The operators $\mathcal{R}_{(A)}$ contains $\mathfrak{M}_{(A)}$ linearly
\[\mathfrak{M}_{(A)} = K_{(A)(B)} \mathfrak{M}_{(B)},\]
\[K_{(A)(B)} = -2n \text{ Im} \{\Lambda_{(B)}^{-1} \langle p | \Lambda_{(A)} + N_{(A)} \rangle \} \langle p | \Lambda_{(B)}^{-1} \langle p \rangle \} \}
(5.6)

If one inserts now $\alpha(p)$ into (5.6), one gets an expression of $K_{(A)(B)}$ in terms of variables $d_1, \cdots, d_n$.

Evidently the method of explicit construction of unitary representations developed for the case of the group $ISL(n, C)$ may be applied to all groups which are subgroups of $ISL(n, C)$. The class of such groups are rather large so that the method described above is of a considerable generality. As an example we have treated the group $IU(m, m)$ in Sec. 3B; a special case $m = 2$, i.e., the group $IU(2, 2)$, was investigated in detail earlier. No additional difficulties arise also if one considers the group $IU(m, m')$ with $m + m' = n$.

The problem of the construction of $\alpha(p)$ for the groups $IU(m, m)$ and $ISL(m, C)$ is equivalent to that of solution of the linear covariant equation of the type $Q\psi = \psi$. Therefore, it would be superfluous to discuss these equations separately.

---

Note on Statistical Mechanics of Random Systems*

T. BURKE AND J. L. LEBOWITZ
Belfer Graduate School of Science, Yeshiva University, New York

(Received 23 October 1967)

We discuss some equilibrium properties of random systems, i.e., systems whose Hamiltonian depends on some random variables $y$ with a distribution $P(y)$ which is independent of the dynamic state of the system. For a system of noninteracting particles which interact with randomly distributed scattering centers, the important quantity is the average density of states of a single particle per unit volume, $\langle \rho \rangle$. Feynman's path-integral formulation of quantum statistics is used to derive some properties of the average partition function for one particle $\langle Z_1 \rangle$, which is the Laplace transform of $\langle \rho \rangle$. In particular, it is shown that $\langle Z_1 \rangle$ is an analytic function of the density of scatterers $\rho$ for a wide class of particle-scattering center potentials $V(x)$, including those with hard cores and those with negative parts. The analyticity of $\rho$ of the equilibrium properties of these systems is very remarkable and is in contrast to the conjectured nonanalytic behavior of their transport (i.e., diffusion) coefficients. We find also upper and lower bounds on $\langle Z_1 \rangle$ for a particle acted upon by a random potential $V(r)$ obeying Gaussian statistics with $\langle V(r)V(r') \rangle \sim \exp [-\alpha^2 (r - r')^2]$. In the limit of “white noise,” $\langle V(r)V(r') \rangle \sim \delta(r - r')$, $\langle Z_1 \rangle$ is shown to diverge in two and three dimensions but remains finite in one dimension. This agrees with approximate results on the density of states.

In appendices we prove the existence, in the thermodynamic limit, of the free-energy density of a system with random scatterers and also of the frequency distribution and, thus, the free-energy density for a random harmonic crystal.

1. INTRODUCTION

It is the purpose of this paper to investigate some equilibrium properties of certain random systems. By a random system we mean a system whose Hamiltonian depends on some parameters $x$ which are, in a sense to be specified, random variables with a distribution $P(y)$ which is independent of the dynamical state of the system. The dynamical (canonical) variables of the system are denoted by $x$ so that the Hamiltonian $H(x, y)$ is a function both of $x$ and $y$ with $x$ varying in time according to some dynamical law.

Typical examples of model random systems discussed in the literature are (i) a lattice in which spins are located randomly on sites with a probability $p$ independent of the other sites, (ii) a harmonic crystal in which the masses or spring constants have random values with some specified distribution, and (iii) a set of particles, usually electrons, acted on by an external potential due to the presence of centers of force (scatterers, impurities) at positions $\{R_1, \cdots, R_N\} = \{R\} \equiv y$. In the last case, which will be our primary concern here, the Hamiltonian of a set of $M$ particles with positions $\{r_1, \cdots, r_M\}$ and momenta $\{p_1, \cdots, p_M\}$ in a box of volume $\Omega$ is given by
\[H = \sum_{i=1}^{M} p_i^2 / 2m + U(r_1, \cdots, r_M) + \lambda \sum_{i=1}^{M} \sum_{n=1}^{N} V(r_i - R_n),\]
(1.1)

where $U$ is the interparticle potential which is independent of the location (or presence) of the impurities.

---

* Supported by the Air Force Office of Scientific Research under Grant No. 508-66.
and $\lambda V(r)$ is the potential energy of a particle in the presence of an impurity located at $r = 0$.

In all these cases the physical situation, idealized in these models, corresponds to starting with the system at a high temperature and quenching it. The imperfections will then remain fixed in space and can be described by the parameters $y$, whereas the other degrees of freedom $x$ come to equilibrium with a Hamiltonian which depends on $y$. (The actual physical situation is more complex, but this is a reasonable approximation to it.) For a given system, $y$ has, of course, some specified set of values $\{y_1, \ldots, y_N\}$, and it is therefore necessary to state what we mean by saying that the $R_i$ are distributed at random. To be more specific, how do we compute the properties, such as the internal energy or specific heat, of a macroscopic system for which the values of the $R_i$ are unknown to us? The simplest attitude one can take is to make measurements on an ensemble of systems prepared in the same way. (This is a superensemble of thermal ensembles for each specified $\{y_1, \ldots, y_N\}$.) Hence the average of any function $A(x, y)$ is given by

$$\langle A \rangle = \int dy P(y) \langle A \rangle_y,$$

(1.2)

where

$$\langle A \rangle_y = \frac{\text{Tr}_y [A(x, y) e^{-\beta H(x,y)}]/Z(y)}{Z(y)} = \text{Tr}_x e^{-\beta H(x,y)},$$

(1.3)

(1.4)

is the partition function for the system represented by a canonical ensemble with inverse temperature $\beta$. Here $P(y)$ is the distribution of random variables $y$ which, for case (iii) above, is

$$P(y) dy = \Omega^{-N} dR_1, \ldots, dR_N; \quad R_i \in \Omega.$$

(1.5)

It is also possible to consider the case where the number of scatterers in $\Omega$ is not fixed, but has an average value $N$. (This is actually used in Appendix B.) The thermodynamic properties of this ensemble would then be obtained from the free energy $F$ defined as

$$F = -\beta^{-1} \langle \ln Z(y) \rangle = -\beta^{-1} \int P(y) \ln Z(y) \, dy.$$

(1.6)

This prescription for obtaining the properties of a system will be satisfactory only when the dispersion in the values of $\ln Z(y)$ is small. This will be true for a macroscopic system when $\ln Z(y)$ is an additive quantity. The existence and some properties of the free-energy density in the thermodynamic limit $\lim_{\Omega \to \infty} F/\Omega$ for the spin system have been discussed previously. A proof of the existence of this quantity, as well as the thermodynamic limit of the frequency distribution function for random harmonic crystals, is given in Appendix A.

In this paper we are primarily interested in case (iii). The existence of $\lim_{\Omega \to \infty} (F/\Omega)$ for this system is discussed in Appendix B. In the special situation when the particles are noninteracting ($U = 0$) and may be treated by Boltzmann statistics, the problem reduces to an investigation of one of the most frequently used models in the study of irreversible phenomena, that in which a single particle interacts with a set of scattering centers randomly distributed in space. General properties of perturbation expansions for the resolvent operator and the density matrix have been discussed in many papers. In Sec. 2 we study properties of this system using the path-integral formulation of quantum statistics which was introduced by Feynman. For $M$ noninteracting particles obeying Boltzmann statistics, (1.4) becomes

$$Z_M = [Z_i(y)]^M/M!$$

(1.7)

where $Z_i(y)$ is the (quantum-mechanical) partition function for a single particle interacting in a volume $\Omega$ with $N$ scatterers located at positions $\{R_1, \ldots, R_N\} \equiv y$. From (1.6)

$$(F/\Omega) = -\langle \beta \rangle^{-1} \langle \ln (Z_i^M/M!) \rangle$$

$$= -\langle \beta \rangle^{-1} \langle 1 - \ln (\Omega/\Omega) + \ln [Z_i(y; \Omega)/\Omega] \rangle,$$

(1.8)

where we have used Stirling's formula for $\ln \Omega$.

We now argue somewhat heuristically that, since $Z_i$ is an extensive quantity in this case, we will have $\langle \ln (Z_i/\Omega) \rangle \sim \ln (Z_i/\Omega)$ in the limit $\Omega \to \infty, N \to \infty, N/\Omega = \rho = \text{const}$. To see this more formally we divide up the volume $\Omega$ into $J$ cubes, $\omega_i (i = 1, \ldots, J)$, each of volume $\omega$; we consider the limits $J \to \infty$ followed by $\omega \to \infty$. For reasonable forms of the interaction potential $V(r)$ we should be able to neglect, for sufficiently large $\omega$, the interaction between a particle in one cube $\omega_i$ with impurities outside $\omega_i$ as well as the precise boundary conditions. Thus

$$\Omega^{-1} Z_i(y; \Omega) \sim \Omega^{-1} \sum_{i=1}^J Z_i(y^{(i)}; \omega) \equiv J^{-1} \sum_{i=1}^J (z_i/\omega).$$

(1.9)

In (1.9) the $z_i$ can be considered independent random variables so that, by the central limit theorem, in the

---


2 See, e.g., papers cited in Refs. 6 and 7.


limit of large $J$, $Z_t(y; \Omega)$ will have a normal distribution
\[
P(Z_t) = \exp \left[ - \frac{(Z_t - \langle Z_t \rangle)^2}{2\langle (\Delta Z_t)^2 \rangle} \right], \tag{1.10}\]
where
\[
\langle (\Delta Z_t)^2 \rangle = J\langle (\Delta z)^2 \rangle
\]
and
\[
\langle \ln (Z_t/\Omega) \rangle = \ln \langle Z_t/\Omega \rangle + \left\langle \ln \left[ 1 + \frac{Z_t - \langle Z_t \rangle}{\langle Z_t \rangle} \right] \right\rangle
\]
\[= \ln \langle Z_t/\Omega \rangle - \frac{1}{2} \left\langle (\Delta z)^2 \right\rangle + \cdots\]
\[= \ln \langle Z_t/\Omega \rangle \]
in the limit $J \to \infty$ when $P(Z_t)$ becomes infinitely sharply peaked about $\langle Z_t \rangle$. Thus from (1.8) in the limit $M \to \infty$, $\Omega \to \infty$, $M/\Omega = \text{const}$,
\[
<F> = -\beta^{-1} (M/\Omega)[1 - \ln \langle M/\Omega \rangle + \ln \langle Z_t/\Omega \rangle].
\tag{1.11}\]
Alternatively, we can consider this system to be represented by a grand canonical ensemble with chemical potential $\mu$, activity $\xi = e^{\beta \mu}$, and mean number of particles $\langle M \rangle$. The grand partition function
\[
\Xi(y; \Omega) = \sum_{M=1}^{\infty} \xi^M Z_t^M/M! = e^{\beta \Xi_t}, \tag{1.12}\]
so that the grand potential
\[
F - \mu <M> = -\beta^{-1} \langle \ln \Xi \rangle = -\beta^{-1} \langle Z_t \rangle \tag{1.13}\]
and
\[
\langle M \rangle = \xi \left\langle \frac{\partial \ln \Xi(y; \Omega)}{\partial \xi} \right\rangle = \xi \langle Z_t \rangle.
\]
For the free energy this gives
\[
F = -\beta^{-1} <M>[1 - \ln \langle <M>/\langle Z_t \rangle \rangle], \tag{1.14}\]
which coincides with (1.11) when $\langle M \rangle$ is associated with the $M$ of the canonical ensemble.

The thermodynamics of this system is thus given entirely in terms of $\langle Z_t \rangle/\Omega$ in the limit when the system is large. In Sec. 2, we use the path-integral method of Feynman to investigate the existence of an expansion of $\langle Z_t \rangle/\Omega$ in the density of scattering centers $\rho = N/\Omega$ in the limit $N, \Omega \to \infty$, and of an expansion in the coupling constant $\lambda$ when certain conditions on the potential $V(r)$ between electron and scattering center are satisfied. This analyticity in $\lambda$ was shown first by Doniach, who used a different representation for the many-temperature Green's functions which arise in the expansion.

\footnote{S. Doniach, "Greens Function Theory of Multiple Scattering. I. Convergence of the Perturbation Series for the Partition Function"; "II. Variational Estimate for the Conductivity under Strong Coupling Conditions" (unpublished).}

The importance of the quantity $\langle Z_t \rangle$ here arises from its linear relation to the average density of states
\[
n(E) \equiv \langle n(E; y) \rangle = \Omega^{-1} \langle \sum_i \delta(E - E_i(y)) \rangle, \tag{1.15}\]
where $E_i$ are the energy eigenvalues of (1.1). We then have
\[
\langle Z_t(\beta) \rangle/\Omega = \int_{-\infty}^{\infty} e^{-\beta E} n(E) \, dE = \int_{-\infty}^{\infty} e^{-\beta E} e^{\beta E} n(E) \, dE.
\tag{1.16}\]
Equation (1.16) is valid for both classical and quantum systems with their respective standard interpretations. For quantum systems in which the particles obey B.E. or F.D. statistics, the grand ensemble approach gives
\[
\Omega^{-1} \langle \ln \Xi(y) \rangle = \mp \int_{-\infty}^{\infty} dE \, n(E) \ln (1 \mp e^{E(\xi - 1)})
\rightarrow e^{\beta n(Z_t)/\Omega}, \tag{1.17}\]
when the particle density is low. In principle we can compute the density of states from $\langle Z_t(\beta) \rangle$ by the inverse of (1.16):
\[
n(E) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\beta \frac{e^{\beta E} \langle Z_t(\beta) \rangle/\Omega}{}, \tag{1.18}\]
but this requires knowledge of $\langle Z_t(\beta) \rangle$ for complex $\beta$. The quantity $n(E)$ has been investigated recently for various kinds of potential and we hope that our results will be of relevance.

In Sec. 3 we consider the properties of a particle in a potential random in space and obeying Gaussian statistics. This corresponds to the high-density limit of the random scatterers model discussed above.\footnote{B. I. Halperin and M. Lax, Phys. Rev. 148, 722 (1966); 153, 802, (1967).} In some nontrivial cases we obtain explicit bounds on the average partition function, which, in the limiting case of "white noise," are consistent with recent approximate calculations of the asymptotic value of the average density of states.

2. EVALUATION OF $\langle Z_t \rangle$

In terms of Feynman's path-integral formalism the partition function for a particle of mass $m$ interacting through a potential $\lambda V(r)$, with $N$ scattering centers at positions $R_1, \ldots, R_N$ in a volume $\Omega$, is given by
\[
Z_s(\beta; \{R\}) = \int dr_0 \int_{r_0}^{r_0 + L} \delta r \exp \left[ - \int_0^\beta \delta m r^2 dt - \int_0^\beta \sum_{n=1}^N \lambda V(r(t) - R_n) \right], \tag{2.1}\]
where $\beta$ is the inverse temperature, the symbol $\sum_{t_0}^{r_0} dr$ denotes the appropriately normalized sum over all paths $r$ in $\Omega$ such that $r(0) = r(\beta) = r_0$, and we have taken $h = 1$. We define the configurational average of $Z_1$ by
\[
\langle Z_1(\beta) \rangle = \frac{1}{\Omega} \prod_{n=1}^{N} \int_{\Omega} d\mathbf{R}_n P(\mathbf{R}_1, \ldots, \mathbf{R}_N) Z_1(\beta; \{\mathbf{R}\}).
\] (2.2)

The case of randomly distributed scatterers corresponds to $P = \Omega^{-N}$ so that
\[
\langle Z_1(\beta) \rangle = \int_{\Omega} d\mathbf{R}_0 \left( \frac{r_0}{r_0} \right) \exp \left( -\int_{0}^{r_0} \frac{1}{2} m \mathbf{t}^2 dt \right)
\times \prod_{n=1}^{N} \left( \Omega^{-1} \int_{\Omega} d\mathbf{R}_n \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}_n) \right) \right).
\]
Each term in the product is identical, and, by adding and subtracting unity, we can write the product as an exponential in the limit $N, \Omega \to \infty, \rho = N/\Omega = \text{const}$, so that
\[
\langle Z_1(\beta) \rangle = \int_{\Omega} d\mathbf{R}_0 \left( \frac{r_0}{r_0} \right) \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right)
+ \rho \int_{\Omega} d\mathbf{R} \left( \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right) - 1 \right).
\]

If we introduce the following notation for the normalized average of a functional of the path $E[F[\mathbf{r}(t)]]$
\[
E[F[\mathbf{r}(t)]] = \frac{1}{\Omega} \int_{\Omega} d\mathbf{R}_0 \left( \frac{r_0}{r_0} \right) \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}_0) \right) \frac{1}{\Omega} \int_{\Omega} d\mathbf{R} \left( \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right) - 1 \right),
\]
then we can write the partition function in the form
\[
\langle Z_1(\beta) \rangle / Z_0 = E \left[ \exp \rho \int_{\Omega} d\mathbf{R} \left( \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right) - 1 \right) \right].
\] (2.3)

Here $Z_0$ is the partition function for a free particle so that
\[
Z_0 = \int_{\Omega} d\mathbf{R}_0 \left( \frac{r_0}{r_0} \right) \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}_0) \right) = \Omega^{1/2} \frac{m^{1/2}}{2\pi\beta^2}.
\] (2.4)

An expression of the type (2.3) can be obtained also for a nonuniform distribution of scatterers of the type
\[
P(\mathbf{R}_1, \ldots, \mathbf{R}_N) = \Omega^{-N} \prod_{n=1}^{N} f(\mathbf{R}_n),
\]
where $f$ is normalized by
\[
\Omega^{-1} \int d\mathbf{R} f(\mathbf{R}) = 1.
\]
However, this will only introduce an additional factor $f(\mathbf{R})$ into the $\mathbf{R}$ integration in (2.3) and will not significantly alter the following discussion. A more realistic distribution which takes into account correlations in the positions of scattering centers will not lead to a simple expression of the form (2.3).

A. Inequalities

Making use of the standard inequality
\[
\int_{-\beta}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \leq \beta^{-1} \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}),
\]
so that one obtains the following upper bound for $\langle Z_1 \rangle$:
\[
\langle Z_1(\beta) \rangle \leq \int_{\Omega} d\mathbf{R}_0 \left( \frac{r_0}{r_0} \right) \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}_0) \right) \exp \left( -\lambda \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right) - 1 \right).
\]
Therefore,
\[
\langle Z_1(\beta) \rangle / Z_0 \leq \exp \left[ \rho \int_{\Omega} d\mathbf{R} \left( \exp \left( -\beta \int_{0}^{\beta} dt V(\mathbf{r}(t) - \mathbf{R}) \right) - 1 \right) \right] \]
\[
\equiv \langle Z_1^{(i)}(\beta) \rangle / Z_0,
\] (2.6)
where $\langle Z_1^{(i)}(\beta) \rangle$ is the configurational average of the classical partition function.

B. Analyticity in $\rho$

Using some results obtained by Ginibre in his work on the analyticity properties of regular systems, it is readily shown that $\langle Z_1(\beta; \rho) / Z_0$ is an entire function of $\rho$ (for real positive $\beta$), for all reasonable (non-Coulomb) potentials $V(\mathbf{r})$. To be more specific, we assume that $V(\mathbf{r})$ can be written as a sum of two terms
\[
V(\mathbf{r}) = V_1(\mathbf{r}) + V_2(\mathbf{r})
\] (2.7)
satisfying the conditions
\[
V_1(\mathbf{r}) \geq 0 \quad \text{for} \quad r \leq a, \quad V_1(\mathbf{r}) = 0 \quad \text{for} \quad r > a,
\] (2.8)
\[\text{J. Ginibre, J. Math. Phys. 6, 1432 (1965); in particular, see Appendix 2.}
and
\[ \int dr [e^{iV(r)} - 1] < \infty. \] (2.9)

For the case where the particle-impurity has a hard core, \( a \) may be taken to be the range of this core. Writing (2.3) in the form
\[ \langle Z_1(\beta; \rho) \rangle / Z_0 = E \{ \exp \left[ \rho Q([r(t)], \beta) \right] \}, \] (2.10)
we have
\[ Q([r(t)], \beta) = Q_1([r(t)], \beta) + Q_2([r(t)], \beta), \] (2.11)
where
\[ Q_1([r(t)], \beta) = \int dR \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) - 1 \right] \] (2.12)
and
\[ Q_2([r(t)], \beta) = \int dR \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) \right] \times \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) - 1 \right]. \] (2.13)

Using (2.5) and (2.8),
\[ |Q_2([r(t)], \beta)| \leq \int dR \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) \right] \times \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) - 1 \right]. \]

Thus finally
\[ |Q_2([r(t)], \beta)| \leq \int dR [e^{i\lambda V_2(R)} - 1], \] (2.14)
which is bounded by (2.9). Also, using (2.8), we have
\[ |Q_1([r(t)], \beta)| \leq v_a([r(t)], \beta), \] (2.15)
the volume of the region containing all points within a distance \( a \) of the path \( r(t) \). The equality in (2.15) holds when \( V_2 \) is a hard-core potential. Ginibre was able to obtain very strong bounds on
\[ E \{ \exp \left[ \rho \omega_a([r(t)], \beta) \right] \} \]
from which the analyticity of \( \langle Z_1 \rangle / Z_0 \) now follows.

Having established the analyticity in \( \rho \) of \( \langle Z_1 \rangle / Z_0 \), it is now possible to show that the average "pressure" of an ideal gas with quantum statistics is also analytic in \( \rho \) for \( V(R) \geq 0 \) and \( e^{\beta \mu} < 1 \). This is readily seen by expanding the integrand in (1.17) in powers of \( e^{\beta \mu} \) for \( \mu < 0 \), since \( n(E) = 0 \) for \( E < 0 \), when \( V(r) \geq 0 \). The coefficient of \( e^{\beta \mu} \) is \((\pm 1)^{1/2}(\pi \beta)^{-1} \langle Z_1(\beta) \rangle \) and is bounded by
\[ \left( \frac{m}{2\pi \beta} \right)^{\nu/2} \exp \left[ \rho \int dR [e^{-\beta V(r)} - 1] \right] \]
according to (2.6), where \( \nu \) is the dimensionality of the space considered. The series will therefore converge to an analytic function of \( \rho \) for \( e^{\beta \mu} < 1 \). It is an interesting but unanswered question whether the Bose–Einstein condensation of an ideal gas, \( \rho = 0 \), will disappear at some finite \( \rho \). This could happen, for example, if \( n(E; \rho) \) was zero for \( E < E_0 \) and
\[ n(E_0 + \rho) \neq 0. \]

C. Analyticity in \( \lambda \)

By expansion of each term in the \( \rho \) series, when (2.11) is satisfied, in powers of the coupling constant \( \lambda \) and rearranging, one can obtain an expansion of \( \langle Z_1(\beta) \rangle \) in powers of \( \lambda \). This series was considered by Doniach,\(^5\) who showed that \( \langle Z_1(\beta) \rangle \) is an analytic function of \( \lambda \) for certain potentials. If we expand the potential in its Fourier components, we find
\[ Q([r(t)], \beta) = \int dR \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) \right] \times \left[ \exp \left( -\lambda \int_0^\beta dt V_2(r(t) - R) \right) - 1 \right]. \]

Each term in the \( \lambda \) expansion will involve many-temperature Green’s functions of the form
\[ G_{k_1, \ldots, k_m}(t_1, \ldots, t_m) = \exp \left[ \sum_{i=1}^m ik_i \cdot r(t_i) \right]. \]

Since
\[ \exp \left[ i \sum_{i=1}^m k_i \cdot r(t_i) \right] = \cos \left( \sum_{i=1}^m k_i \cdot r(t_i) \right) + i \sin \left( \sum_{i=1}^m k_i \cdot r(t_i) \right) \]
and for every path for which
\[ r(t_1) = r_0 + x_1, \quad r(t_2) = r_0 + x_2, \ldots, \]
there is a corresponding path with
\[ r(t_1) = r_0 - x_1, \quad r(t_2) = r_0 - x_2, \ldots, \]
then the imaginary parts cancel out because \( r_0 \cdot \sum k_i = 0 \). Furthermore,

\[
|G| \leq E\{\exp\left[|k_1 \cdot r(t_1)| \cdots |k_m \cdot r(t_m)|\right]\} = 1.
\]

(2.17)

Each term in the \( \lambda \) expansion will be majorized by the absolute value of a product of terms of the type on the right-hand side of Eq. (2.16) in which the exponentials have been replaced by unity. Then the \( \lambda \) expansion will exist for all values of \( \lambda \) if the following conditions on the potential are satisfied:

(i) \[
\sum_k |V_k| \leq \bar{V},
\]

(ii) \[
|V_k| \leq \left(\frac{\alpha^3}{\Omega}\right) \bar{V},
\]

(2.18)

\[
\langle Z_1(\beta) \rangle = \frac{\int \delta \varphi Z_1(\beta, [\varphi]) \exp\left[-\frac{1}{2} \int_0^\beta \int_0^\beta d\tau d\tau' \varphi(\tau) \varphi(\tau') K(\tau - \tau')\right]}{\int \delta \varphi \exp\left[-\frac{1}{2} \int_0^\beta \int_0^\beta d\tau d\tau' \varphi(\tau) \varphi(\tau') K(\tau - \tau')\right]}.
\]

Thus,

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 = E\left\{\exp\left[\int_0^\beta dt_1 \int_0^{2\beta} dt_2 K^{-1}(\tau(t_1) - \tau(t_2))\right]\right\}
\]

(3.2)

where

\[
\int K(x - y)K^{-1}(y - z) \, dy = \delta(x - z).
\]

(3.3)

Comparison with (2.3) shows that (3.2) "corresponds" to the random scatterers case in the limit \( \rho \to \infty, \lambda \to 0 \) such that \( \rho^2 = \text{const} \) with the identification

\[
K^{-1}(r) = \lambda^2 \rho \int dR V(R) V(R + r).
\]

(3.4)

It has also been pointed out by Halperin and Lax\(^6\) that the Gaussian random potential is the high-density limit of the random scatterers model as a consequence of the central limit theorem.

The path integral (3.2) cannot be explicitly evaluated for any physically interesting potential correlation \( K^{-1} \). If \( K^{-1} \) satisfies the inequalities

\[
M_1 \leq K^{-1}(r) \leq M_2,
\]

then \( \langle Z_1(\beta) \rangle / \bar{Z}_0 \) has corresponding bounds

\[
e^{\beta M_1} \leq \langle Z_1(\beta) \rangle / \bar{Z}_0 \leq e^{\beta M_2}
\]

(3.5)

and one easily sees that an expansion in \( \lambda^2 \) exists. One can find a more useful lower bound using the inequality which follows from (2.5):

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 \geq \exp\left[ E\left\{\int_0^\beta dt_1 \int_0^{2\beta} dt_2 K^{-1}(\tau(t_1) - \tau(t_2))\right\}\right].
\]

(3.6)

When \( K^{-1} \) has a Gaussian form

\[
K^{-1}(r) = \nu \left(\frac{x^2}{\pi}\right)^{\nu/2} e^{-x^2 / \nu},
\]

(3.7)

where \( \nu \) is the dimensionality and \( \int dK^{-1}(r) = \nu \), the right-hand side of (3.6) can be evaluated to give in the one-dimensional case

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 \geq \exp\left[\nu \beta \left(\frac{2m}{\pi \beta}\right)^{\nu/2} \sin^{-1}\left(\frac{\alpha}{(\alpha^2 + 2m/\beta)^{1/2}}\right)\right].
\]

(3.8)

In two dimensions we have

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 \geq \exp\left[\frac{-\gamma m \beta \alpha}{\pi (\alpha^2 + 2m/\beta)^{1/2}} \times \ln \left(\frac{\alpha}{\alpha + (\alpha^2 + 2m/\beta)^{1/2}}\right)\right].
\]

(3.9)

In three dimensions we have

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 \geq \exp\left[\frac{2\gamma^2 \beta m z^2}{\pi^3 (\alpha^2 + 2m/\beta)^{3/2}}\right].
\]

(3.10)

From (3.5) the upper bound in the case of Gaussian correlation is given by

\[
\langle Z_1(\beta) \rangle / \bar{Z}_0 \leq \exp\left[\frac{\beta^2 \gamma}{\nu} \left(\frac{\alpha^2}{\pi}\right)^{\nu/2}\right].
\]

When \( \alpha \to 0 \), which can be considered as the limiting
case of a long-range potential correlation, the upper and lower bounds become identical and thus \( \langle Z_1(\beta) \rangle \) is obtained exactly in this limit. In the limit \( \alpha \to \infty \), \( K^{-1} \) becomes a \( \delta \) function and we can make a connection with the work of Halperin and Lax\(^6\) and Zittartz and Langer,\(^7\) who calculated the low-energy behavior \( (E \to -\infty) \) of the average density of states \( n(E) \) in the case of "white noise":

\[
K^{-1}(r) = \gamma \delta(r). \tag{3.11}
\]

In this limit we obtain in the one-dimensional case (3.8)

\[
\langle Z_1(\beta) \rangle / Z_0 \geq \exp \left[ \gamma \beta (\beta m \pi/2) \right], \tag{3.12}
\]

but the two- and three-dimensional bounds (3.9) and (3.10) diverge as \( \alpha \to \infty \) (the exponent diverging logarithmically and linearly, respectively). This is in agreement with the density of states results\(^6\) which, as \( E \to -\infty \), predict a behavior

\[
n(E) \sim \exp \left[ -\text{const.} |E|^{2-\nu/2} \right], \tag{3.13}
\]

which, from (1.16), will lead to a finite value for \( \langle Z_1(\beta) \rangle \) in the one-dimensional case and to an infinite value in three dimensions. The divergence in the two-dimensional problem may be associated with the fact that, as discussed by Halperin and Lax,\(^6\) in the case of two- and three-dimensional "white noise," the second-order corrections to the variational energy diverge due to short wavelength potential fluctuations. This leads to an infinite constant in \( \langle Z_1(\beta) \rangle \) unless those fluctuations are cut off below a certain wavelength, which is the case if \( K^{-1} \) is not a true \( \delta \) function.

A further lower bound on (3.2) may be obtained by application of the methods used in Feynman's treatment of the polaron problem.\(^4\) This leads to a complicated expression which, however, has the same behavior in the "white noise" case as the bounds (3.8)-(3.10). The expression (3.2) for \( \langle Z_1(\beta) \rangle \) also satisfies the condition for applicability of the extension of Feynman's variational principle for the free energy to include dissipative processes, which was introduced by Doniach in his second paper.\(^6\) This condition is that \( \langle Z_1(\beta) \rangle \) is a convex-downward function of any parameter, say \( \lambda \), multiplying \( K \) in (3.2)

\[
\frac{\partial^2 \langle Z_1(\beta) \rangle}{\partial \lambda^2} \geq 0,
\]

which, from (3.2), is true for any function \( K^{-1} \).

**ACKNOWLEDGMENTS**

We wish to thank Dr. S. Doniach, whose work interested us in this subject, and Dr. R. B. Griffiths, Dr. A. Lenard, and Dr. E. Lieb for helpful comments.

We are particularly indebted to Dr. Ginibre for pointing out to us the results he obtained in Ref. 9.

**APPENDIX A**

The free energy of a harmonic crystal can be written in the form\(^10\)

\[
F = \int_0^\infty d\omega f(\omega) g(\omega), \quad (A1)
\]

where \( F(\omega) \) is a smooth function of \( \omega \) and \( g(\omega) \) is the distribution function of normal mode frequencies of the crystal (eigenvalues of the dynamical matrix). If, for simplicity, we consider a crystal with one atom per unit cell, then we can write \( g(\omega) \) in the form

\[
g(\omega) = 2\omega G(\omega^2), \tag{A2}
\]

where

\[
G(\omega^2) = N^{-1} \frac{d}{d\omega^2} N(\omega^2) \tag{A3}
\]

and

\[
N(\omega^2) = \int_0^{\omega^2} dx \sum_k \delta(x - \omega^2(k)) \tag{A4}
\]

is the number of modes in the crystal with frequencies \( \leq \omega^2 \).

In this Appendix we show the existence of

\[
n_\alpha(\omega^2) = N(\omega^2)/\Omega \tag{A5}
\]

in the limit where the number of atoms \( N \) in the crystal and its volume \( \Omega \) become infinite in such a way that \( N/\Omega \) is constant. (A1)-(A4) then lead to the existence of the free energy density \( F/\Omega \) in this limit. The proof also applies to a crystal with random masses or a random distribution of atoms on lattice sites.

For \( m \) identical crystals of cubic geometry each with \( N \) atoms in volume \( \Omega \), \( N(\omega^2) \) and the eigenfrequencies are the same for each crystal. For the system taken as a whole, the number of

\[
\text{(frequencies)} \leq \omega^2,
\]

\[
N_{m\Omega}(\omega^2) = mN(\omega^2) = \int_0^{\omega^2} dx \sum_k \delta(x - \omega^2_m(k)),
\]

when \( \omega_m(k) \) are the eigenvalues of a dynamical matrix which can be decomposed into matrices referring to the individual crystals alone, each having \( O(N) \) elements in the case of finite range interatomic forces.

If the \( m \) crystals are joined together in some way to form a new crystal \( I \) with \( mN \) atoms and volume \( m\Omega \), then

\[
N_{m\Omega}^I(\omega^2) = \int_0^{\omega^2} \sum_k \delta(x - \omega^2_m(k)),
\]

in which \( \omega_m^s \) are eigenvalues of a matrix which differs from the above only by interaction terms between component crystals. These interaction terms correspond to \( O(N^3) \) elements since only surface atoms will contribute such terms to the dynamical matrix. By Ledermann's Theorem\(^{10}\) the number of eigenvalues of this matrix \( \omega_m^s \leq \omega^s \) will differ from the number for the previous matrix \( \omega_m^2 \leq \omega^2 \) by, at most, the number of rows and columns which are changed, i.e., by less than \( \alpha_m N^{\frac{1}{2}} \) where \( \alpha_m \) is some number which depends on \( m \) and on how the crystals are joined but is independent of \( N \).

Hence

\[
n_m^s(\omega^s) = n_m^s(\omega^s)/m\Omega = n_m(\omega^s)/m\Omega + \alpha_m N^{\frac{1}{2}}/m\Omega
\]

where

\[
R_{m}\omega(\omega^s) \sim N^{\frac{1}{2}}/\Omega.
\]

Following the method of Griffiths,\(^{11}\) consider a simple cubic lattice of lattice constant 1. Let the cube \( \Omega_s \) for \( s = 2, 3, 4, \ldots \), be of volume \( \Omega_s = 2^{3s}\Omega \) and contain \( 2^{3s} N \) particles so that it is composed of eight cubes \( \Omega_{s-1} \). The corresponding values of \( n(\omega^s) \) satisfy an inequality of the type

\[
n^{(s)}(\omega^s) \leq n^{(s-1)}(\omega^s) + |R^{(s)}(\omega^s)|,
\]

where

\[
|R^{(s)}(\omega^s)| \leq \frac{\bar{\alpha}_s (2^{3s} N)^{\frac{1}{2}}}{2^{3s}\Omega} = C 2^{-s}\Omega^{-\frac{1}{2}}
\]

in which \( \bar{\alpha}_s \) is the maximum possible value of \( \alpha_s \).

Therefore

\[
n^{(s)}(\omega^s) \leq n^{(s-1)}(\omega^s) + C \Omega^{-\frac{1}{2}}2^{-s}.
\]

Thus the quantity

\[
n^{(s)}(\omega^s) + C \Omega^{-\frac{1}{2}}2^{-s}
\]

is monotonically decreasing as \( s \to \infty \). Since this is bounded below by zero, it will approach a limit \( n(\omega^s) \) in the limit \( s \to \infty \). By a method similar to that of Griffiths, one can show that an arbitrary sequence of cubes of increasing volume will yield the same limit \( n(\omega^s) \) as the particular sequence \( \Omega_s \).

For a random crystal the above argument follows through where each crystal has some particular configuration \( \theta \) and one takes the average

\[
\langle n(\omega^s) \rangle = \sum_\theta P(\theta)n(\omega^s)[\theta],
\]

in which \( P(\theta) \) is the normalized probability of con-figuration \( \theta \). It is easily seen that

\[
\langle n^{(s)}(\omega^s) \rangle \leq \langle n^{(s-1)}(\omega^s) \rangle + C \Omega^{-\frac{1}{2}}2^{-s}
\]

and the argument follows as above.\(^2\)

### APPENDIX B

In this Appendix we shall prove the existence of the thermodynamic limit of the free energy per unit volume defined in (1.6) for a system with a Hamiltonian given in (1.1).

The problem here is more complicated than in the case without scatterers, where the existence of the free-energy density in the thermodynamic limit was proved for very general interactions by Fisher\(^{12}\) and Ruelle.\(^{13}\) While we need not assume any restrictions on the interaction between the particles beyond those necessary for the existence of the thermodynamic limit in the absence of any scattering centers, we shall assume that the potential \( V(r) \) between particle and scattering centers satisfies the "strong tempering" condition of Fisher\(^{12}\):

\[
V(r) \leq 0 \quad \text{when} \quad r \geq D,
\]

as well as the more usual condition that

\[
\int [e^{-\beta V(r)} - 1] \, dr < \infty.
\]

Furthermore, we shall assume that the particles of our system, of which there are \( M \), are confined to a cubical box with sides of length \( L, L^3 = \Omega \). The scattering centers, on the other hand, are located inside a larger cube of sides \( L + 2D, (L + 2D)^3 = \Omega' \), centered on the original cube \( \Omega \). The probability density for having precisely \( l \) scatterers at positions \( R_1, \ldots, R_l \) in some volume element \( \omega \in \Omega' \) is assumed to be given by

\[
P(y) = P_\omega(R_1, \ldots, R_l) = \frac{e^{-\rho \omega} \rho^l}{l!},
\]

so that \( \rho \) is the average density of scatterers.

To prove the existence of

\[
\lim_{\alpha \to -\infty} -\beta(JF) = \lim_{\alpha \to -\infty} \frac{\langle \ln Z(y, M, \Omega') \rangle}{\Omega'}
\]

for \( M/\Omega \) fixed under the assumptions (B1) and (B2) and the special kind of boundary conditions we have used requires only a small modification of the methods of Fisher and Ruelle. We shall therefore give only a brief outline of the proof. There are two parts to the proof: (1) finding an upper bound on \( \langle \ln Z(\Omega') \rangle/\Omega' \)


\(^{13}\) D. Ruelle, Boulder Lectures 1963 (University of Colorado, Theoretical Physics Institute, 1963).
which is independent of $\Omega'$; and (2) showing that, when eight cubes of volume $\Omega'$ are put together to form a larger cube of volume $\Omega'' = 2^4 \Omega'$ with $2^9 M$ particles in it, then

$$
(\ln Z(y'', 2^3 M, 2^9 \Omega'))/2^3 \Omega' \geq (\ln Z(y', M, \Omega'))/\Omega' + o(\Omega'), \quad (B5)
$$

where $y''$ is the configuration of scatterers in $\Omega'$.

An upper bound on $Z(y', M, \Omega')$ is obtained from the condition that

$$
U(r_1, \cdots, r_M) \geq -M\Phi, \quad \Phi \text{ const}, \quad (B6)
$$

for all values of the $r_i$. This condition is required for the existence of the thermodynamic limit of the free energy in the absence of scatterers. Hence

$$
\frac{1}{\Omega'} \left( \ln Z(y, M, \Omega') \right) \leq \frac{\beta M \Phi}{\Omega'} + \frac{1}{\Omega'} \left( \ln \left( \frac{M}{\Omega'} \right) + \frac{M}{\Omega'} \rho \int e^{-\beta V(r)} - 1 \, dr \right) \quad (B7)
$$

$$
\leq \frac{\beta M}{\Omega'} \Phi + 1 - \ln \left( \frac{M}{\Omega'} \right) + \frac{M}{\Omega'} \rho \int e^{-\beta V(r)} - 1 \, dr \quad (B8)
$$

$$
\leq C,
$$

where $C$ is some constant independent of $\Omega$ and use was made of (2.5) in deriving the second inequality. Having obtained the bound in (B8), we can now proceed with our construction of the larger cubes à la Fisher and Ruelle.

The inequality (B5) is obtained by first noting that

$$
\ln Z(y'', 2^3 M, 2^9 \Omega') \geq \ln Z(y'', 2^3 M, 2^9 \Omega'), \quad (B9)
$$

where $y'$ is the partition function when the $2^9 M$ particles are constrained to be inside, and evenly divided between, the original eight cubes $\Omega_i$, $i = 1, \cdots, 8$, of volume $\Omega$. A lower bound on $y'$ is now obtained using (B1) if we neglect the interactions between particles in $\Omega_i$ and scattering centers outside $\Omega_i$. The interaction between particles in different boxes $\Omega_i$ is now bounded by a term of $o(\Omega)$ which is independent of the configuration of scattering centers. Finally, we obtain

$$
\ln Z(y'', 2^3 M, 2^9 \Omega') \geq \sum_{i=1}^{8} \ln Z(y_i, M, \Omega_i) + o(\Omega),
$$

where $y_i$ is the configuration of scatterers in $\Omega_i$. Due to the independence of the distribution of scatterers in the different boxes, averaging of (B9) now yields (B5).

**Quantum Corrections to the Second Virial Coefficient at High Temperatures**

**Robert Nyden Hill**

Department of Physics, University of Delaware, Newark, Delaware

(Received 13 September 1967)

The Laplace transform of $\exp(-\beta H)$ is the Green's operator of the negative-energy Schrödinger equation $(H + W)^{-1}$. Conditions are stated under which a large $|W|$ asymptotic series for the Green's operator can be inverse-Laplace-transformed term-by-term to obtain a small $\beta$ expansion for $\exp(-\beta H)$. This approach and the Watson transformation are used to calculate the first few terms of high-temperature asymptotic expansions for the exchange second virial coefficient for hard spheres and for the Lennard-Jones potential. The known results for the direct second virial coefficient for hard spheres are extended. The Wigner-Kirkwood expansion is calculated to order $\hbar^4$ and used to calculate the direct second virial coefficient for the Lennard-Jones potential through order $\hbar^6$.

**I. INTRODUCTION AND SUMMARY**

The problem of calculating quantum corrections to the second virial coefficient at high temperatures has been only partially solved by previous authors.1


The exchange contribution has been particularly difficult, and it is only in the last year that Lieb,2 by calculating rigorous upper and lower bounds, has obtained the leading term of an asymptotic expansion for the exchange contribution in the particular case of