

higher energies ($e\phi \geq 5$ eV) is 8 cm for the data presented in Fig. 2 and is independent of the frequency of excitation. At higher neutral pressure this distance is reduced. This length corresponds to the ion-neutral collision mean free path, and is much longer than the damping length of the wave. For lower ion energies, however, l is smaller than that for higher ion energies. The low-energy l decreases as the frequency is increased. This behavior of the damping length with frequency in the lower ion energy range suggests that ion-ion collision effects are present.^{9,14,15} Further improvement of the resolution of the energy analyzer will make it possible to measure the ion-ion collision effects as a function of energy. An experimental study of nonlinear effects on the distribution function should also be interesting.

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CONVERGENCE OF COUPLING-PARAMETER EXPANSIONS FOR DISTRIBUTION AND THERMODYNAMIC FUNCTIONS

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It is shown that Maclaurin expansions of properly defined distribution functions and of the density-to-activity ratio in powers of exponential coupling parameters (which multiply the Ursell-Mayer f bonds, instead of pair potentials) converge if the integral of the f bond over all space exists. Therefore various successive approximation schemes can be devised with the assurance that they will converge to the correct solution.

The device of multiplying the interaction potential of one or more particles by a coupling parameter whose value varies from zero (complete decoupling) to unity (full coupling) has been extensively used in quantum as well as classical statistics. Most problems dealt with by this method have been solved only in the weak (linear in the coupling parameters)-coupling limit; for example, for the case of Coulombic potentials, one obtains the Debye distribution.¹ One of the most serious difficulties in extending the method to include higher powers of coupling parameters has been the question of convergence of expansions of distribution and thermodynamic functions in powers of the coupling parameters of one or more particles: It was not known whether such expansions converge.

In this note we prove that expansions of properly chosen distribution and thermodynamic functions in powers of the exponential coupling parameters² (multiplying the Ursell-Mayer f bonds of individual particle pairs) of any number of particles of the system converge for all positive values of the parameters, for all classical systems for which the integral of the Ursell-Mayer f bond over an infinite volume is finite. We also show that expansions in powers of the usual coupling parameters (multiplying

directly the individual pair-interaction potentials) can be put into a convergent form. Expansions in individual coupling parameters in quantum statistics are considerably more complicated owing to the problem of particle indistinguishability. The convergence proof presented here means that one can devise a number of successive approximation schemes for obtaining equations of state, with the assurance that they will converge to the correct solution. The question of rapidity of convergence of such schemes, however, still remains to be investigated.

We treat a system of N particles in a volume V , interacting with a pairwise additive potential $U_N(\vec{N})$, $\vec{N} = \vec{r}_1, \dots, \vec{r}_N$. We write the Boltzmann factor $v_N(\vec{N}) = \exp[-U_N(\vec{N})/kT]$ with each particle i coupled by the parameter λ_i :

$$v_N(\vec{N}; \vec{\lambda}_N) = \prod_{i,j \subset \vec{N}} [1 + \lambda_i \lambda_j f_{ij}], \quad f_{ij} = v_{ij} - 1 = \exp[-U_{ij}/kT] - 1. \quad (1)$$

Here $\vec{\lambda}_N$ denotes the set of parameters $\lambda_1, \dots, \lambda_N$, and $i, j \subset \vec{N}$ means that the pairs i, j are chosen from the set \vec{N} , without permutations. The canonical-configurational partition function is thus

$$Z_N(\vec{\lambda}_N) = \int_V v_N(\vec{\lambda}_N) d(\vec{N}), \quad d(\vec{N}) = d^3r_1 \cdots d^3r_N, \quad (2)$$

with all integrations understood to be over the volume V . As with all coupling parameters of this type, we have

$$\left[\frac{Z_N(\vec{\lambda}_N)}{Z_N(\vec{\lambda}_N)} \right]_{\lambda_j=0} = \frac{\rho}{z_j} = \xi_j = \exp[-\alpha(\lambda_j)], \quad (3)$$

with z_j the activity³ of particle j , coupled by λ_j , $\alpha(\lambda_j)$ the excess chemical potential⁴ of that particle in units of kT , and $\rho = N/V$. The distribution functions are defined by the asymptotic formula⁵

$$g_n(\vec{n}; \vec{\lambda}_n) = \frac{V^n}{Z_N(\vec{\lambda}_N)} \int v_N(\vec{N}; \vec{\lambda}_N) d(\vec{N} - \vec{n}), \quad d(\vec{N} - \vec{n}) = d^3r_{n+1} \cdots d^3r_N. \quad (4)$$

Here also only the "strong"-coupling dependence⁴ is indicated explicitly.

We now define distribution functions $G_n(\vec{n}; \vec{\lambda}_n)$ by

$$G_n(\vec{n}; \vec{\lambda}_n) = \prod_{i=1}^n \xi_i \frac{g_n(\vec{n}; \vec{\lambda}_n)}{v_n(\vec{n}; \vec{\lambda}_n)} \quad (5)$$

with $v_n(\vec{n}; \vec{\lambda}_n)$ the direct Boltzmann factor of the particles of the set \vec{n} . The division by v_n is always permissible because it merely represents a cancellation of the same factor implicit in Eq. (4). The functions ξ_i and $G_n(\vec{n}; \vec{\lambda}_n)$ have the properties

$$(\xi_i)_{\lambda_i=0} = 1; \quad [G_n(\vec{n}; \vec{\lambda}_n)]_{\lambda_i=0} = G_{n-1}(\vec{n}-i, \vec{\lambda}_{n-i}), \quad i \subset \vec{n}. \quad (6)$$

Here $\vec{n}-i$ is the set $1, \dots, n$, with the i th particle omitted, and $\vec{\lambda}_{n-i}$ has the corresponding meaning. Differentiating Eq. (5) with respect to λ_1 we obtain⁶

$$\begin{aligned} \partial G_n(\vec{n}; \vec{\lambda}_n) / \partial \lambda_1 &= z_j \int f_{i,j} v(j|\vec{n}-1; \vec{\lambda}_{n-1}, \lambda_j) G_{n+1}(\vec{n}, j; \vec{\lambda}_n, \lambda_j) d(j), \\ v(j|\vec{n}-1; \vec{\lambda}_{n-1}, \lambda_j) &= \prod_{i \subset \vec{n}-1} (1 + \lambda_i \lambda_j f_{ij}), \quad \vec{n}-1 = 2, \dots, n. \end{aligned} \quad (7)$$

By repeated differentiation with respect to λ_1 , using Eqs. (6) and (7), we obtain the expansion of $G_n(\vec{n}; \vec{\lambda}_n)$ in powers of λ_1 :

$$G_n(\vec{n}; \vec{\lambda}_n) = G_{n-1}(\vec{n}-1; \vec{\lambda}_{n-1}) + \sum_{m=1}^{N-n} \frac{\lambda_1^m}{m!} \int K(\vec{m}|\vec{n}; \vec{\lambda}_{n-1+m}) G_{n-1+m}(\vec{n}-1+\vec{m}; \vec{\lambda}_{n-1+m}) d(\vec{m}) \quad (8)$$

with

$$K(\vec{m}|\vec{n}; \vec{\lambda}_{n-1+m}) = \prod_{j \subset \vec{m}} \lambda_j z_j f_{1j} v(j|\vec{n}-1; \vec{\lambda}_{n-1}, \lambda_j) v_m(\vec{m}; \lambda_m) \quad (9)$$

and the sets $\vec{m} = n+1, \dots, n+m$. We now proceed to prove that the expansion Eq. (8) converges in the thermodynamic limit $N, V \rightarrow \infty, N/V = \rho$.

First, we set all coupling parameters of particles \vec{m} in the product

$$\prod_{j \subset \vec{m}} v(j|\vec{n}-1) v_m G_{n-1+m}$$

equal to zero. We also note that the convergence (or divergence) of the series will not be affected if the coupling parameters of particles of the sets \vec{m} are all set equal: $\lambda_j = \lambda$ (hence $z_j = z$). With these provisos, using (6), and taking the limit $N, V \rightarrow \infty$ in Eq. (8), we obtain from the latter

$$S_0(\vec{n}; \vec{\lambda}_n) = G_{n-1}(\vec{n}-1; \vec{\lambda}_{n-1}) \exp(\lambda_1 \lambda z f_0), \quad f_0 = \int f_{ij} d(j). \quad (10)$$

The summation leading to $S_0(\vec{n}; \vec{\lambda}_n)$ can be performed if f_0 is finite. This condition is fulfilled for all physically reasonable models.⁷ By setting all λ_j 's, except the first m_0 ($\lambda_{n+1}, \dots, \lambda_{n+m_0}$), in the product equal to zero, we obtain in an entirely analogous manner the following sequence of finite sums:

$$S_{m_0}(\vec{n}; \vec{\lambda}_n) = G_{n-1}(\vec{n}-1; \vec{\lambda}_{n-1}) + \sum_{m=1}^{m_0} \frac{\lambda_1^m}{m!} \int K(\vec{m}|\vec{n}; \vec{\lambda}_{n-1+m}) G_{n-1+m}(\vec{n}-1+\vec{m}; \vec{\lambda}_{n-1+m}) d(\vec{m}) + R_{m_0} \quad (11)$$

with

$$R_{m_0} = \int K(\vec{m}_0|\vec{n}; \vec{\lambda}_{n-1+m_0}) G_{n-1+m_0}(\vec{n}-1+\vec{m}_0; \vec{\lambda}_{n-1+m_0}) d(\vec{m}_0) P_{m_0},$$

$$P_{m_0} = \exp(\lambda_1 \lambda z f_0) - \sum_{k=0}^{m_0} \frac{(\lambda_1 \lambda z f_0)^k}{k!}. \quad (12)$$

Since $R_{m_0} \rightarrow 0$ as $m_0 \rightarrow \infty$ (because then $P_{m_0} \rightarrow 0$, and the integral is finite), the sequence converges in this limit. Comparing Eq. (11) for $m_0 = \infty$ with Eq. (8) for $N, V \rightarrow \infty$, we see that in the thermodynamic limit,

$$G_n(\vec{n}; \vec{\lambda}_n) = \lim_{m_0 \rightarrow \infty} S_{m_0}(\vec{n}; \vec{\lambda}_n). \quad (13)$$

This completes the proof. In an analogous manner it is shown that the complete Taylor expansion of $G_n(\vec{n}; \vec{\lambda}_n)$ in powers of all coupling parameters of the set $\vec{\lambda}_n$ converges. The expansion of $\zeta_1(\lambda_1)$ in λ_1 is given by Eq. (8) with $n=1$ and thus is also convergent. When all coupling parameters in Eq. (8) are unity and Eq. (5) is used, one obtains the Kirkwood-Salzburg expansion⁸ of $g_n(\vec{n})$. The usual argument for convergence of the latter depends on the assumption that particles have practically finite hard-core diameters, so that the product

$$v_m(\vec{m}) \prod_{j \subset \vec{m}} f_{1j}$$

becomes vanishingly small for sufficiently large m . The proof given here can be applied also to the expansion of $\zeta(\lambda_1) g_n(\vec{n}; \vec{\lambda}_n)$ in λ_1 ; thus we see that the hard-core condition is unnecessarily restrictive. It is sufficient that f_0 , Eq. (10), be finite.

In the case of the usual coupling parameters, with

$$U_N(\vec{N}; \vec{\xi}_N) = \sum_{i,j \subset \vec{N}} \xi_i \xi_j U_{ij},$$

it can be shown that $G_n(\vec{n}; \vec{\xi}_n)$ can be written in a form similar to Eq. (8) with $\lambda_i \lambda_j f_{1j}$ replaced by $f_{1j}(\xi_1, \xi_j) = \exp(-\xi_1 \xi_j U_{ij}/kT) - 1$ and with the corresponding adjustment for the Boltzmann factors. The convergence of these expansions is proved by the same arguments as for Eq. (8). Such expansions, however, are not Taylor expansions of $G_n(\vec{n}; \vec{\xi}_n)$ in ξ_1 but, rather, resummations of these expansions into convergent forms.

The present proof cannot be applied to the customary distribution functions $g_n(\vec{n}; \vec{\lambda}_n)$. The most that can be said about convergence of an expansion of $g_n(\vec{n}; \vec{\lambda}_n)$ in powers of λ_i , $i \subset \vec{n}$, is that g_n can be expressed as a ratio of two converging series.

The functions $G_n(\vec{n})$ yield the usual thermodynamic functions (with activity instead of density as independent variable) through the same theorems as for $g_n(\vec{n})$.

¹See, e.g., J. G. Kirkwood and J. C. Poirier, *J. Phys. Chem.* **58**, 591 (1964), and references cited therein.

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³Strictly speaking, z_j in Eq. (3) equals thermodynamic activity only after taking the thermodynamic limit on the left-hand side.

⁴The dependence of $\alpha(\lambda_i)$ on any finite number of coupling parameters from among the $N-1$ remaining ones is thermodynamically negligible. The same situation obtains for distribution functions: $g_n(\vec{n}; \vec{\lambda}_n)$ depends strongly only on the \vec{n} coupling parameters of the set \vec{n} [see J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935)].

⁵Kirkwood, Ref. 4.

⁶In order to obtain Eq. (7), the coupling parameters of the set $\vec{N}-\vec{n}$ were all set equal to λ_j , and terms $O(n/V)$ ($\rightarrow 0$ in thermodynamic limit) neglected. Retaining a different value for each coupling parameter merely results in a very cumbersome notation but does not affect our proofs.

⁷In the case of Coulombic potentials with short-range repulsion, $f_0 = \infty$, but the expansion can be resummed so that the Debye potential replaces the Coulombic potential. The corresponding integrals are then finite.

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DIRECT OBSERVATION OF ELECTRON-PAIRING EFFECT IN TYPE-II SUPERCONDUCTORS BY POSITRON ANNIHILATION

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We have performed angular-distribution measurements of the two gammas produced by annihilation of positrons in a type-II superconductor (Nb₃Sn) to detect the superconducting smearing effect on the electrons momentum distribution function. Our results give, for the first time, a direct experimental evidence of the redistribution of K -space states at the superconducting transition.

In a normal metal the electron distribution function is the Fermi-Dirac one, but, for the superconducting state, the BCS theory predicts a redistribution in K space, because of the electron pairing.^{1,2} Although there are, at present, many experimental proofs of this theory, it has been impossible, until now, to obtain a direct observation of the modified distribution in K space. The positron annihilation technique allows the measurement of the electron momentum^{3,4}; we have used it on a sample of Nb₃Sn to show the super-

conducting smearing effect on the electrons' momentum distribution function.

At absolute zero, the smearing range δK of the momentum distribution function in a superconductor is given by¹

$$\delta K = \Delta / \hbar V_F \simeq 1 / \xi, \quad (1)$$

where Δ is the superconducting energy gap, V_F is the Fermi velocity, and ξ is the coherence length. In a type-I superconductor ξ is typically