and biphenyl to 1700A,[8] it is assumed that the intro-
duction of a methylene bridge (fluorene is 2,2'-methyl-
ene-biphenyl) results in an approximately planar struc-
ture in which the phenyl groups are not symmetrical
about an axis through the 4,4'-positions. This is in
agreement with dipole moment measurements which
favor this configuration.[9] The band positions change
due to alkyl substitution (bathochromic shift) and the
intensities of the ^1B_b bands decrease as is indicated by
the decrease in f-values. It is to be noted that essen-
tially the same occurs in the comparison of the spectra
and the f-values of anthracene and phenanthrene.

Similar regularities (bathochromic shifts and de-
crease in f-values) are also observed in the spectra of
2-phenylnaphthalene and its methylene derivative,
1,2-benzfluorene, and in 2-phenylazulene and its
methylene derivative, indeno-azulene, as can be seen
from the data in Fig. 3 and Table II, although in these

compounds the decreases are smaller due probably to
less bending of the molecule. There is seen in these
compounds only the normal bathochromic effect due
to alkyl substitution and not the marked changes in
intensity normally associated with twisting of double
bonds and twisting of rings from planar positions. The
^1C_b band, transversely polarized to the long axis of the
molecule, increases in intensity upon loss of C_{2v} sym-
metry about this long axis as is seen in a comparison
of the f-values of 0.28 for anthracene and 0.60 for
phenanthrene. A similar increase is observed for the
same transition in 2-phenylazulene and indeno-azulene
with f-values of 0.41 and 0.55, respectively, although
this increase is also smaller than that observed in the
case of the more highly bent polyacene, phenanthrene.
The approximated f-values of this singlet ^1C_b(?) band
in biphenyl and fluorene, and 2-phenylnaphthalene and
1,2-benzfluorene are to be expected to show a similar
small increase in going from the linear to the slightly
bent methylene derivative.

[8] J. R. Platt and H. B. Klevens (unpublished results).
[9] Hughes, LeFevre, and LeFevre, J. Chem. Soc., 202 (1937).

On the Notion of Pressure in a Canonical Ensemble

R. J. RIDDELL, JR. AND G. E. UHLENBECK
University of Michigan, Ann Arbor, Michigan
(Received April 6, 1950)

Recently a controversy has arisen between J. De Boer and H. S. Green concerning the notion of pressure
in a canonical ensemble. According to Green, only classically is the pressure as derived from the partition
function equal to that obtained from the virial theorem, while at low temperatures, at which quantum
effects become important, there will be considerable deviations between the two. De Boer attempts to
prove that the two pressures are actually identical. We have come to the same conclusion, and shall show
this in several ways; first, by considering a simple example (Section 2), and then in general using the energy
representation (Section 3). We believe that the discrepancy between the two pressures which Green has
found is in fact due to improper handling of the effect of the wall of the vessel in which the particles are
contained. Finally, we are of the opinion that Green's criticism of De Boer's calculation is not justified,
and in the last section arguments are given to show that the traces of all commutators of interest in quantum
statistical mechanics are zero.

1. INTRODUCTION

RECENTLY a controversy has arisen between J.
De Boer and H. S. Green[1] concerning the notion
of pressure in a canonical ensemble. According to
Green, the pressure as derived from the partition
function Z:

$$p = 1/\beta Z \cdot \partial Z/\partial V, \qquad (1)$$

where $\beta = (kT)^{-1}$, is not necessarily equal to the pressure
as derived from the virial theorem:

$$pV = \tfrac{2}{3}\langle K_n\rangle_{Av} + \tfrac{1}{3}\langle \Phi_n\rangle_{Av} \qquad (2)$$

where K is the kinetic energy, Φ is the virial of the

[1] J. De Boer, Physica XV, 843 (1949); Nuovo Cimento Supple-
ment to the Statistical Mechanics Conference at Florence (May,
1949), p. 199 and discussion. H. S. Green, Physica XV, 882 (1949).
Compare also J. Yvon, Comptes Rendus 227, 763 (1949).

intermolecular forces, and where the $\langle \cdots \rangle_{Av}$ means an
average over the canonical ensemble.* Green asserts
that the first pressure (which he calls the thermody-
namical pressure) is the one exerted by the system in
the equilibrium state, while the second (kinetic pres-
sure) is the one occurring in the hydrodynamical
equations.[2] Only in classical statistical mechanics would
these two pressures be identical. However, according
to Green, as soon as quantum effects become important
(as would be the case at very low temperatures) an

* Compare, for instance, Tolman, *Principles of Statistical
Mechanics*, Chapter IX. If F is any kind of operator then in the
energy representation:

$$\langle F_n\rangle_{Av} = \frac{1}{Z}\Sigma F_n \exp(-\beta E_n),$$

where F_n is the average of F in a state of energy E_n.

[2] H. S. Green, Proc. Roy. Soc. A194, 244 (1949).

appreciable difference between the two pressures will occur.

On the other hand, De Boer has attempted to show that the two pressures as given by (1) and (2) are *always* identical. Since the argument does not seem to have been completely settled, and since Green's result is so different from the usual conception, a further analysis seems justified. In the following we will confirm De Boer's result using a slight modification of his method of proof. Green's criticism of De Boer's proof cannot, in our opinion, be justified. The origin of the discrepancy between Green's kinetic and thermodynamic pressures lies, in our opinion, in the treatment of the boundary conditions due to the potential of the wall of the vessel in which the system is enclosed. Green (and also De Boer) represents the vessel by a sudden infinite potential jump, and it is well known that with such potentials the formulas of the transformation theory have to be used with caution.

2. A SIMPLE EXAMPLE

In order to illustrate in an explicitly soluble case that with a non-singular wall potential the two pressures (1) and (2) are identical, consider the following simple example: two equal one-dimensional particles bound together by a harmonic potential, moving in a "vessel" represented by another, but very weak, harmonic potential. The Hamiltonian for the system is:

$$\mathcal{3C} = (p_1{}^2 + p_2{}^2)/2m + \tfrac{1}{2}m\omega^2(q_1{}^2 + q_2{}^2) + \tfrac{1}{2}m\alpha^2(q_1 - q_2)^2$$

or, introducing the center of gravity and relative coordinates Q, q:

$$\mathcal{3C} = P^2/4m + p^2/m + m\omega^2 Q^2 + \tfrac{1}{4}m\omega_1{}^2 q^2$$

where:

$$\omega_1{}^2 = \omega^2 + 2\alpha^2.$$

Clearly the energy values are:

$$E_{N,\,n} = (N + \tfrac{1}{2})\hbar\omega + (n + \tfrac{1}{2})\hbar\omega_1.$$

To find the "pressure" from the partition function $Z = \sum_{N,\,n} \exp(-\beta E_{N,\,n})$ one has to identify the "volume" of the vessel with $1/\omega$. To prove, therefore, the equality of the thermodynamic and kinetic pressures, one has to show that:

$$-\omega^2/\beta Z \cdot \partial Z/\partial\omega = \omega\langle 2K_n + \Phi_n\rangle_{\text{Av}}. \quad (3)$$

The factor $\tfrac{1}{3}$ in (2) must be omitted since the problem is one dimensional.

Because of the harmonicity of the forces one has immediately:

$$2K_{N,\,n} = E_{N,\,n};$$

$$\Phi_{N,\,n} = -\sum_i \left(q_i \frac{\partial V_{\text{int}}}{\partial q_i}\right)_{N,\,n} = -m\alpha^2\langle q^2\rangle_{N,\,n}$$

$$= -(n + \tfrac{1}{2})2\hbar\alpha^2/\omega_1.$$

On the other hand:

$$-\frac{\omega^2}{\beta Z} \cdot \frac{\partial Z}{\partial\omega}$$

$$= \frac{\omega^2}{Z}\sum_{N,\,n} \frac{\partial E_{N,\,n}}{\partial\omega} \exp(-\beta E_{N,\,n})$$

$$= \omega/Z \sum_{N,\,n} \{E_{N,\,n} - (n + \tfrac{1}{2})2\hbar\alpha^2/\omega_1\} \exp(-\beta E_{N,\,n})$$

so that (3) is evident.

3. THE GENERAL PROOF

To perform the differentiation of Z with respect to the volume in general, Green and also De Boer use the trick of measuring all coordinates with a unit L, which is characteristic of the vessel. In this way they were able to shift the differentiation with respect to the boundary to a differentiation of the operator $\exp(-\beta\mathcal{3C})$. To show how this works, we will use as in Section 2 the energy representation of all operators. If $V = L^3$, then from (1):

$$p = -\frac{1}{3VZ}\sum_n L\frac{\partial E_n}{\partial L}\exp(-\beta E_n). \quad (4)$$

In order to determine $\partial E_n/\partial L$ we must go to the Schroedinger equation for the whole system:

$$\mathcal{3C}\Psi_n \equiv [K + V_{\text{int}} + W(q_i/L)]\Psi_n = E_n\Psi_n, \quad (5)$$

where V_{int} is the potential of the intermolecular forces and where we have explicitly introduced the potential W due to the wall. It is best to consider W as a smooth, though nearly step-like, function near the boundary, becoming infinite for $q_i \rightarrow \pm\infty$. There is then no need to impose a boundary condition on Ψ_n (except for the usual one that $\Psi_n \rightarrow 0$ as $q_i \rightarrow \pm\infty$), and all the coordinates q_i can be taken from $-\infty$ to $+\infty$. Since W depends on L, Ψ_n and E_n are also functions of L. Now let us replace q_i by $L\bar{q}_i$, and then differentiate (5) with respect to L, considering the $\bar{q}_i$ as constant. Thus:

$$\frac{\partial\mathcal{3C}}{\partial L}\Psi_n + \mathcal{3C}\frac{\partial\Psi_n}{\partial L} = \frac{\partial E_n}{\partial L}\Psi_n + E_n\frac{\partial\Psi_n}{\partial L}.$$

Multiplying on the left by $\Psi_n{}^*$ and integrating over all coordinates, one obtains:

$$\frac{\partial E_n}{\partial L} = \int \Psi_n{}^* \frac{\partial\mathcal{3C}}{\partial L}\Psi_n d\tau, \quad (6)$$

since the terms in $(\partial\Psi_n/\partial L)$ cancel using the Hermitian property of $\mathcal{3C}$. Since, in terms of the $\bar{q}_i$:

$$\mathcal{3C} = -\frac{\hbar^2}{2mL^2}\sum_i \frac{\partial^2}{\partial\bar{q}_i{}^2}$$

$$+ V_{\text{int}}(L\bar{q}_1, \cdots, L\bar{q}_N) + W(\bar{q}_1, \cdots, \bar{q}_N) \quad (7)$$

in $(\partial\mathcal{3C}/\partial L)$ the wall potential drops out and one verifies easily:

$$L(\partial\mathcal{3C}/\partial L) = -2K - \Phi,\qquad(8)$$

where

$$\Phi = -\sum_i q_i \frac{\partial V_{\text{int}}}{\partial q_i}$$

is the virial of the intermolecular forces. From (6), therefore,

$$L(\partial E_n/\partial L) = -2K_n - \Phi_n$$

and substituting in (4) gives the virial theorem (2).

4. DISCUSSION OF GREEN'S CALCULATION

Green uses the coordinate representation of all operators, instead of the energy representation used in the previous section. The partition function is now written as:

$$Z = \int dq \langle q | \exp(-\beta\mathcal{3C}) | q \rangle,\qquad(9)$$

where q stands for the coordinates $q_1, \cdots, q_N$ of all the particles and where, if the wall potential is included in $\mathcal{3C}$, the integrals may be taken from $-\infty$ to $+\infty$. Introducing the reduced coordinates $\bar{q}_i = q_i L^{-1}$, one finds:

$$V\frac{\partial Z}{\partial V} = \frac{L}{3}\frac{\partial Z}{\partial L} = NZ$$

$$+\frac{L^{3N}}{3}\int d\bar{q} L\frac{\partial}{\partial L}\langle L\bar{q} | \exp(-\beta\mathcal{3C}) | L\bar{q} \rangle.\quad(10)$$

To carry out the differentiation, one expands the matrix $\exp(-\beta\mathcal{3C})$ in its power series in $\mathcal{3C}$, and then differentiates term by term. Following Green, one obtains for the first term, going back to the original variables q_i after the differentiation is completed:

$$L\frac{\partial}{\partial L}\langle L\bar{q} | \mathcal{3C} | L\bar{q}' \rangle$$

$$= \left(q\cdot\frac{\partial}{\partial q} + q'\cdot\frac{\partial}{\partial q'}\right)\langle q | \mathcal{3C} | q' \rangle + \langle q | \Phi_{\text{wall}} | q' \rangle,$$

where

$$\Phi_{\text{wall}} = -\sum_i q_i \frac{\partial W}{\partial q_i}$$

is the virial of the wall potential. Analogously, one can proceed in the differentiation of the matrix elements of the higher powers of $\mathcal{3C}$, and one can show by induction:

$$L\frac{\partial}{\partial L}\langle L\bar{q} | \exp(-\beta\mathcal{3C}) | L\bar{q}' \rangle$$

$$= \left(q\cdot\frac{\partial}{\partial q} + q'\cdot\frac{\partial}{\partial q'}\right)\langle q | \exp(-\beta\mathcal{3C}) | q' \rangle$$

$$-\sum_{m=0}^{\infty}\frac{\beta^{m+1}}{(m+1)!}\langle q | \mu_m \exp(-\beta\mathcal{3C}) | q' \rangle,\quad(11)$$

where $\mu_0 \equiv \Phi_W$, and $\mu_m = [\mu_{m-1}, \mathcal{3C}]$, and the square brackets indicate as usual the commutator. Introducing (11) in (10) and using (1), one easily verifies:

$$p = \frac{i}{3\beta\hbar VZ}\int dq \langle q | [p\cdot q, \exp(-\beta\mathcal{3C})] | q \rangle$$

$$-\frac{1}{3VZ}\sum_{m=0}^{\infty}\frac{\beta^m}{(m+1)!}\int dq \langle q | \mu_m \exp(-\beta\mathcal{3C}) | q \rangle.\quad(12)$$

The first term in (12) is identical with Green's expression for the pressure. The reason that he does not obtain the second term in (12) is clearly due to the fact that he does not include the wall potential in the Hamiltonian, but instead restricts his coordinates q_i to the finite range $0 \leqslant q_i \leqslant L$. Omitting the wall potential, the matrix element of $\exp(-\beta\mathcal{3C})$ in the coordinate representation is apparently a function of q, q' alone. Therefore with the reduced coordinates the differentiation operation $L(\partial/\partial L)$ is apparently equivalent to the differentiation operation $q\cdot(\partial/\partial q) + q'\cdot(\partial/\partial q')$ on the original matrix element. The second term in (11) would not be there and one would obtain Green's result for the pressure. We do *not* believe that this is correct, because the matrix element of $\exp(-\beta\mathcal{3C})$ besides being a function of q, q' is also implicitly a function of L because of the boundary condition imposed on the wave functions. One can see this, for instance, by going back to the energy representation. One has:

$$\langle q | \exp(-\beta\mathcal{3C}) | q' \rangle = \sum_n \exp(-\beta E_n)\Psi_n^*(q)\Psi_n(q').$$

Following Green, one would neglect, for instance, the dependence of E_n on L. This, however, just gives, as shown in the previous section, De Boer's result. The other terms (including those of Green) obtained from the $L(\partial/\partial L)$ differentiation must, therefore, be zero. This is in fact, we think, the case. Contrary to Green, and in accordance with De Boer, we are of the opinion that the traces of the commutators which occur in the usual applications of quantum statistics and in particular in (12) are all zero,† so that (12) reduces to the trivial result:

$$pV = -\frac{1}{3}\langle(\Phi_{\text{wall}})_n\rangle_{\text{Av}}.\qquad(13)$$

In order to obtain (2) from (9) one must carry out the L-differentiation more directly, essentially as De Boer does. Since

$$\langle q | \exp(-\beta\mathcal{3C}) | q' \rangle = \exp(-\beta\mathcal{3C}_{\text{op}})\delta(q - q')$$

and

$$\delta(L\bar{q} - L\bar{q}') = 1/L\delta(\bar{q} - \bar{q}'),$$

one can write for the partition function

$$Z = \int\int d\bar{q} d\bar{q}' \delta(\bar{q} - \bar{q}')\exp(-\beta\mathcal{3C}_{\text{op}})\delta(\bar{q} - \bar{q}').$$

---

† For some further comments on this point see Section 5. This is the main point of the criticism which Green made against De Boer's method of proof.

Now L appears only in $\mathfrak{K}_{\mathrm{op}}$ (compare Eq. (7)), and one proves that

$$L\frac{\partial}{\partial L}\exp(-\beta\mathfrak{K}_{\mathrm{op}})=-\sum_{m=0}^{\infty}\frac{\mu_m\beta^{m+1}}{(m+1)!}\exp(-\beta\mathfrak{K}_{\mathrm{op}}), \quad (14)$$

where again $\mu_m=[\mu_{m-1},\mathfrak{K}]$, but where now

$$\mu_0\equiv L\frac{\partial\mathfrak{K}_{\mathrm{op}}}{\partial L}=-2K-\Phi,$$

according to (8).†† Omitting the traces of all commutators, this leads immediately to (2).¶

5. ON THE TRACES OF COMMUTATORS IN QUANTUM STATISTICS

Green remarks that the trace of the commutator of two matrices A and B is not necessarily zero, since it depends on the convergence of the double integral (or double sum):

$$\int\int dq'dq''\langle q'|A|q''\rangle\langle q''|B|q'\rangle, \quad (15)$$

and this may not be the case if A and B are singular, as, for instance, p and q. However, in quantum statistics one of the matrices occurring is always the density matrix:

$$\rho(q,q')=\langle q|\exp(-\beta\mathfrak{K})|q'\rangle$$
$$=\sum_n\exp(-\beta E_n)\Psi_n^*(q)\Psi_n(q').$$

For the usual types of Hamiltonians $\rho(q,q')$ is an analytic function of q and q', vanishing exponentially for large values of q and q'. This follows from the fact

---

†† Equation (14) is equivalent to (I) in De Boer's paper after a slight error is corrected.

¶ (13) would result if one carries the L-differentiation out without introducing the reduced coordinates $\bar{q}_i$. One can then use (14) again, but now

$$\mu_0\equiv L(\partial W/\partial L)=+\Phi_{\mathrm{wall}}.$$

that $\rho(q,q')$ is the fundamental solution of the parabolic differential equation:‖

$$\frac{\partial\varphi(q,\beta)}{\partial\beta}=-\mathfrak{K}_{\mathrm{op}}\varphi=\frac{\hbar^2}{2m}\Delta\varphi-V\varphi. \quad (16)$$

For instance, for the harmonic oscillator with

$$\mathfrak{K}=\tfrac{1}{2}(p^2+\omega^2q^2):$$

$$\rho(q,q')=\left\{\frac{\omega}{2\pi\hbar\,\sinh(\hbar\omega\beta)}\right\}^{\frac{1}{2}}\exp\left[-\frac{\omega}{2\hbar[1-\exp(-2\hbar\omega\beta)]}\right.$$
$$\left.\cdot\{(q^2+q'^2)(1+\exp(-2\hbar\omega\beta))-4qq'\exp(-\hbar\omega\beta)\}\right].$$

For such functions we believe that the integrals of the type (15) are always convergent, and therefore the order of integration may be interchanged, as is necessary in order to prove that the trace of the commutator is zero. For example:

$$Tr[p,\exp(-\beta\mathfrak{K})]=\frac{\hbar}{i}\int_{-\infty}^{\infty}dq\left(\frac{\partial\rho}{\partial q}+\frac{\partial\rho}{\partial q'}\right)_{q=q'}$$
$$=\frac{\hbar}{i}\int_C\left[\frac{\partial\rho}{\partial q}dq+\frac{\partial\rho}{\partial q'}dq'\right],$$

where C is the path $q=q'$ from $-\infty$ to $+\infty$. The line integral is clearly zero since ρ is zero at infinity. Analogously, one shows that the trace of the commutator of p^2 and of $p\cdot q$ with $\exp(-\beta\mathfrak{K})$ is zero. In general, the theorems:

$$Tr(AB)=Tr(BA)$$
$$Tr(ABC)=Tr(CAB)=Tr(BCA)$$

and so on, will be valid if only one of the matrices A, B, C, $\cdots$ is the density matrix. The other matrices may then be of the singular kind as, for example, the impulse and coordinate matrices are.

‖ This means that $\rho(q,q')$ is the solution of (16), which for $\beta=0$ becomes $\delta(q-q')$. Of course, certain regularity conditions are necessary for $V(q)$.