure 68) leads seemingly to the

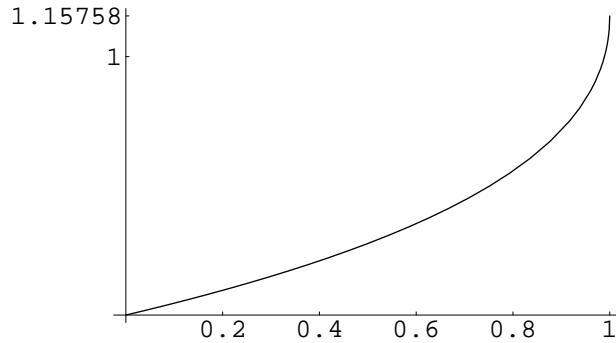


FIGURE 68: Graph of the function  $\frac{\sqrt{\pi}}{4} \text{PolyLog}[\frac{3}{2}, x_0]$ .

conclusion that necessarily

$$0 < \frac{N}{4\pi(V/h^3)(2mkT)^{\frac{3}{2}}} < 1.15758$$

Which is to say: at any given  $T$  there is a maximal number  $N_c$  of bosons that can be packed into a volume  $V$ ; there exists a “lowest temperature”

$$T_c = 0.16781 \frac{h^2}{2mk} \left(\frac{N}{V}\right)^{\frac{2}{3}} \quad (263)$$

sustainable within an ideal bosonic gas of number-density  $N/V$ .  $T_c$  is typically quite small—if we were to pack 100,000  $^{87}\text{Rb}$  atoms ( $m = 1.45 \times 10^{-25}$  kg) into a box measuring one millimeter on a side we would have  $T_c = 39.5 \times 10^{-12}$  K which until the mid-1990’s lay far beyond the reach of cryogenic technique—but any claim of the form

- “if  $N_c$  bosons are already in the box you can’t introduce another”
- “if the bosonic gas stands already to  $T_c$  it can’t be further cooled”

appears on its face to be physically absurd. That—and where—our simple theory appears to have led us astray was first noticed by Einstein (1924, 1925), but for nearly seventy-five years the subject was considered to be of *only* theoretical interest: that changed when Carl Wieman, Eric Cornell and their team at JILA (Joint Institute for Laboratory Astrophysics, Colorado University) produced the first BEC (Bose-Einstein condensate)—an accomplishment for which they were awarded the Nobel Prize in 2001.<sup>150</sup>

So where did we get off track? In a word: where we brought into play the  $\sum \rightarrow \int$  trick. For if we back up to (259) and write out the equation

$$N = \frac{1}{\frac{1}{x_0} e^{\beta\epsilon_1} - 1} + \sum_{\alpha=2} \frac{1}{\frac{1}{x_0} e^{\beta\epsilon_\alpha} - 1}$$

<sup>150</sup> See <http://www.colorado.edu/physics/2000/bec/>.

that when adapted to gases led to (262), we see—as in fact we saw already at (261)—that any number of particles can be inserted into the ground state provided  $x_0$  approaches closely enough to the critical value  $e^{\beta\epsilon_1}$ .

We return, therefore, to page 197 and, in place of an equation that appears there, write

$$N = \frac{1}{\frac{1}{x_0} e^{\beta\epsilon_0}(1^2 + 1^2 + 1^2) - 1} + \sum'_{\alpha_1, \alpha_2, \alpha_3} \frac{1}{\frac{1}{x_0} e^{\beta\epsilon_0}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) - 1}$$

Shift the energy scale (which we can do with impunity) so that the ground state energy becomes zero instead of  $\epsilon_0(1^2 + 1^2 + 1^2)$ : then the critical value of  $x_0$  becomes  $e^0 = 1$  and we find ourselves writing

$$N = (N - N_c) + N_c \quad (264)$$

where

$$\begin{aligned} N_c &= 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \int_0^\infty \frac{u^2}{e^{u^2} - 1} du \\ &= 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{1}{4}\sqrt{\pi}\zeta\left(\frac{3}{2}\right) \\ &= 2.61238 \cdot (V/h^3)(2\pi mkT)^{\frac{3}{2}} \end{aligned} \quad (265.1)$$

and

$$N = 2.61238 \cdot (V/h^3)(2\pi mkT_c)^{\frac{3}{2}} \quad (265.2)$$

serve to define the **critical temperature**  $T_c$  and the number  $N_c$  of particles that remain in the gaseous phase, while

$$N_0 \equiv N - N_c = \begin{cases} \text{number of particles that have} \\ \text{condensed to the ground state} \end{cases}$$

Evidently

$$N_0 = N \left\{ 1 - \frac{N_c}{N} \right\} = N \left\{ 1 - \left( \frac{T}{T_c} \right)^{\frac{3}{2}} \right\} \quad (266)$$

The energy of the system (since we have set the ground state energy to zero) is contributed entirely by the uncondensed phase, and (compare (243)) can be described

$$\begin{aligned} U &= 4\pi kT(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \int_0^\infty \frac{u^4}{e^{u^2} - 1} du \\ &= kT 4\pi(V/h^3)(2mkT)^{\frac{3}{2}} \cdot \frac{3}{8}\sqrt{\pi}\zeta\left(\frac{5}{2}\right) \\ &= kTN_c \cdot \frac{3}{8}\zeta\left(\frac{5}{2}\right) / \frac{1}{4}\zeta\left(\frac{3}{2}\right) \\ &= 0.513512 \cdot \frac{3}{2}N_c kT \quad : \quad T < T_c \end{aligned} \quad (267.1)$$

while at (247) we had

$$\begin{aligned} U &= \mathcal{F}_-(x_0) \cdot \frac{3}{2}NkT \quad : \quad T > T_c \quad (267.2) \\ \mathcal{F}_-(x_0) &\equiv \frac{\text{PolyLog}\left[\frac{5}{2}, x_0\right]}{\text{PolyLog}\left[\frac{3}{2}, x_0\right]} \quad \text{by (249)} \end{aligned}$$

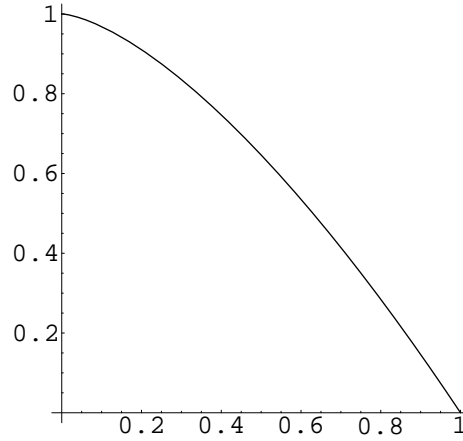


FIGURE 69: Graph—based upon (266)— $N_0/N$  vs.  $T/T_c$ ; i.e., of the sub-critical temperature dependence of the “order parameter.”

From (265.1) we learn that  $N_c \sim T^{\frac{3}{2}}$  so from (267.1) it follows that in the sub-critical region  $U \sim T^{\frac{5}{2}}$ , and therefore that the isovolumetric heat capacity

$$C_v \sim T^{\frac{3}{2}} \quad : \quad T < T_c$$

On page 203 we established at high temperatures  $U = \frac{3}{2}NkT$ , which gives the classical result

$$C_v = \frac{3}{2}Nk \quad (\text{constant}) \quad : \quad T \gg T_c$$

But for  $T$  only slightly higher than  $T_c$  we must, by (267.2), take into account the  $T$ -dependence of  $x_0$ , which is made awkward by the fact that  $x_0$  is got by *functional inversion* of (242):

$$\text{PolyLog}\left[\frac{3}{2}, x_0\right] = \frac{Nh^3}{V(2\pi mkT)^{\frac{3}{2}}}$$

I will not pursue this problem,<sup>151</sup> but will report only that one is led at length to a  $C_v(T)$  of the form shown in Figure 70.

Look more closely to  $C_v$  in the sub-critical regime. From (267.1) it follows readily that

$$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V = \frac{5U}{2T} = \frac{5}{2}(\text{stuff}) T^{\frac{3}{2}}$$

But at (70.1) we had occasion to notice that  $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$  so we have

$$S(T, V) = \int_0^T \left(\frac{\partial S}{\partial T}\right)_V dT = \int_0^T \frac{5}{2}(\text{stuff}) T^{\frac{1}{2}} dT = \frac{5}{3}(\text{stuff}) T^{\frac{3}{2}}$$

<sup>151</sup> See the footnote on page 210 of ter Haar.<sup>108</sup>



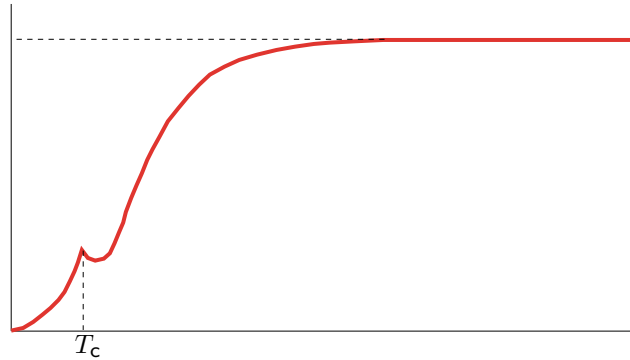


FIGURE 70: Qualitative representation of how the isovolumetric heat capacity of an ideal Bose-Einstein gas varies with temperature. The discontinuity announces the onset of a **phase transition**. The figure is adapted from the figure that appears on page 391 of Reichl’s *A Modern Course in Statistical Physics* (2<sup>nd</sup> edition 1998). Reichl also sketches a clever way to circumvent the computational difficulty mentioned in the text.

The sub-critical free energy is given therefore by

$$\begin{aligned} F &= U - TS = (\text{stuff}) T^{\frac{5}{2}} - \frac{5}{2}(\text{stuff}) T^{\frac{5}{2}} \\ &= -\frac{3}{2}(\text{stuff}) T^{\frac{5}{2}} \\ &= -\frac{3}{2}V(2\pi m/h^2)^{\frac{3}{2}}(kT)^{\frac{5}{2}} \end{aligned}$$

and the sub-critical pressure by

$$p = \left(\frac{\partial F}{\partial V}\right)_T = \frac{3}{2}(2\pi m/h^2)^{\frac{3}{2}}(kT)^{\frac{5}{2}} \quad : \quad T \leq T_c \quad (268)$$

Landau & Lifshitz remark<sup>152</sup> that the volume-independence of pressure, as revealed in the preceding equation, can be understood as “a natural consequence of the fact that [particles in the ground state] have no momentum, and thus do not contribute to the pressure.” The situation here differs radically from that presented by degenerate Fermi-Dirac gases, where we found (page 205) the pressure at  $T \approx 0$  to be typically quite high. We have come upon a vivid instance of the idea (page 187) that “bosons are drawn to each other, fermions find one another repulsive.”

It is instructive to contemplate the isothermal compression of a bosonic gas. Holding both  $T$  and  $N$  ever constant, let us assume that  $V$  is initially so large (and the gas so dilute) that it behaves classically. We begin to compress the gas and the pressure rises by the familiar rule

$$pV = \text{constant}$$

<sup>152</sup> *Statistical Physics* (1958), page 170.

As  $V$  becomes smaller smaller we begin to notice that the pressure rise is *less* than that rule predicts (by an amount we could describe if we could carry out some awkward functional inversions). Continued isothermal compression brings us ultimately to the *critical volume*  $V_c$  set by the condition

$$N = 2.61238 \cdot (V_c/h^3)(2\pi mkT)^{\frac{3}{2}} \quad (269)$$

At that point  $N$  has, according to (265.1), “gone critical,” and the pressure, according to (268), has dropped to only 57% of its classically expected value:

$$\begin{aligned} \frac{NkT}{V_c} &= 2.61238 \frac{NkT \cdot (2\pi mkT)^{\frac{3}{2}}}{Nh^3} \\ &= 2.61238 (2\pi m/h^2)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \quad : \quad \text{CLASSICAL VALUE} \\ &\downarrow \\ p_c &= 1.50000 (2\pi m/h^2)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \quad : \quad \text{BOSONIC VALUE} \end{aligned}$$

Further compression causes no change in the pressure (Figure 71), but does cause the number of particles in the gas phase to decrease, the number of particles in the condensate to increase ... according to rules

$$N_{\text{gas}} + N_{\text{condensate}} = N$$

$$\frac{N_{\text{condensate}}}{N_{\text{gas}}} = \frac{V_c}{V} - 1 \quad : \quad V \leq V_c$$

the first of which is obvious, and the second of which follows directly from (265).

That the phenomena here in question are *profoundly quantum mechanical* in nature is made obvious by the exposed  $h$ 's that appear in our formulæ. For example, we have

$$V_c = N \frac{h^3}{2.61238 (2\pi mkT)^{\frac{3}{2}}} \quad : \quad \text{vanishes as } h \downarrow 0$$

Recall, in this connection, that the ground state energy of a mass  $m$  confined to a cubic box of volume  $\mathcal{V} = \ell^3$  is given by

$$E_0 = \frac{h^2}{8m\ell^2} 3 = \frac{3h^2}{8m\mathcal{V}^{\frac{2}{3}}}$$

and notice that if we were to set  $E_0 = \frac{3}{2}kT$  we would have

$$\mathcal{V} = \left( \frac{h^2}{4mkT} \right)^{\frac{3}{2}} = 1.96870 \frac{h^3}{(2\pi mkT)^{\frac{3}{2}}}$$

So

$$V_c = N \cdot 0.194439 \mathcal{V} \approx \frac{1}{5} N \cdot \mathcal{V}$$

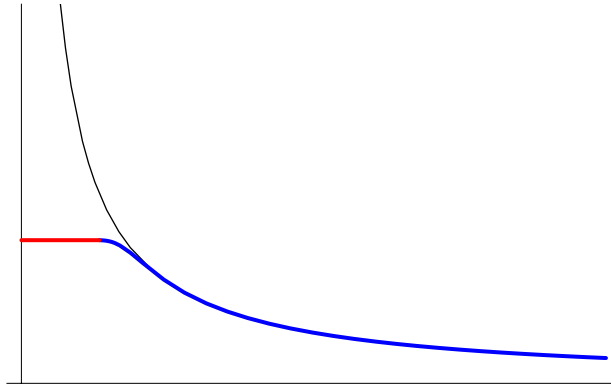


FIGURE 71: Isotherm ( $V$  runs  $\rightarrow$ ,  $p$  runs  $\uparrow$ ) of an ideal classical gas compared with that of an ideal bosonic gas. The bosonic isotherm changes color  $\text{—}$  at the critical point  $(p_c, V_c)$  at which the gas phase starts to condense. The gaseous and condensed phases co-exist at points along the isobaric left leg  $\text{—}$  of the isotherm. In point of practical fact, bosonic condensates are produced in the laboratory not by isothermal compression but by the clever ultra-refrigeration of cleverly confined samples.

The deBroglie wavelength of a mass  $m$  with energy  $kT$  is  $\lambda = h/\sqrt{2mkT}$ , so what we have learned is that at criticality

$$\text{characteristic box dimension} \approx N^{\frac{1}{3}} \cdot (\text{deBroglie wavelength})$$

For example: if  $m$  is the mass of an  $^{87}\text{Rb}$  atom and  $T = 39 \times 10^{-12}\text{K}$  then  $\lambda = 5.3 \times 10^{-3}\text{mm}$ . If we take  $N = 100,000$  then  $N^{\frac{1}{3}} = 46.4$  and we are led to a characteristic box dimension of about 2.5mm—which, though I have abandoned all fussy little numerics, is entirely consistent with the result of a previous calculation.<sup>153</sup> The point I am belaboring is that *it would be a mistake to confuse the size of the confined condensate with the size of the “deBroglie box.”*

For reasons not hard to understand, the high-temperature physics of many-body systems is securely classical, the very low-temperature physics profoundly quantum mechanical. Superconductivity and superfluidity—both of which are low-temperature phenomena—derive their interest in part from the fact that they provide “macroscopic manifestations of quantum mechanics.” So also does the phenomenon of Bose-Einstein condensation, but—excitingly—it presents a uniquely clean and (literally) transparent instance of “macroscopic quantum mechanics.” To discuss the *physics of the condensed state* would be a quantum mechanical (not a thermodynamic) exercise, but it is important to recognize that the objects met in the laboratory are the condensates not of the ideal bosonic gases discussed above but of *real* bosonic gases; *i.e.*, that to understand the data one would have to take theoretical account of particle interactions.

<sup>153</sup> See again page 210, where we first encountered the present example.