Temperature Dependence of Distribution Functions in Quantum Statistical Mechanics*

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The Bloch equation is utilized to derive an integro-differential equation for the temperature dependence of the Wigner distribution function of a canonical ensemble. This equation is solved by two methods; one yields a power series in Planck's constant and the other a power series in the potential energy of the system. Transformation functions for the density matrix and the Wigner function are discussed and their possible application in the treatment of systems obeying Fermi-Dirac or Bose-Einstein statistics is investigated.

I.

THE thermodynamic properties of a system at equilibrium can be derived from the partition function or the related distribution function. The evaluation of these quantities for quantum-statistical systems has been approached by various methods, all with the common purpose of avoiding the direct computation of the energy levels of the system obtained as solutions of the appropriate Schrödinger equation. These methods can be grouped generally into three categories: (1) direct evaluation of the partition function by successive approximation[1,2]; (2) series solution of the Bloch equation for the density matrix[3–11]; and (3) series solution of the quantum-mechanical analog of Liouville's equation (the Wigner equation) for the Wigner function.[7,12]

The present article is a study of the Bloch equation for the Wigner function, which is a quantum statistical phase space distribution function. We first derive the equation obeyed by the Wigner function for a canonical ensemble at an arbitrary temperature and then solve this equation for systems obeying Maxwell-Boltzmann statistics. Two solutions are presented, one of which is an expansion in a power series in Planck's constant, and the other of which is a power series expansion in the potential energy. Both series diverge at low temperatures, and it has not been possible so far to obtain a useful low-temperature expansion. From these solutions for the phase space distribution function, the configuration space and momentum space distribution functions are easily obtained and are compared with previous results, wherever possible.

We next consider systems obeying quantum statistics (Bose-Einstein or Fermi-Dirac) and approach this problem with the aid of transformation functions for the density matrix and the Wigner function. The transformation functions are defined, some of their properties are discussed, and it is shown that a formal separation of the problem of statistics from the problem of quantum dynamics can be effected.

II.

Consider a system of N-identical particles obeying Boltzmann statistics and the laws of quantum mechanics. For a canonical ensemble the partition function Q is given by the expression

$$Q=\sum_n e^{-\beta E_n}, \tag{1}$$

where the sum is over all eigenstates of the system and $\beta=(kT)^{-1}$. The energies E_n are the eigenvalues of the Schrödinger equation

$$\mathbf{H}\psi_n=E_n\psi_n,\quad \mathbf{H}=-(\hbar^2/2m)\nabla_R^2+U(\mathbf{R}); \tag{2}$$

ψ_n is the normalized wave function in coordinate representation, $U(\mathbf{R})$ is the potential energy, $\mathbf{R}$ is a $3N$-dimensional vector denoting the coordinates of the entire system, and $\mathbf{H}$ is the Hamiltonian operator. The unnormalized density matrix of a canonical ensemble in coordinate representation is defined by the relation

$$\rho^{(N)}(\mathbf{R},\mathbf{R}';\beta)=\sum_n e^{-\beta E_n}\psi_n^*(\mathbf{R}')\psi_n(\mathbf{R}), \tag{3}$$

where ψ_n^* is the complex conjugate of ψ_n.[13] Alternate expressions for the density matrix are

$$\rho^{(N)}=\sum_n \exp[-\beta\mathbf{H}(\mathbf{R}')]\psi_n^*(\mathbf{R}')\psi_n(\mathbf{R}), \tag{4}$$

$$\rho^{(N)}=\sum_n \exp[-\beta\mathbf{H}(\mathbf{R})]\psi_n(\mathbf{R})\psi_n^*(\mathbf{R}'). \tag{5}$$

The Wigner function is a Fourier transform of the

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density matrix and can be written as

$$f^{(N)}(\mathbf{R},\mathbf{p};\beta)=\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left(\frac{2i}{\hbar}\mathbf{p}\cdot\mathbf{Y}\right)\rho^{(N)}(\mathbf{R}+\mathbf{Y},\,\mathbf{R}-\mathbf{Y};\beta)d\mathbf{Y},\quad(6)$$

where $\mathbf{p}$ is a $3N$-dimensional vector which denotes all the momenta of the system and the $3N$-dimensional integration extends over all space. This function possesses many pertinent features of the classical distribution function; in particular, phase-space averages may be formed without recourse to operator techniques as required with the density-matrix formalism. The quantum mechanical operator corresponding to the observable whose average is desired must be related to its classical counterpart by means of the Weyl correspondence. Thus the ensemble average of a quantity, $\alpha(\mathbf{R},\mathbf{p})$, a function of the coordinates and momenta of the particles of the system, is, simply,

$$\langle\alpha\rangle=\frac{\int\alpha(\mathbf{R},\mathbf{p})f^{(N)}(\mathbf{R},\mathbf{p};\beta)d\mathbf{R}d\mathbf{p}}{\int f^{(N)}(\mathbf{R},\mathbf{p};\beta)d\mathbf{R}d\mathbf{p}}.\quad(7)$$

Differentiation of Eq. (4) yields the Bloch equation for the density matrix,

$$\partial\rho^{(N)}/\partial\beta=-\mathbf{H}\rho^{(N)},$$

which has been studied by various authors.[3–11] The equation determining the temperature dependence of the Wigner function, Eq. (6), can be derived in the following way. Differentiation of Eq. (4) and Eq. (5) with respect to β leads to

$$\partial\rho^{(N)}/\partial\beta=-\tfrac{1}{2}[\mathbf{H}(\mathbf{R}')\rho^{(N)}(\mathbf{R},\mathbf{R}';\beta)+\mathbf{H}(\mathbf{R})\rho^{(N)}(\mathbf{R},\mathbf{R}';\beta)],\quad(8)$$

and the Fourier transform of this equation becomes

$$\frac{\partial f^{(N)}}{\partial\beta}=-\frac{1}{2}\Bigg\{\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left(\frac{2i}{\hbar}\mathbf{p}\cdot\mathbf{Y}\right)\times\left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{R}+\mathbf{Y}}{}^2-\frac{\hbar^2}{2m}\nabla_{\mathbf{R}-\mathbf{Y}}{}^2\right)\times\rho^{(N)}(\mathbf{R}+\mathbf{Y},\,\mathbf{R}-\mathbf{Y};\beta)d\mathbf{Y}+\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left(\frac{2i}{\hbar}\mathbf{p}\cdot\mathbf{Y}\right)[U(\mathbf{R}+\mathbf{Y})+U(\mathbf{R}-\mathbf{Y})]\rho^{(N)}(\mathbf{R}+\mathbf{Y},\,\mathbf{R}-\mathbf{Y};\beta)d\mathbf{Y}\Bigg\},\quad(9)$$

where $\mathbf{R}$ has been replaced by $(\mathbf{R}-\mathbf{Y})$ and $\mathbf{R}'$ by $(\mathbf{R}+\mathbf{Y})$. The Laplacian operators can be rewritten in terms of the variables $\mathbf{R}$ and $\mathbf{Y}$; this permits integration of the first two terms on the right-hand side of Eq. (9) and we obtain the desired equation,[14]

$$\frac{\partial f^{(N)}}{\partial\beta}=\left(\frac{\hbar^2}{8m}\nabla_{\mathbf{R}}{}^2-\frac{p^2}{2m}\right)f^{(N)}(\mathbf{R},\mathbf{p};\beta)-\boldsymbol{\Theta}'\cdot f^{(N)}(\mathbf{R},\mathbf{p};\beta),\quad(10)$$

where

$$\boldsymbol{\Theta}'\cdot f^{(N)}=\frac{1}{2}\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left(\frac{2i}{\hbar}\mathbf{p}\cdot\mathbf{Y}\right)\times[U(\mathbf{R}+\mathbf{Y})+U(\mathbf{R}-\mathbf{Y})]\times\rho^{(N)}(\mathbf{R}+\mathbf{Y},\,\mathbf{R}-\mathbf{Y};\beta)d\mathbf{Y}\quad(11)$$

$$=\frac{1}{2}\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left[\frac{2i}{\hbar}(\mathbf{p}-\mathbf{p}')\cdot\mathbf{x}\right]\times[U(\mathbf{R}+\mathbf{x})+U(\mathbf{R}-\mathbf{x})]\times f^{(N)}(\mathbf{R},\mathbf{p}';\beta)d\mathbf{x}d\mathbf{p}'\quad(12)$$

$$=\frac{1}{2}\left(\frac{1}{\hbar\pi}\right)^{3N}\int\cdots\int\exp\left[\frac{2i}{\hbar}(\mathbf{R}-\mathbf{x})\cdot\mathbf{p}'\right]\times[f^{(N)}(\mathbf{R},\,\mathbf{p}+\mathbf{p}';\beta)+f^{(N)}(\mathbf{R},\,\mathbf{p}-\mathbf{p}';\beta)]U(\mathbf{x})d\mathbf{x}d\mathbf{p}'\quad(13)$$

$$=\cos(\tfrac{1}{2}\hbar\nabla_{\mathbf{p}}\cdot\nabla_{\mathbf{R}})U(\mathbf{R})f^{(N)}(\mathbf{R},\mathbf{p};\beta).\quad(14)$$

In Eq. (14), $\nabla_{\mathbf{R}}$ operates on $U(\mathbf{R})$ only. The $\boldsymbol{\Theta}'$ operator has been written in a variety of ways for later reference.[15] Equation (10) may be considered a fundamental equation for equilibrium ensembles. Its classical counterpart is

$$\frac{\partial f_{\mathrm{cl}}{}^{(N)}}{\partial\beta}=-\left[\frac{p^2}{2m}+U(\mathbf{R})\right]f_{\mathrm{cl}}{}^{(N)},\quad(15)$$

which is obtained at once from Eq. (10) in the limit as $\hbar\rightarrow 0$ or directly by differentiation with respect to β of the classical unnormalized canonical distribution function,

$$f_{\mathrm{cl}}{}^{(N)}=\left(\frac{1}{2\pi\hbar}\right)^{3N}\exp(-\beta H_{\mathrm{cl}}),\quad H_{\mathrm{cl}}=\frac{p^2}{2m}+U(\mathbf{R}).\quad(16)$$

Comparison of Eqs. (10) and (15) shows the influence of quantum mechanics on the equation for the distribution function: first, in the appearance of the terms $-(\hbar^2/8m)\nabla_{\mathbf{R}}{}^2f^{(N)}$ and secondly, in the more complex effect of the potential energy.

III.

The solution of Eq. (10) for the quantum mechanical distribution function in a power series in Planck's

[14] Compare with H. S. Green, reference 7.

[15] J. H. Irving and R. W. Zwanzig, J. Chem. Phys. 19, 1173 (1951).

constant, appropriate for almost classical systems, can be derived most easily with the representation of the Θ' operator given by Eq. (14). We postulate the solution for $f^{(N)}$ to be

$$f^{(N)}(\mathbf{R},\mathbf{p};\beta)=f_{\mathrm{cl}}^{(N)}(\mathbf{R},\mathbf{p};\beta)\sum_{n=0}^{\infty}\hbar^n\chi_n(\mathbf{R},\mathbf{p};\beta). \quad (17)$$

It can be readily established that the coefficients of odd powers of $\hbar$ in (17) must be zero if $f^{(N)}$ is to reduce to $f_{\mathrm{cl}}^{(N)}$ at infinite temperature, and we may thus rewrite (17) as

$$f^{(N)}(\mathbf{R},\mathbf{p};\beta)=f_{\mathrm{cl}}^{(N)}(\mathbf{R},\mathbf{p};\beta)\sum_{n=0}^{\infty}\hbar^{2n}\phi_n(\mathbf{R},\mathbf{p};\beta). \quad (18)$$

Substitution of Eq. (18) into Eqs. (10) and (14), and equating of the coefficients of like powers of $\hbar$, yields the desired equation for ϕ_n:

$$f_{\mathrm{cl}}^{(N)}\frac{\partial\phi_n}{\partial\beta}-\frac{1}{8m}\nabla_{\mathrm{R}}^2(\phi_{n-1}f_{\mathrm{cl}}^{(N)}) +\sum_{k=0}^{n-1}(-1)^{n-k}\frac{(\frac{1}{2}\nabla_{\mathrm{R}}\cdot\nabla_{\mathrm{p}})^{2(n-k)}}{[2(n-k)]!}U(\mathbf{R})f_{\mathrm{cl}}^{(N)}\phi_k=0, \quad (19)$$

of which the solution is, for $n>0$,

$$\phi_n=\int_0^{\beta}\Bigg[e^{+\beta' U}\left(\frac{1}{8m}\nabla_{\mathrm{R}}^2[\phi_{n-1}(e^{-\beta' U})]\right) +\exp\left(\frac{\beta' p^2}{2m}\right)\sum_{k=0}^{n-1}\frac{(\frac{1}{2}\nabla_{\mathrm{R}}\cdot\nabla_{\mathrm{p}})^{2(n-k)}}{[2(n-k)]!}(-1)^{n-k+1}U(\mathbf{R}) \times\exp\left(-\frac{\beta' p^2}{2m}\right)\phi_k\Bigg]d\beta'. \quad (20)$$

For $n=0$, we have

$$\partial\phi_0/\partial\beta=0,\quad \phi_0=\text{constant};$$

since $f^{(N)}$ approaches $f_{\mathrm{cl}}^{(N)}$ as β approaches zero, we obtain $\phi_0=1$. The equation for ϕ_1 can be reduced to

$$\frac{\partial\phi_1}{\partial\beta}+\frac{1}{8m}\left\{2\beta(\nabla_{\mathrm{R}}^2U) -\beta^2\left[(\nabla_{\mathrm{R}}U)^2+\nabla_{\mathrm{R}}\nabla_{\mathrm{R}}U(\mathbf{R}):\frac{\mathbf{pp}}{m^2}\right]\right\}=0, \quad (21)$$

where $\mathbf{ab}:\mathbf{cd}\equiv(\mathbf{a}\cdot\mathbf{d})(\mathbf{b}\cdot\mathbf{c})$. The integration of Eq. (21), subject to the initial condition $\phi_1\to 0$ as $\beta\to 0$, is trivial and we obtain

$$\phi_1=-\left\{\frac{\beta^2}{8m}(\nabla_{\mathrm{R}}^2U) -\frac{\beta^3}{24m}\left[(\nabla_{\mathrm{R}}U)^2+\nabla_{\mathrm{R}}\nabla_{\mathrm{R}}U(\mathbf{R}):\frac{\mathbf{pp}}{m^2}\right]\right\}. \quad (22)$$

Higher approximations to $f^{(N)}$ can be easily determined by similarly straightforward evaluations of ϕ_2, ϕ_3, etc.

The distribution function in configuration space $\rho^{(N)}(\mathbf{R},\mathbf{R};\beta)\equiv\rho^{(N)}(\mathbf{R};\beta)$ is obtained from $f^{(N)}$ by integration over the momenta,

$$\rho^{(N)}(\mathbf{R};\beta)=\int\cdots\int f^{(N)}(\mathbf{R},\mathbf{p};\beta)d\mathbf{p}. \quad (23)$$

If we approximate $f^{(N)}$ by $f_{\mathrm{cl}}^{(N)}(1+\hbar^2\phi_1)$, $\rho^{(N)}(\mathbf{R};\beta)$ becomes

$$\rho^{(N)}(\mathbf{R};\beta)=\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}N}\left\{1+\hbar^2\left[\left(-\frac{\beta^2}{12m}\right)\nabla_{\mathrm{R}}^2U +\frac{\beta^3}{24m}(\nabla_{\mathrm{R}}U)^2\right]\right\}e^{-\beta U}. \quad (24)$$

This expression has been derived by earlier investigators by considerably more complicated methods. The distribution function in momentum space $\sigma^{(N)}(\mathbf{p};\beta)$ can likewise be easily determined:

$$\sigma^{(N)}(\mathbf{p};\beta)=\int f^{(N)}(\mathbf{R},\mathbf{p};\beta)d\mathbf{R}. \quad (25)$$

To terms of order $\hbar^2$, $\sigma^{(N)}$ is

$$\sigma^{(N)}(\mathbf{p};\beta)=\left(\frac{1}{2\pi\hbar}\right)^{3N}\exp\left(\frac{-\beta p^2}{2m}\right)\left[\int\exp(-\beta U)d\mathbf{R} +\hbar^2\int\exp(-\beta U)\phi_1 d\mathbf{R}\right], \quad (26)$$

where further evaluation depends upon the specific form of the potential energy function. Thus, the present formalism provides the advantage of yielding one solution of the fundamental equation from which the configuration space and momentum space distribution functions, as well as phase-space averages, can be obtained by relatively simple integrations. If, instead of Eq. (17), we had postulated the form

$$f^{(N)}(\mathbf{R},\mathbf{p};\beta)=\left(\frac{1}{2\pi\hbar}\right)^{3N}\left\{\exp\left[-\beta\left(H_{\mathrm{cl}}+\sum_{n=0}^{\infty}\hbar^{2n}\phi_n\right)\right]\right\}$$

as a solution of the fundamental equation, we would have arrived at the results of Mayer and Band. For the calculation of the first-order quantum corrections to thermodynamic functions it is immaterial which approach is used.

The series solution, Eq. (17), is applicable to quantal systems obeying Boltzmann statistics. Consideration of Fermi-Dirac or Bose-Einstein statistics is of importance in regard to the correct dependence of $f^{(N)}$ on N, the number of particles, and leads in the limit as $\hbar$

approaches zero to the proper entropy expression, i.e., a homogeneous function of the mass.[3,4] However, for practical purposes the neglect of Fermi-Dirac or Bose-Einstein statistics is justified as it appears that the power series solution in $\hbar$ for $f^{(N)}$ is not useful for regions of density and temperature where Boltzmann statistics is inadequate.

IV.

The fundamental equation, Eq. (10), is also amenable to solution by a perturbation procedure. Other authors[1,7–9] have considered this method and our results agree with the previous work. We outline the steps briefly for the sake of completeness. For Maxwell-Boltzmann statistics, the unnormalized distribution function reduces to

$$(1/2\pi\hbar)^{3N}\exp(-\beta p^2/2m)$$

in the absence of all forces. We postulate therefore the following solution,

$$f^{(N)}(\mathbf{R},\mathbf{p};\beta)=\left(\frac{1}{2\pi\hbar}\right)^{3N}\exp\left(\frac{-\beta p^2}{2m}\right)\sum_{n=0}^{\infty}\lambda^n\omega_n(\mathbf{R},\mathbf{p};\beta), \quad (27)$$

of the integro-differential equation

$$\frac{\partial f^{(N)}}{\partial\beta}=\left(\frac{\hbar^2}{8m}\nabla_{\mathrm{R}}^2-\frac{p^2}{2m}\right)f^{(N)}-\lambda\boldsymbol{\Theta}'\cdot f^{(N)}, \quad (28)$$

where λ is the expansion parameter and where we shall use the representation of the $\boldsymbol{\Theta}'$ operator given by Eq. (13). Substitution of Eq. (27) into Eq. (28) and equating the coefficients of like powers of λ yields a set of equations with solutions:

$$\omega_0=1,$$

$$\omega_n=-\int_0^\beta \exp\left[-(\beta-\tau)\frac{\hbar^2}{8m}\nabla_{\mathrm{R}}^2\right]\times\left\{\exp\left[\frac{\tau p^2}{2m}\right]\boldsymbol{\Theta}'\left[\exp\left(\frac{-\tau p^2}{2m}\right)\omega_{n-1}\right]\right\}d\tau. \quad (29)$$

To terms of order λ^2, the distribution function in configuration space can be reduced to

$$\rho^{(N)}(\mathbf{R};\beta)=\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}N}-\int_0^\beta\cdots\int\left(\frac{1}{2\pi\hbar}\right)^{6N}\times\left(\frac{4\pi m}{\beta+\tau}\right)^{\frac{3}{2}N}\left(\frac{4\pi m}{\beta-\tau}\right)^{\frac{3}{2}N}\exp\left[-\frac{m(\mathbf{R}-\mathbf{x})^2}{\hbar^2(\beta+\tau)}\right]\times\exp\left[-\frac{m(\mathbf{R}-\mathbf{x})^2}{\hbar^2(\beta-\tau)}\right]U(\mathbf{x})d\mathbf{x}d\tau, \quad (30)$$

which can be shown to agree with the results of Green,[7] Goldberger and Adams,[8] and Chester.[1] In the same approximation the distribution function in momentum space,

$$\sigma^{(N)}(\mathbf{p};\beta)=\left(\frac{1}{2\pi\hbar}\right)^{3N}\exp\left(\frac{-\beta p^2}{2m}\right)\times\left[V^N-\beta\int U(\mathbf{R})d\mathbf{R}\cdots\right], \quad (31)$$

is identical to the classical distribution function, a result which becomes invalid when higher order terms are included or when Bose-Einstein or Fermi-Dirac statistics are considered.

V.

So far we have confined the discussion to systems obeying Boltzmann statistics. We propose to approach the problem of quantal systems obeying Fermi-Dirac or Bose-Einstein statistics with the aid of transformation functions and turn now to such considerations.

We define a transformation function[16] for the density matrix, $\kappa^{(N)}(\mathbf{R},\mathbf{R}';\beta+\tau|\mathbf{q},\mathbf{q}';\beta)$, by the integral equation

$$\rho^{(N)}(\mathbf{R},\mathbf{R}';\beta+\tau)=\int\cdots\int\kappa^{(N)}(\mathbf{R},\mathbf{R}';\beta+\tau|\mathbf{q},\mathbf{q}';\beta)\times\rho^{(N)}(\mathbf{q},\mathbf{q}';\beta)d\mathbf{q}d\mathbf{q}'. \quad (32)$$

By use of the representation,

$$\rho^{(N)}(\mathbf{R},\mathbf{R}';\beta)=\exp[-\beta\mathbf{H}(\mathbf{R})]\delta(\mathbf{R}-\mathbf{R}')=\exp[-\beta\mathbf{H}(\mathbf{R})]\rho^{(N)}(\mathbf{R},\mathbf{R}';0), \quad (33)$$

for the density matrix, one easily finds

$$\kappa^{(N)}=\delta(\mathbf{R}-\mathbf{q})\delta(\mathbf{R}'-\mathbf{q}')\exp[-\tau\mathbf{H}(\mathbf{q})],$$
$$\kappa^{(N)}=\exp[-\tau\mathbf{H}(\mathbf{R})]\delta(\mathbf{R}-\mathbf{q})\delta(\mathbf{R}'-\mathbf{q}')=\rho^{(N)}(\mathbf{R},\mathbf{q};\tau)\delta(\mathbf{R}'-\mathbf{q}'), \quad (34)$$

as formal representations for the transformation function. In a similar manner, the transformation function for the Wigner function, $K^{(N)}(\mathbf{R},\mathbf{p};\beta+\tau|\mathbf{R}',\mathbf{p}';\beta)$, is defined by the integral equation

$$f^{(N)}(\mathbf{R},\mathbf{p};\ \beta+\tau)=\int\cdots\int K^{(N)}(\mathbf{R},\mathbf{p};\ \beta+\tau|\mathbf{R}',\mathbf{p}';\ \beta)\times f^{(N)}(\mathbf{R}',\mathbf{p}';\beta)d\mathbf{R}'d\mathbf{p}'. \quad (35)$$

The transformation function $K^{(N)}$ represents a description of the formal transition of the system at one

[16] The transformation functions defined here differ from the Green's functions discussed by Husimi,[6] Goldberger and Adams,[8] and Siegert.[9] The present functions are analogous to the time-dependent transformation functions, developed by J. E. Moyal, Proc. Cambridge Phil. Soc. 45, 99 (1949) and by J. Ross and J. G. Kirkwood, J. Chem. Phys. 22, 1094 (1954).

temperature and position in phase space to another temperature and position in phase space.

It can be seen readily from the definitions of the transformation functions that $\kappa^{(N)}$ obeys Bloch's equation,

$$\partial\kappa^{(N)}/\partial\tau = -\mathbf{H}(\mathbf{R})\kappa^{(N)} \tag{36}$$

or

$$\partial\kappa^{(N)}/\partial\tau = -\kappa^{(N)}\mathbf{H}(\mathbf{q}),$$

with the initial condition

$$\kappa^{(N)}(\mathbf{R},\mathbf{R}';\beta|\mathbf{q},\mathbf{q}';\beta)=\delta(\mathbf{R}-\mathbf{q})\delta(\mathbf{R}'-\mathbf{q}'). \tag{37}$$

Similarly, the function $K^{(N)}$ obeys the fundamental equation, Eq. (10),

$$\frac{\partial K^{(N)}}{\partial\tau}=\left(\frac{\hbar^2}{8m}\nabla_{\mathrm{R}}^2-\frac{p^2}{2m}\right)K^{(N)}-\Theta'\cdot K^{(N)}, \tag{38}$$

with initial condition

$$K^{(N)}(\mathbf{R},\mathbf{p};\beta|\mathbf{R}',\mathbf{p}';\beta)=\delta(\mathbf{R}-\mathbf{R}')\delta(\mathbf{p}-\mathbf{p}'). \tag{39}$$

Thus, the transformation functions can be determined by solving the appropriate equation, Eq. (36) or Eq. (38). For example, power series solutions of Eq. (38) can be effected in a manner analogous to that presented above for the determination of the distribution function $f^{(N)}$; the details are omitted.

The formal separation of the problem of statistics (proper symmetrization) from the quantal problem of solving the Bloch equation or the corresponding equation for the Wigner function can now be accomplished. Suppose that in Eq. (32) for the density matrix or Eq. (35) for the Wigner function we choose an initial state and construct a properly symmetrized function for that state. The transition to any other state with the preservation of the proper symmetry is effected by the appropriate transformation function which, in this scheme, is *independent* of statistics as it is determined uniquely by Eq. (36) or Eq. (38) and the corresponding initial conditions. Let us follow this procedure for the density matrix and select the initial state at $\beta=0$. The density matrix with a subscript s to indicate a symmetrized function,

$$\begin{aligned}\rho_s^{(N)}(\mathbf{R},\mathbf{R}';\beta)&=\textstyle\sum_n \exp[-\beta\mathbf{H}(\mathbf{R})]\psi_n^*(\mathbf{R}')\psi_n(\mathbf{R})\\&=\exp[-\beta\mathbf{H}(\mathbf{R})]\rho_s^{(N)}(\mathbf{R},\mathbf{R}';0),\end{aligned} \tag{40}$$

can be evaluated by means of any complete set of symmetrized wave functions. The use of plane wave functions,

$$\psi_p(\mathbf{R})=\frac{1}{N!}\left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}N}\sum_P(\pm1)^{|P|}\exp\left(\frac{i}{\hbar}\mathbf{p}\cdot P\mathbf{R}\right), \tag{41}$$

leads very simply to the completeness relation:

$$\rho_s^{(N)}(\mathbf{R},\mathbf{R}';0)=\frac{1}{N!}\sum_P(\pm1)^{|P|}\delta(P\mathbf{R}-\mathbf{R}'). \tag{42}$$

In Eq. (41) the operator P permutes the components of $\mathbf{R}$ and the sum extends over all $N!$ permutations. Use of Eqs. (32), (34), and (42) leads now at once to the proof of the result

$$\begin{aligned}&\int\kappa^{(N)}(\mathbf{R},\mathbf{R}';\beta|\mathbf{q},\mathbf{q}';0)\rho_s^{(N)}(\mathbf{q},\mathbf{q}';0)d\mathbf{q}d\mathbf{q}'\\&\quad=\int\delta(\mathbf{R}-\mathbf{q})\delta(\mathbf{R}'-\mathbf{q}')\exp[-\beta\mathbf{H}(\mathbf{q})]\frac{1}{N!}\\&\qquad\times\sum_P(\pm1)^{|P|}\delta(P\mathbf{R}-\mathbf{R}')d\mathbf{q}d\mathbf{q}'\\&\quad=\exp[-\beta\mathbf{H}(\mathbf{R})]\frac{1}{N!}\sum_P(\pm1)^{|P|}\delta(P\mathbf{R}-\mathbf{R}')\\&\quad=\rho_s^{(N)}(\mathbf{R},\mathbf{R}';\beta),\end{aligned} \tag{43}$$

or, symbolically,

$$\rho_s^{(N)}(\beta)=\kappa^{(N)}(\beta|0)\cdot\rho_s^{(N)}(0). \tag{44}$$

A similar equation can be written for the Wigner function.

An alternative approach consists of considering an initial state described by Boltzmann statistics and constructing a transformation function which effects the transition from this initial state to a final state of the proper symmetry and at a different temperature. Equation (36) or (38) still suffice for the determination of the transformation functions, but must now be supplemented by the appropriate initial conditions. Thus, symbolically, we write

$$\rho_s^{(N)}(\beta)=\kappa_s^{(N)}(\beta|0)\cdot\rho^{(N)}(0), \tag{45}$$

where

$$\kappa_s^{(N)}(0|0)=\frac{1}{N!}\sum_P(\pm1)^{|P|}\delta(P\mathbf{R}-\mathbf{q})\delta(\mathbf{R}'-\mathbf{q}'), \tag{46}$$

and

$$\begin{aligned}\kappa_s^{(N)}(\beta|0)&=\exp[-\beta\mathbf{H}(\mathbf{R})]\frac{1}{N!}\sum_P(\pm1)^{|P|}\delta(P\mathbf{R}-\mathbf{q})\\&\quad\times\delta(\mathbf{R}'-\mathbf{q}')=\rho_s^{(N)}(\mathbf{R},\mathbf{q};\beta)\delta(\mathbf{R}'-\mathbf{q}'),\end{aligned}$$

and we observe that the permutation of one variable, $\mathbf{R}$ or $\mathbf{R}'$ is sufficient. It is interesting to note that the relation

$$\rho_s^{(N)}(\beta)=\kappa_s^{(N)}(\beta|0)\rho_s^{(N)}(0) \tag{47}$$

also holds. Equations similar to Eqs. (46) and (47) can again be written for the Wigner function.

Application of this formalism to problems in statistical mechanics and quantum mechanics of molecules is under consideration.