International Journal of Theoretical Physics, Vol. 3, No. 3 (1970), pp. 245–251

Classical Statistical Mechanics of Identical Particles and Quantum Effects

E. C. G. SUDARSHAN

Center for Particle Theory, The University of Texas,
Austin, Texas 78712

and

J. MEHRA

Center for Statistical Mechanics and Thermodynamics,
The University of Texas, Austin, Texas 78712

Received: 24 *December* 1969

Abstract

The identification of the phase space of N classical identical particles with the equivalence class of points is of crucial importance for statistical mechanics. We show that the refined phase space leads to the correct statistical mechanics for an ideal gas; moreover, Gibbs's paradox is resolved and the Third Law of Thermodynamics is recovered. The presence of both induced and stimulated transitions is shown as a consequence of the identity of the particles. Other results are the 'quantum' contribution to the second virial coefficient and the Bose–Einstein condensation. Photon bunching and Hanbury Brown–Twiss effect are also seen to follow from the classical model. The only element of quantum theory involved is the notion of phase cells necessary to make the entropy dimensionless. Assuming the existence of the light quantum or the phonon hypothesis we could derive the Planck distribution law for blackbody radiation or the Debye formula for specific heats respectively.

Classical mechanics idealizes certain objects as particles; thus dust particles, billiard balls, apples and automobiles may be considered as particles in the appropriate framework. In cosmology, even galaxies are considered as particles 'streaming with the substratum'. The idealization of macroscopic objects as point masses is, in many cases, only for treating their dynamics, and not to abolish the possibility of distinguishing between them. For example, two bullets may be identical in their relevant mechanical properties but distinguishable (since a detective may have put his identification marks on them); thus two objects may be 'identical but distinguishable'. For macroscopic objects there is never complete identity of two separate objects, hence identical particles are quite correctly treated as distinguishable.

If we extend this consideration to truly elementary objects (microscopic in fact, although not necessarily) which are points or collections of points, then the identical objects are not only identical but also indistinguishable. Two objects such as two classical helium atoms are completely *identical and indistinguishable*; there is no provision for these objects to carry any identification marks. The distinguishability has to do with unused structures in the objects that are not dynamically relevant (the engine number of an automobile does not affect its functioning), and for a system with no such redundant structure 'identical' implies 'indistinguishable'. The identity of two classical point particles has nothing to do with quantum mechanics or the structure of the atom; it is a basic postulate of the physical model.

Phase Space of a Classical System

Phase space is the theater in which classical Hamiltonian mechanics is best represented. The transformations implied by dynamics, motions, symmetries, most general propositions, and even stochastic states, are all best displayed in phase space. There is probably a lack of precision in the concept of phase space for a system of classical particles some of which may be identical. If we imagine the coordinates and momenta of two identical particles to be interchanged, there is no discernible difference for the state. Thus if we are interested only in the dynamical behavior of a system of identical particles it would be logical to *identify the phase space* of the classical system not with the $6N$-dimensional Euclidean space but *with the equivalence class of points* of this space, any two points obtained by interchange of the coordinates and momenta of identical particles being considered equivalent. This does not reduce the dimensionality of the phase space. (In the language of the mathematician, the phase space is not the Kronecker product of the phase spaces of the individual particles, but the symmetrized Kronecker product.)

It is often argued that since we could follow the motion of each particle in classical mechanics, if we so chose, it must be possible to distinguish the states obtained from each other by interchange of identical particles. But this argument is invalid when only dynamical behavior is considered as in statistical physics. The canonical equations of motion are symmetric under the interchange of identical particles, and *if in the initial state we cannot distinguish two states obtained by exchange of identical particles the indistinguishability propagates itself.* If I claimed that during the instant you blinked your eyes I had carried out such an interchange, you would not be able to verify or refute my claim if the particles are truly identical.

The Thermodynamic System

Let us consider *as a model of a thermodynamic system* a set of N identical particles in a volume V. The phase space is the equivalence class of points in a $6N$-dimensional phase space. To make the entropy of the system dimensionless we should be able to divide μ-space, which is the six-dimensional phase space associated with p and q of a single particle, into cells with a constant volume. This would lead to a division of the γ-space, the $6N$-dimensional phase space of N particles, into cells. We choose the constant μ-space volume to be h^3, where h has the dimensions of an action (Planck, 1932).† Then the number of ways of assigning N particles with a

---

† In statistical mechanics we need a phase volume measured in units of action. We must have a suitable number as the measure of the phase volume so that we can take its logarithm. For many purposes it does not matter what the precise value of the action constant is. In entropy per unit volume of a Boltzmann gas it enters as an additive constant; the equation of state is unaffected by it, as are the specific heat, latent heat, etc. If the absolute entropy is measured we are in some difficulty, since no additive constants are permitted then in the entropy; we cannot change from h to h_1, say.

At this point, problems arise with respect to the Gibbs paradox and the Nernst heat theorem. Taking Gibbs's paradox, the entropy could not be made an extensive quantity without introducing some correction factor; that this is not automatically satisfied by classical statistical mechanics in the usual formulation is due to the fact that the particles are treated as identical but not indistinguishable. If we mix two volumes of a gas I and II, a particle from I is considered distinguishable from a particle from II, and hence there is more than twice the 'disorder' in mixing up the two volumes.

At this point a fundamental choice must be made. Is there any increase in entropy for the case mentioned? Does entropy increase on mixing of two identical volumes? If the particles are 'identical' but 'distinguishable' it *does* increase; if they are 'identical' and 'indistinguishable' it *does not* increase. (Of course, if they are not 'identical' they are not 'indistinguishable', and the entropy certainly does increase!) Now, an entropy which increases when identical gases are mixed is not very good as a definition of a thermodynamic quantity. Thus *if the statistical entropy should coincide with (or, serve as) thermodynamic entropy, then the particles ought to be identical and indistinguishable.*

The 'resolution' of Boltzmann overcomes this difficulty, not by any fundamental change but by fiat; he does not have a natural unit for action, nor does he solve the problem of the Nernst heat theorem. The latter provides an absolute zero for entropy by strengthening the result

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT$$

in the form

$$S(T) = \int_{0}^{T} \frac{C_v(T)}{T} dT$$

Given this strengthened form we can no longer change from h to h_1, since such a change would change the absolute entropy. Now the question arises, which of the choices of h gives the correct (Nernst theorem) value? Could we not use this to choose a numerical value for h?

The tragedy is that with the scheme proposed by Boltzmann, we cannot! This is because every value of h gives $-\infty$ for the entropy; no value of h is classically appropriate. If, however, we use the notion of indistinguishability *and employ phase cells* then, as $T \to 0$, all the particles cluster into the lowest cell and the statistical phase space volume becomes 1 (not zero) *for all choices of h*, and the entropy goes to zero. We have a 'scaling law' (law of corresponding states) which states that if $h \to h_1 = yh$, then the entropy, fugacity and specific heat remain unchanged, provided $T \to T_1 = yT$ and $m \to m_1 = ym$, for other temperatures.

total energy E to these cells is to be calculated. Each cell may be chosen to have a more or less specified energy; moreover, there will be many levels with the same energy. If ϵ_j denotes the energy levels for the cells, g_j the number of cells in μ-space with this value of energy, and n_j the number of particles with the energy ϵ_j, then the distinct number of ways of arriving at this distribution is given by

$$W(n) = \prod_j \frac{(n_j + g_j - 1)!}{n_j!\,(g_j - 1)!} \tag{1}$$

where the particles have been assumed to be indistinguishable.†

The maximization of $W(n)$ subject to the constraints

$$\sum n_j = N; \qquad \sum n_j \epsilon_j = E$$

is given by the distribution

$$n_j = g_j[-1 + z^{-1} \exp(\beta\epsilon) j]^{-1} \tag{2}$$

where z and β are two parameters determined in terms of N and E. This is identical with the Bose–Einstein distribution (Bose, 1924) for a gas with fugacity z and temperature k/β. *Apart from the subdivision of the phase space into cells, no concepts of quantum theory have entered the derivation.*

It is clear that the entropy of the system calculated from this model does behave as an extensive quantity. The entropy is given by

$$S = k \sum_j g_j \left\{ \frac{\beta\epsilon_j - \log z}{z^{-1} \exp(\beta\epsilon) j - 1} - \log[1 - z\exp(-\beta\epsilon_j)] \right\} \tag{3}$$

When two volumes of a gas with the same fugacity and temperature are mixed, the degeneracies g_j simply add, so that the entropies simply add. There is therefore no Gibbs's paradox (Gibbs, 1948).

---

† 'Conventional' classical statistical mechanics involves equal *a priori* probability of the unsymmetrized $6N$-dimensional phase space, which corresponds to equal probability for every distinctive set of occupation numbers in the μ-space, with all the particles being *distinguishable*. However, if we accept the group-theoretical argument for suitable *irreducible* representations of the Kronecker product space, only phase spaces with either single occupation of phase cells (Fermi statistics) or unlimited occupation of phase cells (Bose statistics) are allowed. In the symmetrical case the equal *a priori* probability hypothesis leads immediately to equal probability for *every* distinctive set of occupation numbers in the μ-space, with the particles being *indistinguishable*. The phase space so defined takes care of the factor $1/N!$ traditionally introduced in Boltzmann statistics.

From the above argument it is apparent that $W(n)$ can be identified as the relative probability of the particular state. In the symmetrized single occupation case it leads to equal probability for those sets with the occupation numbers not exceeding 1. This leads to a relative probability

$$W(n) = \prod_j \frac{g_j!}{n_j!\,(g_j - n_j)!}$$

and Fermi-Dirac statistics is retrieved.

Boltzmann Equation and Stimulated Emission

Let us now consider the stability of the equilibrium distribution (2) under collisions. Let $\omega(jk \to lm)$ be the probability per unit time that two isolated atoms in the cells j and k will go into the cells l and m. If these cells are already occupied, the physical transition probability will depend upon the occupation numbers n_j, n_k, n_l, n_m. Hence the collisional rate of change of the distribution function $f(n)$ is given by†

$$\frac{\partial f}{\partial t}_{\text{collision}} = \sum \{n_j n_k \omega(jk \to lm) \phi(n_l) \phi(n_m) - n_l n_m \omega(lm \to jk) \phi(n_j) \phi(n_k)\} \tag{4}$$

where $\phi(n)$ is a function yet to be specified. It is customary to take $\phi(n) = 1$, but this is not warranted as we shall see presently. Microscopic reversibility implies

$$\omega(jk \to lm) = \omega(lm \to jk)$$

and the equilibrium is achieved when

$$\frac{n_j}{\phi(n_j)} \frac{n_k}{\phi(n_k)} = \frac{n_l}{\phi(n_l)} \frac{n_m}{\phi(n_m)} \tag{5}$$

In order to obtain the equilibrium distribution (2) we must choose

$$\phi(n) = 1 + n \tag{6‡}$$

In other words, the physical transition probability for a transition *from* a cell with n particles is proportional to n, but for transition *into* a cell with n particles it is proportional to $1 + n$. The term 'proportional to unity' is the Clausius–Boltzmann term; but there is an additional contribution proportional to n which corresponds to 'stimulated emission'. The latter is considered to be of quantum origin, but we see here that it can be derived purely classically and can be traced to the indistinguishability of equivalent states.

Consequences

The proper treatment of the phase space leads to the phenomena of positive distance correlations (Uhlenbeck & Gropper, 1932) and bunching

---

† The derivation of equation (4) is independent of quantum theory. Essentially it involves the following assumptions:

(1) The existence of a collision rate ω.
(2) The assumption that ω obeys the principle of micro-reversibility.
(3) The assumption that owing to correlations introduced by indistinguishability the occupation numbers in the final states influence the rate of change of f via multiplication of the first term on the right-hand side by some function $\psi(n_l, n_m)$, and the second by $\psi(n_j, n_k)$.
(4) An assumption of independence (the simplest!) implying that ψ factorizes: that is, $\psi(n_l, n_m) = \phi(n_l) \phi(n_m)$.

With these assumptions, the steady-state solution of (4) agrees with the equilibrium distribution (2) (obtained by a combinatorial argument) if and only if $\phi(n) = n + 1$.

‡ The choice of $\phi(n) = n$ is ruled out because that would imply $\partial f / \partial t = 0$ identically.

of particles in phase cells. This may be understood as follows: when the phase space was (incorrectly!) identified with the entire $6N$-dimensional space there were no distance correlations; each state was equally probable. But if the phase space is now identified with only the equivalence classes of points, as formulated above, there is an added preference for states in which more and more particles are in the same cell in μ-space. This is reflected in the expression (1). Hence there is a preference for situations in which the particles tend to be bunched into cells in μ-space; that is, the probability for a state is larger when the occupation number (in the cells in μ-space) is uneven. Thus positive distance correlations are expected.

Another consequence of the distribution (2) is that the non-interacting classical gas now has a second virial coefficient

$$b_2 = 2^{-5/2} \tag{7}$$

in dimensionless units. This is also tranditionally traced to the quantum nature of the particles, but is here seen to be derived from first principles of a classical gas.

Another phenomenon of great interest is the approach of the gas to the absolute zero of temperature. Clearly, as the temperature of the system becomes lower, the lower energy group of phase cells would be preferred, until at last all the particles would cluster in the lowest energy cell (or cells). Since the phase cell has voume h^3 the lowest energy is of order

$$\frac{(p_0)^2}{2m} = \frac{1}{2m}\left(\frac{h^3}{V}\right)^{2/3} = \frac{h^2}{2mV^{2/3}} = \epsilon_0 \tag{8}$$

and this tends to zero with increasing V. The fugacity decreases as $\exp(-\beta\epsilon_0)$ when $\beta \to \infty$ and a finite fraction of the particles end up in the lowest energy state (London, 1938; Einstein, 1925). The entropy decreases rapidly as the temperature decreases, until at last, at $\beta = \infty$, the entropy becomes equal to $k \log g_0$, where g_0 is the degeneracy of the lowest energy state. If this is taken to be a unique state the entropy goes to zero in accordance with the Third Law of Thermodynamics (Nernst, 1906, 1918).

Thus many of the results normally believed to be a consequence of quantum mechanics are seen to follow from classical mechanics provided the notion of phase cells is introduced. If we add Einstein's hypothesis of light quanta, i.e., that light consists of particles with energy $\epsilon = h\nu$, where h is Planck's constant and ν is the frequency of light, we can deduce Planck's distribution law for the intensity of blackbody radiation (Planck, 1900):

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{\exp(\beta h\nu) - 1} \tag{9}$$

which is a specialization of (2). Similarly, the Debye T^3-law (Debye, 1912) of the specific heat for a solid can be obtained if we introduce the notion of phonons with frequencies $0 < \nu < \nu_{\max}$ and energies $\epsilon = h\nu$.

The photon equilibrium distribution (9) will remain steady in the presence of matter which can absorb and emit photons only if the emission process contains both spontaneous emission and stimulated emission contributions. To see this in more detail, let us consider an atomic species which collides with the photon; during this process the photon is absorbed and a different photon is emitted. By considerations analogous to the one employed in deriving (5) and (6) we deduce that the rate of emission into a phase cell with $\hat{n}$ photons is proportional to $\hat{n} + 1$, while the rate of absorption from this state is proportional to $\hat{n}$. The difference is to be attributed to the possibility of spontaneous emission. Our 'classical' theory includes both stimulated and spontaneous emission contributions.†

We remark, in passing, that the introduction of phase cells automatically introduces the notion of zero-point energy, since the lowest energy phase cell still has a finite extension in energy and hence the average energy in the 'ground state cell' is finite and non-zero. This conclusion was reached by Planck himself long before quantum mechanics was formulated (Planck, 1932). A simple example is given by (8).

The fluctuations in the number of photons can also be calculated on the basis of the formulation of a classical photon gas. If $\hat{n}_j$ is the occupation number of the group of g_j phase cells, all with the same energy ϵ_j, then one can show that the mean square of $\hat{n}_j$ is

$$\langle \hat{n}_j^2 \rangle = (1 + g_j^{-1}) \langle \hat{n}_j \rangle^2 + \langle \hat{n}_j \rangle$$

so that the variance is

$$\sigma_j^2 = \hat{n}_j (1 + (\hat{n}_j / g_j)) = \hat{n}_j + \frac{\hat{n}_j^2}{g_j}$$

The term $(\hat{n}_j^2 / g_j)$ may be associated with a wave noise and the term $\hat{n}_j$ with the (Poisson-like) particle noise (Wolf & Mandel, 1965). These may be compared with the fluctuations calculated by Einstein (Einstein, 1909). The Hanbury Brown–Twiss effect (Hanbury Brown & Twiss, 1956, 1957a, b) is a direct consequence of such fluctuations.

Undoubtedly, quantum mechanics govern the motion of atoms and subatomic particles. But the proper use of classical concepts can explain much of the behavior of matter in bulk that is relevant to statistical mechanics. The ultimate origin of the phase cells, and even of the particles and light quanta, is to be sought within a quantum-mechanical framework. But granted the existence of these, a proper application of classical statistical mechanics can lead to a satisfactory theory including many 'quantum' effects.

Appendix

Refinement of Einstein's Derivation of the Planck Distribution

Einstein rederived the Planck distribution formula for blackbody radiation by considering the equilibrium between matter and radiation.

---

† Compare this with the derivation in Einstein, A. (1917). *Physikalische Zeitschrift*, **18**, 121.

He argued as follows: If n_1 and n_2 are the populations of the ground state and excited states of the atom and the energy density per unit frequency interval is $\rho(\nu)$, then the number of transitions exciting the atoms is given by $n_1\rho(\nu_{12})B_{12}$, where $h\nu_{12}$ is excitation energy and B_{12} is a constant characterizing the atom. The reverse transitions contain stimulated transitions at the rate of $n_2\rho(\nu_{12})B_{21}$ and spontaneous transitions at the rate of n_2A_{21} per unit time. The constant A_{21} is related to B_{21} by the formula

$$A_{21} = \frac{8\pi h\nu^3}{c^3}\cdot B_{21} = \frac{8\pi h\nu^3}{c^3} B_{12}$$

Using the Boltzmann distribution

$$n_2/n_1 = \exp(-h\nu/kT)$$

Einstein deduces

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3[\exp(h\nu/kT) - 1]}$$

In this derivation matter and radiation are treated asymmetrically, the former obeying Boltzmann statistics. We could obtain a more satisfactory derivation by considering both the photons and the matter to behave as 'classical' indistinguishable particles. For both species of objects the transition rate has a stimulated and spontaneous contribution. Let us denote the number of photons of the appropriate frequency per phase cell by $\hat{n}$, while the number of atoms in the ground state and excited state *per phase cell* are denoted by n_1 and n_2. Then we get, by considering the equilibrium between absorption and emission of light, the equality

$$n_1(1 + n_2)n_2(\hat{n} + 1)$$

$$\log\left(\frac{n_2}{1 + n_2}\right) - \log\left(\frac{n_1}{1 + n_1}\right) = \log\left(\frac{\hat{n}}{1 + \hat{n}}\right)$$

Comparing this with the conservation laws of energy and atoms

$$E_2 - E_1 = h\nu = E$$

$$n_1 + n_2 = \text{constant}$$

we get

$$\log\frac{\hat{n}}{1 + \hat{n}} = -\beta h\nu$$

$$\log\frac{n_1}{1 + n_1} = -\beta E_1 + \mu$$

$$\log\frac{n_2}{1 + n_2} = -\beta E_2 + \mu,$$

where β is a constant of proportionality and eventually identified with $1/RT$ we obtain

$$n = [\exp(\beta h\nu) - 1]^{-1}$$

Remembering that there are $(8\pi/c^3)\nu^2$ phase cells per unit volume per unit frequency, this yields the Planck distribution formula and at the same time yields the Bose–Einstein distribution for the atoms.

Acknowledgements

We gratefully acknowledge discussions with Professor Eugene P. Wigner. One of us (J.M.) would like to thank Professor Nathan Ginsburg for his hospitality in the Physics Department, Syracuse University during several visits to Syracuse, where this work was done. This work was supported in part by the U.S. Atomic Energy Commission.

References

Bose, S. N. (1924). *Zeitschrift für physik*, **26**, 178.
Debye, P. (1912). *Annalen der Physik*, **39**, 789.
Einstein, A. (1925). *Berliner Berichte*, 3.
Einstein, A. (1909). *Physikalische Zeitschrift*, **10**, 185.
Gibbs, J. W. (1948). *Collected Works*, Vol. II. New Haven.
Hanbury Brown, R. and Twiss, R. Q. (1956). *Nature* (*London*), **177**, **27**.
Hanbury Brown, R. and Twiss, R. Q. (1957a). *Proceedings of the Royal Society* (*London*), **A242**, 300.
Hanbury Brown, R. and Twiss, R. Q. (1957b). *Proceedings of the Royal Society* (*London*), **A243**, 291.
London, F. (1938). *Physical Review*, **54**, 947.
Nernst, W. (1906a). *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen* (*Mathematisch-physikalische Klasse*), Heft I.
Nernst, W. (1906b). *Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin*, V. 20, December 1906.
Nernst, W. (1918). *Die theoretischen und Experimentellen Gundlagen des neven Warmesatzes*. Halle.
Planck, M. (1900). *Verkandlungen der Deutschen physikalischen Gesellschaft*. **ii**, 237.
Planck, M. (1932). *Theory of Heat*. London, Originally published in German in 1906.
Uhlenbeck, G. E. and Gropper, L. (1932). *Physical Review*, **41**, 79.
Wolf, E., and Mandel, L. (1965). *Review of Modern Physics*, **37**, 231.