

JOHN GAMBLE KIRKWOOD COLLECTED WORKS

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Quantum Statistics and Cooperative Phenomena

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Introduction

by F. H. STILLINGER, Jr.

The following set of papers written or coauthored by Professor Kirkwood have been selected as falling into either of two categories: Quantum Statistics, or Cooperative Phenomena. Under each of these headings, the papers are arranged chronologically. One unavoidably concludes that it is much to Professor Kirkwood's credit to have contributed original and notable ideas in the evolution of these fields, which even today rank among the most active and fashionable areas of theoretical physics.

The general excitement prevalent in physical and chemical circles during the early years of quantum mechanics undoubtedly held strong attraction for theorists of that period. The early papers on intermolecular forces, polarizabilities, and susceptibilities written by Professor Kirkwood (contained in another section of this Collection) clearly show he was no exception. To one trained specifically in the Gibbsian methods of statistical mechanics it was, therefore, entirely natural to inquire about the effects that quantization has on the equilibrium properties of matter. The initial investigations (the articles are included with the others on intermolecular forces) were concerned with the quantum mechanical second virial coefficient of monatomic gases.

The first paper included here, "Quantum Statistics of Almost Classical Assemblies", represents a systematic procedure (supplementing that of Wigner¹) for generating asymptotic quantum corrections to the canonical partition function in powers of Planck's constant. This paper, along with "Statistical Theory of Low Frequency Intermolecular Forces", which follows it, verify that for most applications of interest in physical chemistry the quantum corrections to predictions of classical statistical mechanics are indeed small. Since so much of Kirkwood's later research was devoted to the regime of classical statistics, these two papers conceivably formed a strong personal justification for the subsequent specialization.

Included here as well is a correction to "Quantum Statistics of Almost Classical Assemblies", required by the failure of the final partition function expression, Eq. (21) in that paper, to yield an extensive free energy. Strangely enough, although the correction does indeed satisfy that condition by insertion of the necessary reciprocal factorial of particle number, it is not itself quite correct. The functions $S_n(p)$ appearing in Eq. (3) of the correction unfortunately are not uniquely defined. One easily sees, for example, that in the case of free particles, where the wave functions themselves have the form shown in Eq. (2) of the correction, that one might choose:

$$S_n(p) = \delta(p_1 - \bar{p}_1) \dots \delta(p_N - \bar{p}_N),$$

where the set of momenta $\bar{p}_1 \dots \bar{p}_N$ are specified by the index n . Since no more than $2S + 1$ \bar{p}_j 's can be equal for fermions with spin S , and since the \bar{p}_j 's which are equal to one another for bosons are not distinguishable, the S_n can never form a complete set in the usual sense. Equally well, and perhaps more appropriately for the problem considered, the symmetrized (Bose

¹ E. Wigner, *Phys. Rev.* **40**, 749 (1932).

statistics) or antisymmetrized (Fermi statistics) average form also satisfies Eq. (3):

$$S_n(p) = \frac{1}{N!} \sum_P (\pm 1)^{|P|} \delta(p_1 - P\bar{p}_1) \dots \delta(p_N - P\bar{p}_N).$$

If one then adopts this additional symmetry convention for the S_n , it is then possible to show (easily for small numbers of free particles by direct calculation) that Eq. (5) in the correction should read:

$$\sum_n S_n^*(p') S_n(p) = \frac{1}{(2\pi\hbar)^{3N} (N!)^2} \sum_P (\pm 1)^{|P|} \delta(p_1 - P\bar{p}_1) \dots \delta(p_N - P\bar{p}_N),$$

where h (in the obsolete notation of the time) is Planck's constant divided by 2π . The partition function with properly extensive free energy subsequently follows.

Considering the large amount of thought and computational effort devoted during his career to the classical liquid pair correlation function, Professor Kirkwood must surely have found gratification in the fundamental idea behind the three papers on liquid helium written in collaboration with R. M. Mazo. Thus, in spite of the fact that liquid helium vividly provides an example of matter about as far removed from the classical limit as one ordinarily encounters, it was shown at least approximately that the preceding classical calculations could be directly applied to the pair distribution in helium, simply by choosing a suitable temperature-, density-, and statistics-dependent effective temperature, τ . This parameter, which absorbs the entire manifestation of nonclassical behavior, was not calculated, but could be estimated from measured thermodynamic data.

In the last of these three articles ("Statistical Thermodynamics of Quantum Fluids") appears the statement that the classically useful superposition approximation applied to the diagonal elements of the triplet density matrix:

$$\rho_3(123 | 123) \cong \frac{\rho_2(12 | 12)\rho_2(13 | 13)\rho_2(23 | 23)}{\rho_1(1 | 1)\rho_1(2 | 2)\rho_1(3 | 3)}.$$

is less accurate than the corresponding classical limiting case. To account properly for particle indistinguishability, the appropriate quantum superposition principle should read:

$$\rho_3(123 | 123) \cong \begin{vmatrix} \rho_1(1 | 1) & \rho_1(1 | 2) & \rho_1(1 | 3) \\ \rho_1(2 | 1) & \rho_1(2 | 2) & \rho_1(2 | 3) \\ \rho_1(3 | 1) & \rho_1(3 | 2) & \rho_1(3 | 3) \end{vmatrix} \pm g(12)g(13)g(23),$$

where g is defined by:

$$\rho_2(12 | 12) = \begin{vmatrix} \rho_1(1 | 1) & \rho_1(1 | 2) \\ \rho_1(2 | 1) & \rho_1(2 | 2) \end{vmatrix} \pm g(12),$$

and the subscripts \pm indicate interpretation as permanent or determinant for **Bose** or **Fermi** statistics, respectively. It is interesting to note that by means of this closure relation, the coupled equations for the singlet density matrix

and the diagonal part of the pair matrix (both of which may be deduced from Eq. (3) of this third liquid helium paper) are jointly soluble in principle, and would hence permit calculation of the central quantity τ .

The work devoted to application of finite-temperature Thomas-Fermi theory to correlation effects in systems with a degenerate electron gas ("Quantum Statistical Theory of Plasmas and Liquid Metals", and "Quantum Statistical Theory of Electron Correlation") are notable for their use of electrolyte solution theory techniques, especially the charging process. Besides the acknowledged neglect of exchange energy, which can readily be inserted into the development, it is perhaps also worth noting here that another conceptually desirable refinement could also be incorporated, although final numerical analysis might be materially lengthened. This stems from the fact that electrons are not static point charges, but have a finite velocity; consequently, for an electron moving with momentum \mathbf{p} , the density of other electrons surrounding it must be measured in a frame of reference moving with respect to the Fermi sphere. In place of Eq. (2) of the second of these two papers, say, one should write:

$$n(\mathbf{r}, \mathbf{p}) = \frac{2}{h^3} \int \frac{d\mathbf{p}'}{1 + \exp \{[(\mathbf{p}' - \mathbf{p})^2/2m - e\psi(\mathbf{r}, \mathbf{p}) - \mu]/kT\}},$$

where $\psi(\mathbf{r}, \mathbf{p})$ is the generally aspherical mean potential at distance \mathbf{r} from the electron of interest. Inclusion of both exchange and this velocity dependence presumably would lead to better agreement in the high density region with the known electron gas correlation energy limit.

The last paper under the quantum statistics heading was written after Professor Kirkwood's death. Since the fundamental ideas were his, one is not surprised to see in its beginnings a similarity in approach to the first paper in this section. The intention, however, was to analyze the full range of quantum behavior in interacting many-body systems, without being restricted to asymptotic deviations from the classical region. Although no mention of the fact was given in the article, it is easily possible to find explicitly the statistics-independent interaction function $F^{(n)}$ appearing in the development, for certain simple cases, such as harmonic oscillators, and pairs of rigid spheres.

The earliest type of cooperative phenomenon to receive scrutiny in the Kirkwood papers was the order-disorder transformation in binary alloys. It is generally recognized that the approach outlined in the three articles entitled: "Order and Disorder in Binary Solid Solutions," "Critical Behavior of Solid Solutions in the Order-Disorder Transformation," and "Statistical Mechanics of Cooperative Phenomena," constitutes the first comprehensive and systematic theoretical analysis of this broad class of problems in classical statistical mechanics. Thus, by a well-defined (but possibly tedious) procedure, it was shown possible to generate an approximate evaluation of the order-disorder partition function valid to any finite pre-assigned order in inverse temperature. This "semi-invariant expansion" was carried out to fourth order for the lattices considered; later, Chang² extended the calculation to sixth order. More recently, Brout³ has examined in detail a re-ordering of the

² T. S. Chang, *J. Chem. Phys.* **9**, 169 (1941).

³ R. Brout, *Phys. Rev.* **118**, 1009 (1960).

semi-invariant expansion to improve convergence over the entire temperature range.

The nature of the critical point in a given order-disorder model is still a largely unsettled problem. Apparently, carrying the Kirkwood scheme through some finite order always yields a finite, but discontinuous, specific heat, and a coexistence curve parabolic at the critical point. Actually, in the exactly soluble two-dimensional Ising model, and almost certainly as well in three dimensions, the specific heat suffers an infinite singularity, and the coexistence curve is considerably flatter than parabolic.⁴ Probably the implication ought to be drawn that expansions in long-range order, such as exhibited in Eq. (7) of the second of these three papers, fail to converge at the critical point.

The opinion has often prevailed that the significant analytic features of the various kinds of phase transitions should be common to theories of all of them, and so it has become common to refer to *the* phase transition problem. The application of the semi-invariant technique to systems other than binary alloys was consequently a natural step, and some of the papers collected under the heading "Solutions" display precisely this application for liquid mixtures.

It was clearly recognized, and stated, in the early cooperative phenomena investigations reprinted here, that the vibrational contributions to the free energy were assumed to be independent of the mixing order parameters. That this decoupling is much less appropriate for the assumed mixing of molecules and voids in the "hole" theory of liquid-vapor coexistence than in true solid or liquid state mixture theories, forms the basis of "Remarks on the Hole Theory of Condensation." The final cooperative phenomena article, "Contribution of Lattice Vibrations to the Order-Disorder Transformation in Alloys" explicitly calculates the effect of vibrational coupling, and demonstrates thereby an enhanced specific heat anomaly.

In the hole theory critique, it was stated (at the beginning of Part II) that if cellularization of space were to be carried out by means of nearest-neighbor (Voronoi) polyhedra for the face-centered cubic lattice of close-packed rigid molecular cores, that at most one molecular center could lie in each cell. Actually, it is possible to place up to four such centers in each polyhedron, but the amount of freedom left for movement of two or more particles in the same cell, though finite, is very small. The assumption of at most single occupancy is hence a reasonably good one with this cell choice.

"On Phase Changes in Crystals Arising from Hindered Molecular Rotation," and "Phase Transitions in Monolayers Due to Hindered Molecular Rotation" are, respectively, the theories of cooperative molecular orientation in three and two dimensions. The type of interaction chosen, depending only on a single angle between the axes of a pair of neighboring molecules, probably oversimplifies the physical situation. Instead, it is more suitable to have an interaction similar to the classic dipole-dipole energy (though perhaps of shorter-range character) depending on the orientation vectors of the molecular axes, \mathbf{a}_1 and \mathbf{a}_2 , and the separation \mathbf{r}_{12} between the centroids, in the form:

$$f(r_{12})\mathbf{a}_1 \cdot \mathbf{T}_{12} \cdot \mathbf{a}_2,$$

where the dyadic tensor \mathbf{T}_{12} is defined:

$$\mathbf{T}_{12} = r_{12}^{-3} \mathbf{1} - 3r_{12}^{-5} \mathbf{r}_{12}\mathbf{r}_{12},$$

⁴ M. E. Fisher, *J. Math. Phys.* **4**, 278 (1963).

and f is some suitable function of scalar distance. As a trial calculation, however, the case worked out with the simpler and easier to handle potential may be regarded as a suggestive feasibility investigation for the general method, with satisfactory results.

Perhaps partly because of concern over the complication of coupling to vibrational motions, and partly due to his extensive development of condensed matter distribution function theory, Professor Kirkwood proposed a theory of melting based upon the existence of spatially periodic crystalline, versus constant fluid, singlet density solutions to the relevant integral equations, with good results when applied to argon. At the time this calculation was done, the liquid state pair distribution functions that had to be utilized were not known with the accuracy available at present. It would be interesting to see these same calculations performed again with the full assistance of the now-available rapid electronic computers.

The short "Note on the Theory of Fusion" raises a fundamental and deep question bearing upon the problem of transition to ordered crystalline phases: namely, whether the solid phase singlet density should truly possess long-range periodicity. The tentative resolution proposed is that by suitable constraints on the configurations allowed in the complete N -particle distribution function, which would have no visible effect on the form of the low-order distribution function integral equations, that the crystal lattice would be essentially "held in place," and that the singlet density should clearly exhibit periodically localized (vibrating) particle behavior. Unfortunately, though, it has never been demonstrated that the finite concentration of each of the various types of lattice defects that must be present at any positive temperature, do not introduce enough disorder to destroy the coherence of local periodicity in the infinitely long-ranged limit. In addition, it is known that in two dimensions even harmonic vibrations destroy long-range order: the mean square relative displacement of pairs of particles increases without bound as their equilibrium pair separation increases.

In "Crystallization as a Cooperative Phenomenon," the fluid-solid transition is, so to say, attacked from the opposite direction, by calculating a limit of instability of the liquid state, rather than by finding directly the range of *stability* of the solid. Since liquid-solid transitions are first order, this limit must correspond to the attainable limit of metastability for the supercooled liquid. That the distribution function formalism should apply in this nonequilibrium regime must also require introduction of suitable constraints into the original complete phase space distribution for the entire set of particles; one presumably can split up particle arrangements into liquid-like and solid-like types, and admit only the former before integration down to the distribution functions for the small set of particles of interest.

Our understanding of the nature of, and criteria for, cooperative phenomena will, of course, broaden and deepen with the passage of time. It seems certain that the stepwise systematic Kirkwood approach will constitute an important stylistic tool in this development.