Fermi and Bose pressures in statistical mechanics

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I show how the pressure in Fermi and Bose systems, identified in standard discussions of quantum statistical mechanics by the use of thermodynamic analogies, can be derived directly in terms of the flux of momentum across a surface by using the quantum mechanical stress tensor. In this approach, which is analogous to classical kinetic theory, the pressure is naturally defined locally. The approach leads to a simple interpretation of the pressure in terms of the momentum flow encoded in the wave functions. The stress-tensor and thermodynamic approaches are related by an interesting application of boundary perturbation theory for quantum systems. I investigate the properties of quasi-continuous systems, the relations for Fermi and Bose pressures, shape-dependent effects and anisotropies, and the treatment of particles in external fields, and note several interesting problems for graduate courses in statistical mechanics. © *2004 American Association of Physics Teachers.*
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I. INTRODUCTION

The concept of pressure in quantum systems is usually introduced in equilibrium statistical mechanics using thermodynamic analogies. For example, the Helmholtz free energy F is identified with the logarithm of the canonical partition function Z, and the thermodynamic potential Ω, with the logarithm of the grand partition function $\mathcal{Z}$ by the relations

$$F = -k_B T \ln Z, \quad \Omega = -k_B T \ln \mathcal{Z}. \tag{1}$$

Here, Z is the usual sum over the energies in the system

$$Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}} = \sum_\alpha e^{-\beta E_\alpha}, \tag{2}$$

with $\beta = 1/k_B T$. A separate partition function Z_N can be defined for each particle number N. $\mathcal{Z}$ is then defined as

$$\mathcal{Z} = \sum_N e^{N\beta\mu} Z_N, \tag{3}$$

where μ is the chemical potential.

The pressure is customarily determined by one of the standard thermodymanic relations

$$P = -\partial F/\partial V = (k_B T/Z)(\partial Z/\partial V), \tag{4a}$$

or

$$PV = -\Omega, \tag{4b}$$

with F evaluated at fixed temperature T and particle number N, and Ω at fixed T and μ. In the second case, the average particle number and chemical potential are related by $N = -\partial\Omega/\partial\mu$.

The relations in Eqs. (4) can be confirmed in classical particle statistical mechanics by an appeal to the results of kinetic theory, and can be further motivated by an appeal to the concept of generalized forces when the energy of a system depends explicitly on external parameters such as its volume. However, standard discussions do not show directly how the pressure relations arise in a kinetic-theory-like context in quantum statistical mechanics. For a sampling of standard treatments, see Refs. 1–9.

The objective of this paper is to derive the pressure in Fermi and Bose systems using ideas analogous to those in kinetic theory; specifically, the relation of pressure to momentum flow and the quantum stress tensor. These ideas are well defined in quantum systems, give a "quantum kinetic theory" approach to pressure, and lead to a direct interpretation of the pressure in Fermi and Bose systems in terms of the momentum flow encoded in the wave functions. I will show that the pressure is naturally defined locally, a point that is obvious in the stress-tensor approach but that is hidden in the usual thermodynamic approach. The two approaches are connected by an interesting application of boundary perturbation theory for quantum systems.

The basic ideas and relations are developed in Sec. II, and their use for systems of noninteracting fermions and bosons is given in Sec. III. I then consider several examples, including the properties of quasi-continuous systems, relations for Fermi and Bose pressures, shape-dependent effects and anisotropies in Sec. IV A, and examples for particles in external fields in Sec. IV B. The results lead to several interesting problems for graduate courses in statistical mechanics.

II. PRESSURE IN STATISTICAL SYSTEMS

A. Pressure and the stress tensor

The pressure $P(\boldsymbol{x},t)$ of a system at a point $\boldsymbol{x}$ on a surface S at time t can be defined as the rate of momentum flow per unit area across a surface element $d\boldsymbol{S} = \hat{n}\,dS$, that is, in terms of the force per unit area or stress acting across the surface. P depends implicitly on the orientation of the surface through $\hat{n}$, but I will not indicate this dependence explicitly for notational simplicity, and because the apparent $\hat{n}$ dependence is absent for extensive, quasi-continuous systems. I will apply this definition in the quantum context, and will show that

$$P(\boldsymbol{x},t) = -\langle \hat{n} \cdot \overset{\leftrightarrow}{\mathbf{T}} \cdot \hat{n} \rangle, \tag{5}$$

where $\overset{\leftrightarrow}{\mathbf{T}}$ is the quantum mechanical stress tensor, and the average is over the statistical distribution of the quantum states occupied at temperature T.

For definiteness, consider a quantum system of N identical particles with the Lagrangian density

$$\mathcal{L} = \frac{i\hbar}{2}(\psi^* \partial_t \psi - \partial_t \psi^* \psi) - \frac{\hbar^2}{2m}\sum_{l=1}^{N}(\nabla_l \psi^*)\cdot(\nabla_l \psi)$$

$$- \psi^* V \psi, \tag{6}$$

where $\psi = \psi(x_1,\ldots,x_N,t)$ is the many-particle wave function of the system and $V(x_1,\ldots,x_N)$ is the potential. The corresponding Schrödinger equation is

$$i\hbar \partial_t \psi = -\frac{\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2 \psi + V\psi. \tag{7}$$

The momentum density at the point x for a system in a state $|\alpha\rangle$ with wave function ψ_α is

$$p_\alpha(x,t) = \frac{\hbar}{2i}\sum_{l=1}^{N}\int (\psi_\alpha^* \nabla_l \psi_\alpha - \nabla_l \psi_\alpha^* \psi_\alpha)\delta^3$$

$$\times(x-x_l)d^3 x_1 \cdots d^3 x_N, \tag{8}$$

a result obtained by integrating the sum of single-particle momentum operators $(\hbar/2i)(\psi_\alpha^* \nabla_l \psi_\alpha - \nabla_l \psi_\alpha^* \psi_\alpha)$ over the coordinates of the particles that are not observed. The integrations are over the volume V in which the system is confined. Similarly, the local number density is

$$n_\alpha(x,t) = \sum_{l=1}^{N}\int \psi_\alpha^* \psi_\alpha \delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N. \tag{9}$$

After some rearrangements, the time derivative of p_α can be written as

$$\frac{dp_\alpha(x,t)}{dt} = \frac{\hbar}{i}\sum_{l=1}^{N}\int (\partial_t \psi_\alpha^* \nabla_l \psi_\alpha - \nabla_l \psi_\alpha^* \partial_t \psi_\alpha)\delta^3$$

$$\times(x-x_l)d^3 x_1 \cdots d^3 x_N$$

$$+ \frac{\hbar}{2i}\sum_{l=1}^{N}\int \nabla_l(\psi_\alpha^* \partial_t \psi_\alpha - \partial_t \psi_\alpha^* \psi_\alpha)\delta^3$$

$$\times(x-x_l)d^3 x_1 \cdots d^3 x_N. \tag{10}$$

It is convenient to switch to a component labeling of p_α and consider $\partial_t p_{\alpha,i}$. I use the Schrödinger equation (7) to eliminate the time derivatives in Eq. (10), split the double sums that appear into terms with identical and different particle labels, and organize the results as much as possible into a set of divergences. After a straightforward calculation, I find that

$$\frac{dp_{\alpha,i}(x,t)}{dt} = -\sum_{l=1}^{N}\int \psi_\alpha^*(\nabla_{l,i}V)\psi_\alpha \delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N - \frac{\hbar^2}{2m}\sum_{l=1}^{N}\sum_{k=1}^{3}\int \nabla_{l,k}(\nabla_{l,i}\psi_\alpha^* \nabla_{l,k}\psi_\alpha + \nabla_{l,k}\psi_\alpha^* \nabla_{l,i}\psi_\alpha)$$

$$\times \delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N + \frac{\hbar^2}{2m}\sum_{l=1}^{N}\int \nabla_{l,i}(\nabla_{l,k}\psi_\alpha^* \nabla_{l,k}\psi_\alpha)\delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N$$

$$+ \frac{\hbar^2}{4m}\sum_{l=1}^{N}\int \nabla_{l,i}(\psi_\alpha^* \nabla_l^2 \psi_\alpha + \nabla_l^2 \psi_\alpha^* \psi_\alpha)\delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N + \text{surface terms}. \tag{11}$$

The surface terms result from the integration of divergences $\nabla_{l'}\cdot(\cdot)$ in variables $x_{l'}$ other than the selected variable $x = x_l$ using Gauss' theorem. These terms vanish for the usual boundary condition for the energy eigenstates; that is, $\psi_\alpha = 0$ for any of the coordinates on the boundary of the confining volume V.

The first term on the right-hand side of Eq. (11) is the force density $F_{\alpha,i}(x,t)$ at x. The remaining terms are in the form of a divergence, and the result can be written as

$$\frac{dp_{\alpha,i}}{dt}(x,t) = F_{\alpha,i}(x,t) + \nabla_k T_{ki}^\alpha(x,t), \tag{12}$$

or, in dyadic notation,

$$\frac{dp_\alpha}{dt}(x,t) = F_\alpha(x,t) + \nabla \cdot \overleftrightarrow{T}^\alpha(x,t), \tag{13}$$

where T_{ki}^α is the quantum stress tensor evaluated in the state $|\alpha\rangle$,

$$T_{ki}^\alpha = \frac{\partial \mathcal{L}}{\partial(\partial_k \psi^*)}\partial_i \psi^* + \frac{\partial \mathcal{L}}{\partial(\partial_k \psi)}\partial_i \psi - \mathcal{L}\delta_{k,i}$$

$$= -\frac{\hbar^2}{2m}\sum_{l=1}^{N}\int \Bigg[\nabla_{l,i}\psi_\alpha^* \nabla_{l,k}\psi_\alpha + \nabla_{l,k}\psi_\alpha^* \nabla_{l,i}\psi_\alpha$$

$$- \delta_{k,i}\nabla_l \psi_\alpha^* \cdot \nabla_l \psi_\alpha - \frac{1}{2}\delta_{k,i}(\psi_\alpha^* \nabla_l^2 \psi_\alpha$$

$$+ \nabla_l^2 \psi_\alpha^* \psi_\alpha)\Bigg]\delta^3(x-x_l)d^3 x_1 \cdots d^3 x_N. \tag{14}$$

Upon integrating Eq. (12) over a volume $V' \subseteq V$, one finds that the total momentum P in V' changes both because of the bulk action of the forces, and from the flow of momentum across the boundary surface $S' = \partial V'$,

$$\frac{dP_{\alpha,i}}{dt}(t) = \int_{V'}\frac{dp_{\alpha,i}}{dt}(x,t)d^3 x$$

$$= \int_{V'}F_{\alpha,i}(x,t)d^3 x + \int_{S'}dS_k T_{ki}^\alpha(x,t), \tag{15}$$

or, in dyadic notation,

$$\frac{dP_\alpha}{dt}(t) = \int_{V'}F_\alpha(x,t)d^3 x + \int_{S'}dS \cdot \overleftrightarrow{T}^\alpha(x,t). \tag{16}$$

With the conventional definition of the quantum mechanical stress tensor in Eq. (14), $d\boldsymbol{S} \cdot \overset{\leftrightarrow}{\boldsymbol{T}}$ is the rate of momentum flow across the surface element $d\boldsymbol{S} = \hat{n} dS$ *into* the volume V', with $\hat{n}$ the outward normal to the surface. The pressure at $\boldsymbol{x}$ is given by the momentum-flow per unit area *out* of V'. That is,

$$P_\alpha(\boldsymbol{x}, t) = -\hat{n} \cdot \overset{\leftrightarrow}{\boldsymbol{T}}^\alpha(\boldsymbol{x}, t) \cdot \hat{n}, \quad (\boldsymbol{x} \in S'). \tag{17}$$

For equilibrium quantum statistical mechanics, the relevant states $|\alpha\rangle$ are stationary states (that is, energy eigenstates), with $\psi_\alpha = \psi_\alpha(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) e^{-iE_\alpha t/\hbar}$. In this case, the explicit time dependence drops out in Eqs. (11)–(17), and ψ_α can be taken in these and the following expressions as the spatial wave function $\psi_\alpha(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$. The pressure, stress tensor, and force density are then independent of t; that is $\boldsymbol{P}_\alpha(\boldsymbol{x}, t) \rightarrow \boldsymbol{P}_\alpha(\boldsymbol{x})$, $\overset{\leftrightarrow}{\boldsymbol{T}}^\alpha(\boldsymbol{x}, t) \rightarrow \overset{\leftrightarrow}{\boldsymbol{T}}^\alpha(\boldsymbol{x})$, and $\boldsymbol{F}_\alpha(\boldsymbol{x}, t) \rightarrow \boldsymbol{F}_\alpha(\boldsymbol{x})$. Furthermore, $d\boldsymbol{p}_\alpha/dt = 0$, so that $-\boldsymbol{\nabla} \cdot \overset{\leftrightarrow}{\boldsymbol{T}} = \boldsymbol{F}$, and the divergence of the local stress is balanced by the force density. I will focus on this case for the remainder of the paper and use the definition

$$P_\alpha(\boldsymbol{x}) = -\hat{n} \cdot \overset{\leftrightarrow}{\boldsymbol{T}}^\alpha(\boldsymbol{x}) \cdot \hat{n}, \quad (\boldsymbol{x} \in S') \tag{18}$$

for the pressure at $\boldsymbol{x}$ in the state $|\alpha\rangle$, where $\overset{\leftrightarrow}{\boldsymbol{T}}^\alpha(\boldsymbol{x})$ given by Eq. (14) with ψ_α the spatial wave function.

I will first consider the case in which $V' = V$ is the volume in which the system is confined, and will consider a more general case in Sec. III. For $\boldsymbol{x}$ on the boundary surface $S = \partial V$, ψ_α and the derivatives of ψ parallel to the surface vanish. Thus, from Eq. (14),

$$P_\alpha(\boldsymbol{x}) = \frac{\hbar^2}{2m} \sum_{l=1}^N \int (\hat{n} \cdot \boldsymbol{\nabla}_l \psi_\alpha^*)(\hat{n} \cdot \boldsymbol{\nabla}_l \psi_\alpha) \delta^3$$
$$\times (\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N, \tag{19}$$

and the pressure $P_\alpha(\boldsymbol{x})$ in the state $|\alpha\rangle$ depends only on the normal derivatives of ψ_α at $\boldsymbol{x}$. To obtain the average pressure $P(\boldsymbol{x})$, I weight P_α by the statistical factor $e^{-\beta E_\alpha}/Z$ and sum over all energy eigenstates, with the result

$$P(\boldsymbol{x}) = \frac{1}{Z} \frac{\hbar^2}{2m} \sum_\alpha \sum_{l=1}^N \int (\hat{n} \cdot \boldsymbol{\nabla}_l \psi_\alpha^*)(\hat{n} \cdot \boldsymbol{\nabla}_l \psi_\alpha) e^{-\beta E_\alpha} \delta^3$$
$$\times (\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N. \tag{20}$$

Here, Z is the canonical partition function in Eq. (2). The sums are over all the completely symmetric states for Bose systems, and over all the completely antisymmetric states for Fermi systems.

The sums over eigenstates include sums over the extra quantum numbers necessary to label the states completely. For observables such as the total number density or pressure, which do not depend on the internal structure, the ψ's can be reduced to spatial wave functions, and the right-hand side of Eq. (20) multiplied by the appropriate degeneracy factor g. I will follow this convention throughout the paper.

Equation (20), or the more general form in Eq. (18), gives my basic "quantum kinetic theory" result. The differences between fermions and bosons enter only through the symmetry properties of the wave functions and the resulting differences in the sums over states. Before investigating these expressions in simple cases, I emphasize that the kinetic

definition of the pressure is intrinsically local and is expressed through the action of the momentum operators $-i\hbar\boldsymbol{\nabla}$, as would be expected on the basis of classical kinetic theory. It is not immediately clear how this definition of the pressure is connected with the usual thermodynamic definition in Eq. (4). I will first show that the two definitions are equivalent when one considers local variations of the volume in the relation $P = k_B T \partial \ln Z / \partial V$.

B. Pressure from the partition function

The thermodynamic definition (4) of the pressure in terms of the canonical partition function gives the relation

$$P = -\frac{1}{Z} \sum_\alpha \frac{\partial E_\alpha}{\partial V} e^{-\beta E_\alpha}. \tag{21}$$

A comparison of Eq. (21) with Eq. (20) suggests that $\partial E_\alpha/\partial V$ should be expressible in terms of the normal derivative of ψ_α on the boundary surface for local variations in V. This relation is easy to show using boundary perturbation theory. I consider a small change in the volume of the system implemented by displacing the boundary surface outward over a small surface patch ΔS through a normal displacement $\delta\boldsymbol{x} = \hat{n}\,\delta x(\boldsymbol{x})$ that varies smoothly over ΔS and vanishes elsewhere. The energy E'_α of the system in the distorted volume will differ from the energy E_α of the original system, with $E'_\alpha = E_\alpha + \delta E_\alpha$. The perturbed spatial wave function ψ'_α and the original wave function ψ_α satisfy the time-independent Schrödinger equation (7), as follows:

$$E'_\alpha \psi'_\alpha = -\frac{\hbar^2}{2m} \sum_{l=1}^N \boldsymbol{\nabla}_l^2 \psi'_\alpha + \mathrm{V}\psi'_\alpha, \tag{22a}$$

$$E_\alpha \psi_\alpha = -\frac{\hbar^2}{2m} \sum_{l=1}^N \boldsymbol{\nabla}_l^2 \psi + \mathrm{V}\psi. \tag{22b}$$

I multiply the adjoint of Eq. (22a) on the right by ψ_α and Eq. (22b) on the left by ψ'^*_α, subtract the resultant expressions, and find

$$\delta E_\alpha \psi'^*_\alpha \psi_\alpha = -\frac{\hbar^2}{2m} \sum_{l=1}^N \boldsymbol{\nabla}_l \cdot (\boldsymbol{\nabla}_l \psi'^*_\alpha \psi_\alpha - \psi'^*_\alpha \boldsymbol{\nabla}_l \psi_\alpha), \tag{23}$$

where I have assumed that the potential V is unchanged. An integration over the original volume gives

$$\delta E_\alpha \int_V \psi'^*_\alpha \psi_\alpha d^3 x_1 \cdots d^3 x_N$$
$$= -\frac{\hbar^2}{2m} \sum_{l=1}^N \int_S d\boldsymbol{S}(\boldsymbol{x}) \cdot \int_V (\boldsymbol{\nabla}_l \psi'^*_\alpha \psi_\alpha$$
$$- \psi'^*_\alpha \boldsymbol{\nabla}_l \psi_\alpha) \delta^3(\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N, \tag{24}$$

where the surface integration is defined in terms the variable $\boldsymbol{x}$.

The wave function ψ_α vanishes on the original surface S, so that the first term in parentheses in Eq. (24) vanishes. Similarly, $\psi'^*_\alpha = 0$ on the distorted surface S', so that the second term vanishes, except on the patch ΔS where the two surfaces differ, and the surface integration reduces to the

patch ΔS. For small normal displacements $\delta x = \hat{n} \, \delta x(x)$, ψ'_α can be approximated to first order on ΔS using the first non-zero term in its Taylor series expansion relative to S', $\psi'_\alpha \approx -\delta x \cdot \nabla \psi'_\alpha \approx -(\hat{n} \cdot \nabla \psi'_\alpha) \, \delta x$, where the variation of ψ'_α for small displacements parallel to ΔS does not contribute to the first order. Finally, taking ψ'_α equal to ψ_α in leading order and using the normalization condition for the wave function, I find a first-order expression for δE_α,

$$\delta E_\alpha = -\frac{\hbar^2}{2m} \sum_{l=1}^{N} \int_{\Delta S} dS \, \delta x \int_V (\hat{n} \cdot \nabla_l \psi_\alpha^*)(\hat{n} \cdot \nabla_l \psi_\alpha^*) \, \delta^3$$
$$\times (x - x_l) d^3 x_1 \cdots d^3 x_N. \tag{25}$$

The integrand in the volume integral can again be taken as constant to leading order for x on ΔS. The remaining surface integral gives the volume change $\delta V = \int_{\Delta S} dS \, \delta x$, so that

$$\frac{\partial E_\alpha(x)}{\partial V} = -\frac{\hbar^2}{2m} \sum_{l=1}^{N} \int_V (\hat{n} \cdot \nabla_l \psi_\alpha^*)(\hat{n} \cdot \nabla_l \psi_\alpha^*) \, \delta^3$$
$$\times (x - x_l) d^3 x_1 \cdots d^3 x_N. \tag{26}$$

The substitution of this expression in Eq. (21) reproduces Eq. (20), and the kinetic and thermodynamic definitions of the local pressure $P(x)$ agree. For homogeneous isotropic systems, the factor $(\hat{n} \cdot \nabla \psi_\alpha^*)(\hat{n} \cdot \nabla \psi_\alpha^*)$ in the integral in Eq. (25) has the same value at all points on S, the surface integral can be extended to the entire surface, and the calculation reproduces the usual x-independent expression $P = k_B T \partial \ln Z / \partial V$.

C. Generalizations

1. Electromagnetic interactions

The results described in Sec. II can be generalized in various ways. For example, in the presence of electromagnetic interactions, the Lagrangian in Eq. (6) becomes

$$\mathcal{L} = \frac{i\hbar}{2} (\psi^* \partial_t \psi - \partial_t \psi^* \psi) - \frac{1}{2m} \sum_{l=1}^{N} \left[\left(i\hbar \nabla_l - \frac{e}{c} A_l \right) \psi^* \right.$$
$$\left. \cdot \left(-i\hbar \nabla_l - \frac{e}{c} A_l \right) \psi - \psi^* \Phi_i \psi \right], \tag{27}$$

where A_l and Φ_l are the respective vector and scalar potentials evaluated at the position x_l of particle l, and the particles are treated as identical, with charge e. The pressure of the system is related to the rate of change of the kinetic momentum $mv = p - eA/c$ summed over the particles. A rather lengthy calculation for a state $|\alpha\rangle$ gives

$$\frac{d}{dt} \left(p - \frac{e}{c} A \right)_\alpha (x,t) = F_\alpha(x,t) + \nabla \cdot \overset{\leftrightarrow}{T}^\alpha(x,t), \tag{28}$$

where F is the Lorentz force density

$$F_\alpha(x,t) = \sum_{l=1}^{N} \int e \psi_\alpha^* E \psi_\alpha \delta^3 (x - x_l) d^3 x_1 \cdots d^3 x_N$$
$$+ \frac{e}{2mc} \sum_{l=1}^{N} \int \left[\left(i\hbar \nabla_l - \frac{e}{c} A_l \right) \psi_\alpha^* \times B_l \psi_\alpha \right.$$
$$\left. - \psi_\alpha^* B_l \times \left(i\hbar \nabla_l - \frac{e}{c} A_l \right) \psi_\alpha \right] \delta^3$$
$$\times (x - x_l) d^3 x_1 \cdots d^3 x_N, \tag{29}$$

and T_{ki}^α is the gauge-invariant stress tensor

$$T_{k,i}^\alpha = -\frac{1}{2m} \sum_{l=1}^{N} \int \left[\left[\left(i\hbar \nabla - \frac{e}{c} A \right)_{l,i} \psi_\alpha^* \left(-i\hbar \nabla - \frac{e}{c} A \right)_{l,k} \right. \right.$$
$$\times \psi_\alpha + \left(i\hbar \nabla - \frac{e}{c} A \right)_{l,k} \psi_\alpha^* \left(-i\hbar \nabla - \frac{e}{c} A \right)_{l,i}$$
$$\times \psi_\alpha - \delta_{k,i} \left(i\hbar \nabla - \frac{e}{c} A \right)_l \psi_\alpha^* \cdot \left(-i\hbar \nabla - \frac{e}{c} A \right)_l \psi_\alpha$$
$$+ \frac{1}{2} \delta_{k,i} \left(\psi_\alpha^* \left(-i\hbar \nabla - \frac{e}{c} A \right)_l^2 \psi_\alpha \right)$$
$$\left. + \left(i\hbar \nabla - \frac{e}{c} A \right)_l^2 \psi_\alpha^* \psi_\alpha \right) \right] \delta^3 (x - x_l) d^3 x_1 \cdots d^3 x_N. \tag{30}$$

The force density has the expected form, $F \sim eE + (e/c)v \times B$.

The pressure is given by Eq. (17), or, for the case of static fields A and Φ and stationary states $|\alpha\rangle$, by Eq. (18). If the latter is evaluated on the confining surface where the spatial wave function ψ_α vanishes, the A-dependent terms in Eq. (30) vanish, and the time-independent pressure $P_\alpha(x)$ is again given by the expression in Eq. (19) and depends only on the normal derivatives of ψ and ψ^*. The more general expression in Eq. (18) can be used for a surface element in the interior of the confining volume.

A calculation similar to that in Sec. II B also reproduces Eq. (19) for static fields and stationary systems. The A-dependent terms again drop out on the confining surface, and the expression for δE_α obtained in boundary perturbation theory reduces to Eq. (25).

2. Wave-type equations

Quantized systems of bosons such as photons, mesons, or phonons in a solid satisfy wave-type equations; for example, the standard wave equation

$$\frac{1}{c^2} \partial_t^2 \phi - \sum_{l=1}^{N} \nabla_l^2 \phi + \frac{m^2 c^2}{\hbar^2} \phi = 0, \tag{31}$$

with or without the extra mass term or potential $m^2(x_1, \ldots, x_N)$. The normalization of ϕ is given in terms of the covariant current density,[10] and reduces for positive energy eigenstates to

$$\int \frac{i}{c}(\phi^* \partial_t \phi - \partial_t \phi^* \phi) d^3 x_1 \cdots d^3 x_N$$

$$= \frac{2E}{\hbar c} \int \phi^* \phi \, d^3 x_1 \cdots d^3 x_N = 1. \tag{32}$$

An appropriate Lagrangian density for such systems is

$$\mathcal{L} = \hbar c \left(\frac{1}{c^2} \partial_t \phi^* \partial_t \phi - \sum_{l=1}^{N} \boldsymbol{\nabla}_l \phi^* \cdot \boldsymbol{\nabla}_l \phi - \phi^* \frac{m^2 c^2}{\hbar^2} \phi \right). \tag{33}$$

The corresponding momentum density $\boldsymbol{p}(\boldsymbol{x},t)$ is

$$\boldsymbol{p}(\boldsymbol{x},t) = -\frac{\hbar}{c} \sum_{l=1}^{N} \int (\boldsymbol{\nabla}_l \phi^* \partial_t \phi + \partial_t \phi^* \boldsymbol{\nabla}_l \phi) \delta^3$$

$$\times (\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N. \tag{34}$$

Calculations of $d\boldsymbol{p}/dt$ similar to those above give the same formal result for the pressure as in Eq. (18), but with the stress tensor now given by

$$T_{ki} = -\hbar c \sum_{l=1}^{N} \int (\boldsymbol{\nabla}_{l,i} \phi^* \boldsymbol{\nabla}_{l,k} \phi + \boldsymbol{\nabla}_{l,k} \phi^* \boldsymbol{\nabla}_{l,i} \phi$$

$$- \delta_{k,i} \mathcal{L}) \delta^3(\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N. \tag{35}$$

Equation (35) can be written in an energy eigenstate $|\alpha\rangle$ with wave function $\phi = \phi_\alpha(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) e^{-iE_\alpha t/\hbar}$ as

$$T_{ki}^\alpha = -\hbar c \sum_{l=1}^{N} \int [\boldsymbol{\nabla}_{l,i} \phi_\alpha^* \boldsymbol{\nabla}_{l,k} \phi_\alpha + \boldsymbol{\nabla}_{l,k} \phi_\alpha^* \boldsymbol{\nabla}_{l,i} \phi_\alpha$$

$$- \delta_{k,i} \boldsymbol{\nabla}_l \phi_\alpha^* \cdot \boldsymbol{\nabla}_l \phi_\alpha - \tfrac{1}{2} \delta_{k,i} (\phi_\alpha^* \boldsymbol{\nabla}_l^2 \phi_\alpha + \boldsymbol{\nabla}_l^2 \phi_\alpha^* \phi_\alpha)]$$

$$\times \delta^3(\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N. \tag{36}$$

The corresponding pressure for $\boldsymbol{x}$ on a boundary surface $S = \partial V$ where $\phi \equiv 0$ is given by

$$P_\alpha(\boldsymbol{x}) = \hbar c \sum_{l=1}^{N} \int (\hat{n} \cdot \boldsymbol{\nabla}_l \phi_\alpha^*)(\hat{n} \cdot \boldsymbol{\nabla}_l \phi_\alpha) \delta^3$$

$$\times (\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N, \tag{37}$$

and depends only on the normal derivatives of ϕ on the boundary. For a general surface $S' \subset V$, the full form of T_{ki}^α must be used. The pressure in the canonical ensemble is

$$P(\boldsymbol{x}) = \frac{1}{Z} \sum_\alpha P_\alpha(\boldsymbol{x}) e^{-\beta E_\alpha}. \tag{38}$$

It is easy to show that the same result follows from the usual thermodynamic relation in Eq. (21). Thus, from Eq. (31),

$$\frac{E_\alpha^2}{\hbar^2 c^2} \phi_\alpha = -\boldsymbol{\nabla}^2 \phi_\alpha + \frac{m^2 c^2}{\hbar^2} \phi_\alpha. \tag{39}$$

An equation of the same form with a perturbed energy E_α' holds for the perturbed wave function ϕ_α' that results from a local displacement of the boundary. By combining the two equations, I find, as the analog of Eq. (23), that

$$\frac{2E_\alpha \delta E_\alpha}{\hbar c} \phi_\alpha'^* \phi_\alpha = -\hbar c \sum_{l=1}^{N} \boldsymbol{\nabla}_l \cdot (\boldsymbol{\nabla}_l \phi_\alpha'^* \phi_\alpha$$

$$- \phi_\alpha'^* \boldsymbol{\nabla}_l \phi_\alpha). \tag{40}$$

Manipulations equivalent to those following Eq. (23) and the use of the normalization condition (32) give the result

$$\frac{\partial E_\alpha}{\partial V}(\boldsymbol{x}) = -\hbar c \sum_{l=1}^{N} \int (\hat{n} \cdot \boldsymbol{\nabla}_l \phi_\alpha^*)(\hat{n} \cdot \boldsymbol{\nabla}_l \phi_\alpha) \delta^3$$

$$\times (\boldsymbol{x} - \boldsymbol{x}_l) d^3 x_1 \cdots d^3 x_N, \tag{41}$$

for local variations of the boundary surface. Finally, the use of the thermodynamic relation Eq. (21) reproduces the expression for the local pressure in Eq. (38). I emphasize, however, that the equation $P_\alpha(\boldsymbol{x}) = -\hat{n} \cdot \boldsymbol{T}_\alpha \cdot \hat{n}$ for the local pressure in a state $|\alpha\rangle$ holds more generally than Eq. (37) and does not require that $\boldsymbol{x}$ be on the boundary surface.

III. PRESSURE IN NONINTERACTING BOSE AND FERMI SYSTEMS

A. Bose systems

As a first example, I consider the important case of noninteracting bosons in an external field. The Hamiltonian for N noninteracting particles is a sum of N identical single-particle Hamiltonians H_1: $H = \sum_{l=1}^{N} H_1(\boldsymbol{x}_l)$. The wave functions ψ_k for the single-particle states $|k\rangle$ satisfy the Schrödinger equations $H_1 \psi_k(\boldsymbol{x}_1) = E_k \psi_k(\boldsymbol{x}_1)$. I will suppose that the energy eigenvalues have been ordered so that $E_1 < E_2 < E_3 < \cdots$. The total energies are simply sums of single-particle energies E_k, and can be labeled by the number of particles in each single-particle eigenstate $|k\rangle$, as

$$E_{n_1,n_2,\ldots} = n_1 E_1 + n_2 E_2 + \cdots, \tag{42}$$

where $n_1 + n_2 + \cdots = N$. The full wave function for N bosons with n_1 in state $|k_1\rangle$, n_2 in state $|k_2\rangle, \cdots$ is then a fully symmetric sum of product wave functions,

$$\psi_{n_1,n_2,\ldots}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \sum_P [\overbrace{\psi_1 \cdots \psi_1}^{n_1 \text{ factors}} \overbrace{\psi_2 \cdots \psi_2}^{n_2 \text{ factors}} \cdots]$$

$$\times (P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)), \tag{43}$$

where the sum is over all permutations P of N objects, and wave function factors with $n_k = 0$ are to be replaced by 1. The coordinates of the successive wave functions with $n_k \neq 0$ are given in each term in the sum by the corresponding coordinates in the permutation P of $\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N$. The set of n_k's gives a unique labeling of the state. Their values are restricted by the condition $\sum_k n_k = N$.

The number density of particles at a point $\boldsymbol{x}$ is given for a definite state by Eq. (9). The total density reduces after the integrations to

$$n_{n_1,n_2,\ldots}(\boldsymbol{x}) = \sum_k n_k \psi_k^*(\boldsymbol{x}) \psi_k(\boldsymbol{x}), \tag{44}$$

and a final integration over $\boldsymbol{x}$ gives the total number of particles N because $\sum_k n_k = N$. Similarly, from Eq. (19), the pressure on the boundary surface associated with the given state is

$$P_{n_1,n_2,...}(\boldsymbol{x}) = \frac{\hbar^2}{2m} \sum_k n_k (\hat{n} \cdot \boldsymbol{\nabla} \psi_k^*(\boldsymbol{x}))(\hat{n} \cdot \boldsymbol{\nabla} \psi_k(\boldsymbol{x})). \tag{45}$$

More generally, for a surface $S' = \partial V'$, $V' \subset V$,

$$P_{n_1,n_2,...}(\boldsymbol{x}) = -\sum_k n_k \hat{n} \cdot \overleftrightarrow{\boldsymbol{T}}^k \cdot \hat{n}, \quad \boldsymbol{x} \in S', \tag{46}$$

where the tensor T_{ij}^k is given in Eq. (14).

It is difficult to work with the canonical distribution for bosons because of the restriction $\Sigma_k n_k = N$. I will therefore change to the grand distribution as is usually done. I multiply Eq. (44) by the Boltzmann factor $e^{-\beta E_{n_1,n_2,...}}$ for the specified energy and by a factor $e^{\beta \mu N}$, which will be used to enforce the correct average number of particles, sum over the n_k and N, and find that

$$\begin{aligned}
n(\boldsymbol{x}) &= \frac{1}{\mathcal{Z}} \sum_k \sum_{n_1,n_2,...} \sum_N \delta_{n_1+n_2+...,N} n_k \\
&\quad \times \psi_k^*(\boldsymbol{x}) \psi_k(\boldsymbol{x}) e^{\beta(\mu N - \Sigma_j n_j E_j)} \\
&= \frac{1}{\mathcal{Z}} \sum_k \left(\sum_{n_k} n_k \psi_k^*(\boldsymbol{x}) \psi_k(\boldsymbol{x}) e^{-\beta(E_k-\mu)n_k} \right) \\
&\quad \times \prod_{k' \neq k} \left(\sum_{n_{k'}} e^{-\beta(E_{k'}-\mu)n_{k'}} \right) \\
&= \frac{1}{\mathcal{Z}} \sum_k \psi_k^*(\boldsymbol{x}) \psi_k(\boldsymbol{x}) \frac{e^{-\beta(E_k-\mu)}}{(1-e^{-\beta(E_k-\mu)})^2} \\
&\quad \times \prod_{k' \neq k} \left(\frac{1}{1-e^{-\beta(E_{k'}-\mu)}} \right), \tag{47}
\end{aligned}$$

where convergence of the sum requires that $E_k - \mu > 0$. $\mathcal{Z}$ is the grand partition function

$$\mathcal{Z} = \prod_k \left(\frac{1}{1-e^{-\beta(E_k-\mu)}} \right), \tag{48}$$

so that Eq. (47) reduces to

$$n(\boldsymbol{x}) = \sum_k \psi_k^*(\boldsymbol{x}) \psi_k(\boldsymbol{x}) (e^{\beta(E_k-\mu)}-1)^{-1}. \tag{49}$$

Equation (49) is just the result that would be expected. Each product of wave functions $\psi_k^* \psi_k$ appears with a weight that is just the average occupation number of the state $|k\rangle$, as calculated for the usual Bose distribution for noninteracting particles.[1-9]

If there are spin or other internal degeneracies, the internal factors in the wave functions ψ's in Eq. (49) can be suppressed and the wave functions reduced to their spatial components, provided that the right-hand side of Eq. (49) is multiplied by the appropriate degeneracy factor g and the sum is taken to run only over nondegenerate energies.

The integral of $n(\boldsymbol{x})$ gives the average number of particles N in the entire distribution,

$$N = \sum_k (e^{\beta(E_k-\mu)}-1)^{-1}. \tag{50}$$

Equation (50) gives an implicit relation for μ in agreement with the thermodynamic expression $N = k_B T (\partial \ln \mathcal{Z}/\partial \mu)$.

A similar calculation gives the result for the pressure at $\boldsymbol{x}$, again of a form that could be anticipated from the single-particle forms of Eqs. (14), (18), and (19):

$$P(\boldsymbol{x}) = -\sum_k \hat{n} \cdot \overleftrightarrow{\boldsymbol{T}}^k \cdot \hat{n} (e^{\beta(E_k-\mu)}-1)^{-1} \tag{51}$$

$$\begin{aligned}
&= \frac{\hbar^2}{2m} \sum_k (\hat{n} \cdot \boldsymbol{\nabla} \psi_k^*(\boldsymbol{x}))(\hat{n} \cdot \boldsymbol{\nabla} \psi_k(\boldsymbol{x})) \\
&\quad \times (e^{\beta(E_k-\mu)}-1)^{-1}. \tag{52}
\end{aligned}$$

The first form holds for $\boldsymbol{x}$ on a surface S' inside the confining volume, and the second form for $\boldsymbol{x}$ on the confining surface $S = \partial V$. For $T \to 0$, Eq. (52) gives $P(\boldsymbol{x}) \to (N\hbar^2/2m)(\hat{n} \cdot \boldsymbol{\nabla} \psi_0^*(\boldsymbol{x}))(\hat{n} \cdot \boldsymbol{\nabla} \psi_0(\boldsymbol{x}))$. Note that the pressure does not vanish exactly for a system confined in a finite volume even at $T = 0$, a result connected to the kinetic picture and the uncertainty relation.

The pressure in systems of noninteracting bosons also satisfying the wave equation (31) is given formally by the expression in Eq. (51), with $\boldsymbol{T}$ now given by the single-particle form of Eq. (37). The analog of Eq. (52) is therefore

$$\begin{aligned}
P(\boldsymbol{x}) &= \hbar c \sum_k (\hat{n} \cdot \boldsymbol{\nabla} \phi_k^*(\boldsymbol{x}))(\hat{n} \cdot \boldsymbol{\nabla} \phi_k(\boldsymbol{x})) \\
&\quad \times (e^{\beta(E_k-\mu)}-1)^{-1}. \tag{53}
\end{aligned}$$

B. Fermi systems

The composite state of N noninteracting fermions is specified completely by the number of particles n_k in each single-particle state $|k\rangle$ where $n_k = 0$ or 1. The energy of the state $|n_1,n_2,...\rangle$ is just $E_{n_1,n_2,...} = \Sigma_k n_k E_k$, as in Eq. (42). The corresponding wave function is given by the completely antisymmetric sum

$$\begin{aligned}
\psi_{n_1,n_2,...}(\boldsymbol{x}_1,...,\boldsymbol{x}_N) &= \frac{1}{\sqrt{N!}} \sum_P (-)^P \left[\overset{n_1}{\overbrace{\psi_1}} \overset{n_2}{\overbrace{\psi_2}} ... \right] \\
&\quad \times (P(\boldsymbol{x}_1,...,\boldsymbol{x}_N)), \tag{54}
\end{aligned}$$

where $(-)^P$ is the signature of the permutation P of N objects and $\Sigma_k n_k = N$. The factors of wave functions ψ_k with $n_k = 0$ are to be replaced by 1. The coordinates of successive wave functions with $n_k = 1$ are given in each term in the sum by the corresponding coordinates in the permutation P of $\boldsymbol{x}_1,...,\boldsymbol{x}_N$. The n's are restricted by the condition that their sum be N.

The number density and pressure of the particles in the specified state are given at a point $\boldsymbol{x}$ by Eqs. (9) and (19), respectively, and reduce after the integrations are performed to the expressions in Eqs. (44) and (45), or more generally Eq. (46), just as for bosons. The difference between the two cases is entirely in the allowed values of the n's. The sum for fermions can be performed simply in the grand statistical distribution, with, for example,

$$n(x) = \frac{1}{\mathcal{Z}} \sum_k \sum_{n_1, n_2, \cdots = 0,1} \sum_N \delta_{n_1 + n_2 + \dots, N} n_k$$

$$\times \psi_k^*(x)\psi_k(x) e^{\beta(\mu N - \Sigma_j n_j E_j)}$$

$$= \frac{1}{\mathcal{Z}} \sum_k \psi_k^*(x)\psi_k(x) e^{-\beta(E_k - \mu)}$$

$$\times \prod_{k' \neq k} (1 + e^{-\beta(E_{k'} - \mu)})$$

$$= \sum_k \psi_k^*(x)\psi_k(x)(e^{\beta(E_k - \mu)} + 1)^{-1}, \tag{55}$$

where I have used the relation

$$\mathcal{Z} = \prod_k (1 + e^{-\beta(E_k - \mu)}). \tag{56}$$

The expression in Eq. (55) is again what would be expected because the final factor is the average occupation number of the state $|k\rangle$ in the grand ensemble. Similarly, using Eq. (45),

$$P(x) = \frac{\hbar^2}{2m} \sum_k (\hat{n} \cdot \nabla \psi_k^*(x))(\hat{n} \cdot \nabla \psi(x))$$

$$\times (e^{\beta(E_k - \mu)} + 1)^{-1}, \tag{57}$$

or, more generally,

$$P(x) = -\sum_k \hat{n} \cdot \overleftrightarrow{T}^k \cdot \hat{n} (e^{\beta(E_k - \mu)} + 1)^{-1}, \tag{58}$$

where $\overleftrightarrow{T}^k$ is the single-particle version of Eq. (14). If the system has internal spin-type degeneracies, the ψ's in Eq. (57) can be reduced to the spatial factors in the full wave functions, and the sum restricted to the nondegenerate spatial eigenstates after multiplying the right-hand side of Eq. (14) by the degeneracy factor g.

IV. EXAMPLES

A. Quasi-continuous systems

1. General considerations

The systems to which statistical descriptions are applied most frequently are large, extensive systems in which the potentials are uniform or periodic. A well-known theorem shows that the number of eigenvalues E_k smaller than a fixed value E increases proportionally with the volume of the system for $V \to \infty$. [See Kac[11] for a famous discussion of this result and its history in the context of the spectrum of a drum.] The eigenvalues therefore pack together for large V, surface effects on the spectrum become negligible, and it is plausible that the sums over states in the preceding sections can be converted to integrals when there are many states with energies less than $k_B T$. The main question concerns the behavior of the wave functions in the limit of large V. We expect that the products $\psi^*(x)\psi(x)$ and $\nabla\psi^*(x) \cdot \nabla\psi(x)$ will each reduce for large V to the sum of a term describing their smooth average behavior, and extra rapidly oscillating terms that average approximately to zero. The result should again be insensitive to surface effects for sufficiently large V.

These ideas can be illustrated for a uniform system in D dimensions in a box with sides L_i, $i = 1, 2, \dots, D$. The wave functions and energies are

$$\psi_{\{n\}}(x) = \prod_{i=1}^D \sqrt{\frac{2}{L_i}} \sin \frac{\pi n_i x_i}{L_i}, \quad E_{\{n\}} = \sum_{i=1}^D n_i^2 \frac{h^2}{8mL_i^2}, \tag{59}$$

where $\{n\} = (n_1, \dots, n_D)$ with $n_i = 1, 2, \dots$ only. Equation (59) gives

$$\psi_{\{n\}}^*(x)\psi_{\{n\}}(x) = \frac{1}{V_D} \prod_{i=1}^D \left(1 - 2\cos\frac{2\pi n_i x_i}{L_i}\right), \tag{60}$$

where $V_D = \Pi_i L_i$ is the volume of the D-dimensional parallelepiped in which the system is confined, and the state label k in earlier equations is now given explicitly by the multi-index $n_1, n_2, \dots, n_D$.

The typical index for states excited at temperature T is $n_{ex} \sim (8mk_B T V^{2/D}/h^2)^{1/2}$. If n_{ex} is large, many states will be excited as required for the conversion of sums to integrals, and the oscillating terms in Eq. (60) will average to zero over small regions of the box. Then, for observations over such regions, $\psi^*\psi \approx 1/V_D$, a result independent of the shape of V_D. This result is the same as that obtained using the standard approximation of running waves with periodic boundary conditions, $\psi \approx (1/\sqrt{V})\exp(i\Sigma_j \pi n_j x_j/L_j)$. An independent argument shows that the sums of the oscillating terms vanish rapidly at fixed x as the numbers of significant terms in the summations grow. Because the level spacings tend to zero for $V_D \to \infty$, either argument shows that only the leading term in Eq. (60) is important for large systems.

If I drop the oscillating terms in Eq. (60), the expression for the local number density for uniform Fermi and Bose systems becomes

$$n(x) \approx \frac{1}{V_D} \sum_{n_1, \dots, n_D} (e^{\beta(E_{n_1, \dots, n_D} - \mu)} \pm 1)^{-1}, \tag{61}$$

where the upper and lower signs refer to Fermi and Bose systems, respectively. The sums can be converted approximately to integrals by repeated use of the Euler–Maclaurin summation formula

$$\sum_{n=1}^\infty f(n) = \int_0^\infty f(n)dn - \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0)$$

$$+ \cdots. \tag{62}$$

The odd-order derivatives $f^{(2k+1)}$ that appear in the Euler–Maclaurin formula vanish at $n_i = 0, \infty$ for the function in Eq. (61). The first two terms in Eq. (62) are therefore all that survive up to exponentially small corrections that can be investigated using Poisson summation. I retain only the leading corrections, which yields

$$n(x) \approx \frac{1}{V_D} \int_0^\infty dn_1 dn_2 \cdots dn_D (e^{\beta(\Sigma_i (h^2/8mL_i^2)n_i^2 - \mu)} \pm 1)^{-1}$$

$$\times \left(1 - \frac{1}{2}\sum_i \delta(n_i) + \cdots\right). \tag{63}$$

At this point, a change to the momentum variables $p_i = (h/2L_i)n_i$ gives the familiar expression for the leading term, plus corrections that vanish as $V_D^{-1/D}$ for $V_D \to \infty$:

$$n(\boldsymbol{x}) = \int \frac{d^D p}{h^D} (e^{\beta(\mathrm{p}_D^2/2m - \mu)} \pm 1)^{-1}$$

$$- \sum_i \frac{h}{2L_i} \int \frac{d^{D-1}p}{h^{D-1}} (e^{\beta(\mathrm{p}_{D-1}^2/2m - \mu)} \pm 1)^{-1}$$

$$+ O(1/L^2), \qquad (64)$$

where $\boldsymbol{p}_{D-1}$ is the momentum vector in the $D-1$ dimensional subspace orthogonal to the i direction. The momentum integrations extend over the infinite interval $(-\infty, \infty)$, a Brillouin zone, or otherwise as appropriate. The corrections are of order $\hbar/\bar{p}_i L_i$ for $\bar{p}_i$, the typical value of the ith component of the momentum in the leading term; that is, of order $\hbar/\sqrt{mk_B T} L_i$ for nondegenerate systems.

Note that the final result for the leading term is isotropic in momentum space even though the original spectrum in Eq. (59) involves different excitations for motions in the different directions. With enough energy levels occupied in the thermal distribution, the shape-dependent features of the spectrum become unimportant, as noted by Kac.[11] This isotropy in leading order appears to be general for quasi-continuous systems; see, for example, Sec. IV B 1.

2. Fermi and Bose pressures

A calculation of the pressure using the above method and either of Eqs. (51) or (52) for nonrelativistic Bose systems, or Eqs. (57) or (58) for Fermi systems, leads to analogous results for the pressure on a surface with normal $\hat{n}$,

$$P(\boldsymbol{x}) = \int \frac{d^D p}{h^D} \frac{(\hat{n} \cdot \boldsymbol{p})^2}{m} (e^{\beta(\mathrm{p}_D^2/2m - \mu)} \pm 1)^{-1} + \cdots \qquad (65)$$

$$= \frac{2}{D} \int \frac{d^D p}{h^D} E(\boldsymbol{p}) (e^{\beta(E(\mathrm{p}) - \mu)} \pm 1)^{-1} + \cdots$$

$$= \frac{2}{D} \langle E \rangle + \cdots, \qquad (66)$$

with corrections that again vanish as $V_D^{-1/D}$ for $V_D \rightarrow \infty$. The Bose and Fermi statistical factors in the integrals are isotropic in momentum space. Thus, the leading term in the expression for the pressure is independent of the direction of $\hat{n}$, and the results can be expressed in terms of the average energies as indicated.

I emphasize that this result for the local pressure follows directly from the definition of the pressure in terms of the stress on a surface. The factors of $\hat{n} \cdot \boldsymbol{p}$ in Eq. (65) arise from the momentum operators $-i\hbar \boldsymbol{\nabla}$ in $-\hat{n} \cdot \overleftrightarrow{T} \cdot \hat{n}$, and correspond directly to the momenta that appear in the elementary classical derivation of the pressure in a gas. That is, the pressure is associated with "particles bouncing off the wall."

The thermodynamic definition gives the same pressure for the quasi-homogeneous system under consideration, and the two definitions are connected by boundary perturbation theory, as shown in Sec. II B. The derivation given there can be generalized to an arbitrary surface inside the volume V, but is only useful provided that, as here, enough is known about the wave functions to allow explicit evaluation of their derivatives.

It is easy to derive the nonclassical properties of the Fermi and Bose pressures. An integration by parts in spherical coordinates brings Eq. (66) to the form

$$P(\boldsymbol{x}) = \pm k_B T \int \frac{d^D p}{h^D} \ln(1 \pm e^{-\beta(\mathrm{p}_D^2/2m - \mu)})$$

$$= \mp k_B T \int \frac{d^D p}{h^D} \ln(1 \mp \tilde{n}(\boldsymbol{p})), \qquad (67)$$

where $\tilde{n}(\boldsymbol{p})$ is the Fermi or Bose statistical factor in Eq. (66). If I use the inequalities $-\ln(1-x) > x$ and $\ln(1+x) < x$, and the fact that the integral of $\tilde{n}(\boldsymbol{p})$ gives the number density $n(\boldsymbol{x})$, I find that

$$P_{\mathrm{Bose}}(\boldsymbol{x}) < n(\boldsymbol{x}) k_B T < P_{\mathrm{Fermi}}(\boldsymbol{x}). \qquad (68)$$

The difference clearly arises in the momentum flow or stress picture from the necessity that the occupied single-particle states all be different for Fermi–Dirac statistics. This requirement forces the appearance of higher momentum states than are needed in the Bose–Einstein case, and a higher pressure for fixed N and T.

As an example of Bose pressure, I will calculate the pressure of an equilibrium system of noninteracting neutral mesons with mass m. The system will be taken as extensive or quasi-continuous in dimension D. The pressure on the boundary surface is given in a state $|\alpha\rangle$ by Eq. (37). It also can be calculated on an interior surface using the stress tensor in Eq. (36) and the definition in Eq. (18), giving the same average result for large volumes V_D. I will use Eq. (37) and the single-particle wave functions in a box normalized according to Eq. (32):

$$\phi_{p_1, \ldots, p_D}(\boldsymbol{x}) = \sqrt{\frac{\hbar c}{2E(\boldsymbol{p})}}^D \prod_{i=1}^{D} \sqrt{\frac{2}{L_i}} \sin \frac{p_i x_i}{\hbar},$$

$$p_i = \frac{h}{2L_i} n_i, \quad (n_i = 1, 2, \ldots). \qquad (69)$$

By averaging with the Bose statistical factor, I obtain the pressure P_i in the i direction as

$$P_i(\boldsymbol{x}) = \frac{1}{V_D} \int \frac{d^D p}{h^D} \frac{(p_i c)^2}{2E(\boldsymbol{p})} (e^{\beta(E(\mathrm{p}) - \mu)} - 1)^{-1}, \qquad (70)$$

where $E(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4}$. In the limit $m \rightarrow 0$, Eq. (70) reduces to the expression for the pressure for black-body radiation or for phonons in a solid up to the necessary inclusion of the statistical factors for spins or polarizations and the use of the correct ranges of integration in the case of phonons. Thus, for black-body radiation in three dimensions, including the spin degeneracy factor 2, and using the isotropy in momentum space and the fact that $\mu = 0$ because photon number is not conserved, I find

$$P(\boldsymbol{x}) = \frac{1}{3V} \int \frac{d^3 p}{h^3} \frac{pc}{e^{\beta pc} - 1}$$

$$= \frac{\hbar}{3\pi^2 c^3 V} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta \hbar \omega} - 1} = \frac{\langle E \rangle}{3V}, \qquad (71)$$

which is the usual result. However, I again emphasize that the calculation is direct, and is clearly connected to the flow of momentum across the surface through the discussion in Sec. II C 1. No thermodynamic relations were used.

An example for Fermi systems that makes a good homework problem and shows the relation of pressure to momentum flow is the calculation of the Fermi pressure at $T = 0$ starting from the stress tensor. The usual argument for com-

pletely degenerate Fermi systems shows that all energy levels up to a Fermi energy E_F determined by N must be occupied. Then, from Eq. (58), $P(\boldsymbol{x}) = -\Sigma_k \theta(E_F - E_k)\hat{n} \cdot \vec{\boldsymbol{T}}^k \cdot \hat{n}$, where θ is the step function, and $\theta(x) = 1(0)$ for $x > 0$ ($x < 0$). The remaining calculation is simple for continuous systems, and leads directly to the thermodynamic result without the use of any thermodynamic relations.

3. Anisotropic pressures

The corrections from the conversion of sums to integrals in Eq. (64) and the corrections from finite-sized effects in the spectrum[11] are shape dependent. This shape dependence leads to anisotropic stresses or pressures for finite systems. Consider, for example, the limit in which one of the dimensions of the rectangular box, say L_1, becomes small while the other dimensions remain large. If the lowest energy for motion in the 1 direction is large on the scale of $k_B T$, $h^2/8mL_1^2 \gg k_B T$, the sum over n_1 converges rapidly, and conversion of that sum to an integral with only small residual corrections is not possible. If I keep only the leading term in n_1 and treat the large dimensions in the continuum limit, the number density becomes

$$n(\boldsymbol{x}) \rightarrow \frac{2}{L_1} \sin^2 \frac{\pi x_1}{L_1} \int \frac{d^{D-1}p}{h^{D-1}} (e^{-\beta(p_{D-1}^2/2m - \mu')} \pm 1)^{-1},$$
(72)

where $\mu' = \mu - E_1$ with $E_1 = h^2/8mL_1^2$ the ground state energy for motion in direction 1. Higher terms in the sum on n_1 are nominally suppressed by powers of $\exp[-(n_1^2 - 1)E_1/k_B T] \ll 1$, $n_1 > 1$, but the situation becomes more complicated and some excitation must occur for Fermi systems in which the Fermi energy for N particles in $D-1$ dimensions exceeds E_1. I will not consider this refinement.

The leading factor in Eq. (72) is the absolute square of the normalized wave function $\psi_1(x_1)$ and integrates to unity. The momentum integral is independent of the remaining coordinates $x_2, \ldots, x_D$, so that an integration of $n(\boldsymbol{x})$ over the full volume V_D gives the total particle number N as

$$N = V_{D-1} \int \frac{d^{D-1}p}{h^{D-1}} (e^{-\beta(p_{D-1}^2/2m - \mu')} \pm 1)^{-1}.$$
(73)

The number density can therefore be written as

$$n(\boldsymbol{x}) = \frac{N}{V_{D-1}} \frac{2}{L_1} \sin^2 \frac{\pi x_1}{L_1}.$$
(74)

The pressure on the wall of the box at $x_1 = 0$ can be calculated using the expressions in Eqs. (53) and (58), with the result

$$P_1 = \frac{h^2}{4mL_1^3} \frac{N}{V_{D-1}} = 2E_1 \frac{N}{V_D}.$$
(75)

All particles must be in the $n_1 = 1$ state in x_1 for $k_B T \ll E_1$, with the effects of Fermi or Bose statistics absorbed in the integral factor in Eq. (72) and the corresponding factor in the expression for P_1. The same result for P_1 holds on the surface $x_i = L_1$. Note that P_1 is independent of the coordinates $x_2, \ldots, x_D$ that specify the locations on the surfaces at $x_1 = 0, L_1$ on which the pressure is observed.

In contrast, the pressure on any of the remaining walls is

$$P_{j \neq 1}(\boldsymbol{x}) = \frac{2}{L_1} \sin^2 \frac{\pi x_1}{L_1} \int \frac{d^{D-1}p}{h^{D-1}} \frac{p_j^2}{m}$$
$$\times (e^{-\beta(p_{D-1}^2/2m - \mu')} \pm 1)^{-1}$$
$$= \frac{2\langle E \rangle_{D-1}}{D-1} \frac{N}{V_{D-1}} \frac{2}{L_1} \sin^2 \frac{\pi x_1}{L_1}$$
$$= P_{D-1} \frac{2}{L_1} \sin^2 \frac{\pi x_1}{L_1},$$
(76)

where $\langle E \rangle_{D-1}$ is the average single-particle excitation energy for a continuous system in $D-1$ dimensions and P_{D-1} is the corresponding pressure. The pressure P_j is independent of the coordinates $x_2, \ldots, x_D$, but is modulated with respect to x_1 by the factor $|\psi_1(x_1)|^2 = (2/L_1)\sin^2(\pi x_1/L_1)$ which specifies how the N particles are distributed with respect to x_1. When the distribution in x_1 is not observed, x_1 can be integrated out and P_j reduces to P_{D-1}. The effective dimensionality of the system is therefore reduced by one for $k_B T \ll E_1$, the limit in which the no thermal excitations in the 1 direction are possible.

The effects of anisotropies are small in practice, with $E_1/k = 0.2$ K for a helium atom confined in a gap with $L_1 = 1$ nm. Anisotropies in the pressure would only be observable at lower temperatures. The situation is more complicated for electrons because of the effects of Fermi–Dirac statistics.

B. Pressure and number density in an external field
1. WKB approximation

It is simple to treat the problem of otherwise noninteracting particles in a one-dimensional external potential $V(x)$ using the standard Wentzel–Kramers–Brillouin (WKB) approximation discussed in most texts on quantum mechanics (see, for example, Ref. 12). The single-particle energies E_k are determined in this approximation by the semiclassical quantization condition that

$$\left(k + \frac{1}{2}\right)h = 2\int_{x_1}^{x_2} p(E,x)dx,$$
(77)

for $E = E_k$, $k = 0,1,2,\ldots$, Here, $p(E,x) = \sqrt{2m[E - V(x)]}$ is the local momentum, h is Planck's constant, and x_1, x_2 are turning points in the classical motion where $p(E,x) = 0$. The approximation can be shown to be good when there are many local wavelengths h/p between the turning points, but tends to be good even for low-lying states in the spectrum. Because the typical excitation energy in statistical systems is $E \approx k_B T$, the WKB approximation will be valid provided that $h^{-1} \int p(k_B T, x)dx \gg 1$. If I treat k and E as continuous, the density of states dk/dE implied by Eq. (77) is

$$\frac{dk}{dE} = \frac{1}{h} \int_{x_1}^{x_2} \sqrt{\frac{2m}{E - V(x)}} dx.$$
(78)

The WKB wave functions can be written between the turning points as[12]

$$\psi_k(x) \approx \mathcal{N}_k \left(\frac{2m}{E_k - V(x)}\right)^{1/4} \cos\left(\xi_k(x) - \frac{\pi}{4}\right)dx,$$
(79)

$$\xi_k(x) = \frac{1}{\hbar} \int_{x_1}^{x} \sqrt{2m[E_k - V(x)]}dx,$$
(80)

and decrease exponentially outside that region. If I ignore the small contributions from the exponential regions and replace the square of the cosine by its average value of 1/2 for many oscillations over regions in which $E - V$ changes significantly, I find that the normalization constant is related to the density of states by

$$\mathcal{N}_k^2 = \frac{2}{h} \frac{dE}{dk}. \tag{81}$$

Thus, following the previous discussion of quasi-continuous systems, the local number density in the system is

$$n(x) \approx \sum_k \mathcal{N}_k^2 \sqrt{\frac{2m}{E_k - V(x)}} \cos^2\left(\xi(x) - \frac{\pi}{4}\right)$$
$$\times (e^{\beta(E_k - \mu)} \pm 1)^{-1}$$
$$\approx \frac{1}{h} \int dE \sqrt{\frac{2m}{E - V(x)}} (e^{\beta(E - \mu)} \pm 1)^{-1}$$
$$= \int_{-\infty}^{\infty} \frac{dp}{h} (e^{\beta[p^2/2m - \mu + V(x)]} \pm 1)^{-1}, \tag{82}$$

where in the last two lines I have first replaced the square of the cosine in $\psi_k^* \psi_k$ by its average value 1/2 and converted the sum over k to an integral over E using Eq. (81), and then converted from E to p as the integration variable with p defined by the relation $p^2/2m = E - V(x)$. The replacement $\cos^2 \rightarrow 1/2$ may be taken as a local averaging when there are many oscillations in the region observed. Alternatively, I note that the zeros of successive eigenfunctions interweave, so that the zeros in the individual terms in $n(x)$ are washed out in the sum when many states are excited.

The result in Eq. (82) is just that obtained through thermodynamic arguments[6] by dividing the system into small volumes over which $V(x)$ can be taken as constant, and then considering the equilibrium of the subsystems. The result is to replace the chemical potential μ in the corresponding expression for free particles by $\mu - V(x)$. However, it is clear from the WKB-based derivation that there are two key points in the quantum treatment. First, the average number k of excited states must be large enough and vary smoothly enough for energies on the scale of $k_B T$ that the sum over states can be replaced by an integral. Second, the square of the wave function must oscillate sufficiently rapidly over regions in which $E - V(x)$ changes significantly so that the replacement $\cos^2 \rightarrow 1/2$ is valid in the sum in Eq. (82). The second requirement is closely linked to the conditions needed for the validity of the WKB approximation, and for the replacement of the sum by an integral. It is worth noting in this connection that the wave function is defined over the entire volume in which the system is confined, and not just the subvolumes as in Ref. 6.

The expression in Eq. (82) can be extended immediately to three dimensions for systems with additive potentials, $V = \Sigma_i V_i(x_i)$. It can be extended to general potentials $V(\boldsymbol{x})$ in the form

$$n(\boldsymbol{x}) = \int \frac{d^3 p}{h^3} (e^{\beta[p^2/2m - \mu + V(\boldsymbol{x})]} \pm 1)^{-1}, \tag{83}$$

using thermodynamic arguments as in Ref. 6, or directly using functional integral methods such as those in Refs. 13 and 14. It is again required that the oscillations in ψ be rapid on

the scale at which $E - V(\boldsymbol{x})$ changes significantly. The general result in Eq. (83) could probably also be derived in three dimensions using a WKB-like phase-integral approximation such as that investigated by Gutzwiller,[15] but I have not attempted it.

Finally, the total number of particles in the system is given by the spatial integral of $n(\boldsymbol{x})$ over the confining volume,

$$N = \int \frac{d^3 x\, d^3 p}{h^3} (e^{\beta[p^2/2m - \mu + V(\boldsymbol{x})]} \pm 1)^{-1}, \tag{84}$$

giving a result that can be used to determine μ.

The pressure or stress in the external potential can be treated similarly. I will work in the interior of the total volume and use the general expression for the pressure given in Eq. (18), and the single-particle form of the stress tensor in Eq. (14), specialized to one dimension. The key step involves the recognition that the derivatives in Eq. (14) can be taken to act only on the cosine factor in ψ_k, Eq. (79). This assumption gives

$$\frac{d\psi_k}{dx} \approx -\mathcal{N}_k \frac{1}{\hbar} \left(\frac{2m}{E_k - V(x)}\right)^{1/4} \sqrt{2m[E_k - V(x)]}$$
$$\times \sin\left(\xi_k(x) - \frac{\pi}{4}\right) dx. \tag{85}$$

The term omitted is of relative order $\lambda (dV/dx)/8\pi(E - V)$, and can be neglected in the region in which the WKB approximation is valid;[12] namely, when the change in the potential over a wavelength $\lambda = h/p$ is small, on the scale of $E - V$. Furthermore, the correction term oscillates out of phase with the main term, and interference effects can be neglected in averaging $\psi_k^* \psi_k$ A similar result holds for the second derivatives, with the neglected terms just those for which the WKB wave function fails to satisfy the exact Schrödinger equation. The result of the calculation is

$$P(x) \approx \sum_k \mathcal{N}_k^2 \sqrt{2m[E_k - V(x)]} (e^{\beta(E_k - \mu)} \pm 1)^{-1}$$
$$\approx \frac{2}{h} \int dE \sqrt{2m[E - V(x)]} (e^{\beta(E - \mu)} \pm 1)^{-1}$$
$$= \int_{-\infty}^{\infty} \frac{dp}{h} \frac{p^2}{m} (e^{\beta[p^2/2m - \mu + V(x)]} \pm 1)^{-1}. \tag{86}$$

The expression in Eq. (86) can be generalized to more dimensions using thermodynamic arguments or functional integral methods, and should be properly stated in terms of the stress across a surface with normal $\hat{n}$, as

$$-\hat{n} \cdot \vec{\vec{T}} \cdot \hat{n} = \int \frac{d^D p}{h^D} \frac{(\hat{n} \cdot \boldsymbol{p})^2}{m} (e^{\beta[p^2/2m - \mu + V(\boldsymbol{x})]} \pm 1)^{-1}. \tag{87}$$

The final factor in parentheses in Eq. (87) is isotropic in $\boldsymbol{p}$, so that the stress at a given point $\mathbf{x}$ is the same in all directions even for $V(\boldsymbol{x})$ anisotropic. Thus, $\langle (\hat{n} \cdot \boldsymbol{p})^2 \rangle = \langle \boldsymbol{p}^2/D \rangle$, and $P(\boldsymbol{x}) = (2/D) K(\boldsymbol{x})$, where $K(\boldsymbol{x})$ is the average kinetic energy density at $\mathbf{x}$ with the average taken over the local statistical distribution.

I next consider two examples that illustrate the effects of external fields in interesting physical situations. Both lead to useful homework problems for graduate courses in statistical physics.

2. Example: Particles in a linear potential

For particles in a linear potential $V(z) = zV_0/z_0$ with zero potential for the motion in the transverse directions, the motion in z can be described in the WKB approximation as in Sec. IV B 1. while the motion in the transverse coordinates can be described in terms of running waves with momenta $\mathbf{p}_\perp = (p_x, p_y)$. The single-particle energies are

$$E_n(\mathbf{p}_\perp) = \frac{p_\perp^2}{2m} + \frac{V_0}{z_0}\left(\frac{9h^2 z_0}{32 m V_0}\right)^{1/3}\left(n - \frac{1}{4}\right)^{2/3},$$
$$(n = 1, 2, \ldots), \tag{88}$$

where the second term is the WKB energy of the vertical motion. Many states of the vertical moton will be excited at the thermal energy $k_B T$ for $(k_B T/V_0)^{3/2}(8m V_0 z_0^2/9\pi^2\hbar^2)^{1/2} \gg 1$, a condition that is always satisfied under realistic conditions for gases in a gravitational field with $V_0 = mgz_0$ or electrons in a constant electric field E_0, $V_0 = eE_0 z_0$. The sums over k can be replaced by integrals over a momentum p_z defined to reduce the second term in Eq. (88) to the standard form

$$\frac{p_z^2}{2m} \equiv \frac{p_0^2}{2m}\left(n - \frac{1}{4}\right)^{2/3}, \tag{89}$$

where $p_0^2/m \equiv V_0/z_0 (9h^2 z_0/32 m V_0)^{1/3}$. The corrections for Fermi or Bose statistics are unimportant for gases in a gravitational field under normal conditions. I follow the development in Sec. IV B 1 with the Fermi or Bose factors replaced by the simple Boltzmann factor $e^{-\beta(E_k - \mu)}$ and obtain the classical barometric equations

$$P(z) = P(0)e^{-mgz/k_B T}, \quad n(z) = n(0)e^{-mgz/k_B T},$$
$$P(0) = n(0)k_B T. \tag{90}$$

For a system with area A, the number density $n(0)$ at $z = 0$ is given in terms of the total number of particles N by

$$N = \int d^3x\, n(\mathbf{x}) = n(0)\int_0^\infty d^3x\, e^{-mgz/k_B T} = n(0)A\frac{k_B T}{mg}. \tag{91}$$

Hence, $n(0) = (N/A)(mg/k_B T)$ and $P(0) = Nmg/A$, as expected. Note that, as remarked previously, the pressure is isotropic at any point, $T_{x,x} = T_{y,y} = T_{z,z}$, even though the potential is not, and isotropy was not used in the derivation. This result holds generally for quasi-continuous systems at sufficiently high excitation.

A more interesting result with respect to the gravitational field is the existence of a Bose–Einstein condensate in an ideal system at sufficiently low temperatures, an example that makes a good homework problem. The particle number for the Bose system is given in Eq. (50), which becomes

$$N \approx \frac{3A}{p_0^3 h^2}\int d^2 p_\perp \int_0^\infty dp_z\, p_z^2 (e^{\beta[p^2/2m - \mu]} - 1)^{-1}$$
$$< \frac{3A}{p_0^3 h^2}\int d^2 p_\perp \int_0^\infty dp_z\, p_z^2 (e^{p^2/2m} - 1)^{-1} \tag{92}$$

for the energy spectrum in Eq. (88), with sums converted to integrals and p_z defined through Eq. (89). The inequality follows from the convergence requirement that $E_0 - \mu > 0$ and the approximation in Eq. (92) that $E_0 \approx 0$.

The inequality is clearly violated for a fixed N at sufficiently low temperatures or large values of β. It is then necessary to single out the ground state because this state is given zero weight in the transition from a sum over states to an integral over E or $\mathbf{p}$, and include its occupation number N_0 explicitly. N is then given by

$$N = N_0 + \frac{3A}{p_0^3 h^2}\int d^2 p_\perp \int_0^\infty dp_z\, p_z^2 (e^{p^2/2mk_B T} - 1)^{-1}. \tag{93}$$

The integrals can be evaluated by changing to spherical coordinates, and then to the variable $t = p^2/2m$ after performing the angular integration. The final integral gives a product of a generalized factorial or gamma function with the Riemann zeta function

$$\int_0^\infty dt\, \frac{t^{z-1}}{e^t - 1} = \Gamma(z)\zeta(z). \tag{94}$$

The inequality in Eq. (92) can just be satisfied for a given N at a temperature $T = T_c$ determined by setting the right-hand term equal to N, and fails at lower temperatures. The calculation gives

$$N = \frac{3\pi^{3/2}A}{4 p_0^3 h^2}(2m k_B T_c)^{5/2}\zeta(5/2), \tag{95}$$

corresponding for a gravitational potential to

$$k_B T_c = \left[\frac{mg}{\zeta(5/2)}\left(\frac{h^2}{2\pi m}\right)^{3/2}\frac{N}{A}\right]^{2/5}. \tag{96}$$

At lower temperatures,

$$N_0 = N[1 - (T/T_c)^{5/2}]. \tag{97}$$

The power of T/T_c in Eq. (97) is different from that for an ideal system with no field present. The critical temperature T_c also is higher for fixed N than the critical temperature T_c^0 in the absence of the gravitational field, $T_c/T_c^0 = [\zeta(3/2)/\zeta(5/2)]^{2/3} \approx 1.56$, a difference attributable to the greater density of the gas near the ground. Finally, the ground-state wave function is compact in z with a characteristic extent $z_{max} \approx E_1/mg = (81h^2/512mg)^{1/3} \approx 5.4$ μm for helium, and the condensate "falls to the floor."

It is interesting that the presence of a gravitational potential leads to the appearance of Bose–Einstein condensation in a two-dimensional system with $V(z) = zV_0/z_0$ and free motion in a box of length L in the transverse direction, with

$$N_0 = [1 - (T/T_c)^2], \quad k_B T_c = \frac{1}{m}\left(\frac{2p_0^3 h}{\pi^3}\frac{N}{L}\right)^{1/2}. \tag{98}$$

In contrast, there is no condensation for free motion in two dimensions.

The calculations of the local number density and pressure in an external field are simple for dilute systems for which the Fermi and Bose statistical factors reduce in leading order to the usual Boltzmann factor. The calculations cannot be done exactly when quantum corrections are important, with many particles within a volume of of linear dimension equal to the thermal wavelength, but are similar numerically to the calculation of $N(\mathbf{x})$ in the following example.

3. Example: Bosons in a harmonic trap

An example of interest in connection with Bose-Einstein condensation is that of atoms confined in a harmonic trap with $V(\boldsymbol{x}) = \Sigma_{i=1}^3 1/2 m \omega_i^2 x_i^2$. The total number of particles in the system is given by Eq. (84), specifically,

$$N = \int \frac{d^3x\,d^3p}{h^3} (e^{\beta \Sigma_i [p_i^2/2m + (m\omega_i^2/2)x_i^2] - \beta\mu} - 1)^{-1}. \quad (99)$$

The integral can be simplified by changing to the dimensionless variables $x_i' = \omega_i \sqrt{m/2k_{\rm B}T}\, x_i$, $p_i' = p_i / \sqrt{2mk_{\rm B}T}$, and then going to the six-dimensional coordinates $\boldsymbol{s} = (\boldsymbol{x}', \boldsymbol{p}')$, $s^2 = \Sigma_i (p_i'^2 + x_i'^2)$, and working in the spherical representation. The result is

$$N = \frac{1}{\pi^3} \left(\frac{k_{\rm B}T}{\hbar}\right)^3 \frac{1}{\omega_1\omega_2\omega_3} \int_0^\infty \frac{s^5 ds}{e^{s^2 - \beta\mu} - 1} \int d\Omega_6. \quad (100)$$

Here, $d\Omega_6$ is the element of solid angle in six dimensions, and $\int d\Omega_6 = \pi^3$.

The remaining integral is maximized for $\mu = 0$, and can be evaluated exactly in this limit by changing the integration variable from s to $t = s^2$ and using Eq. (94). The resulting equation determines the critical temperature T_c for the onset of Bose–Einstein condensation for fixed particle number N,

$$k_{\rm B}T_c = \hbar \left(\omega_1\omega_2\omega_3 \frac{N}{\zeta(3)}\right)^{1/3}. \quad (101)$$

For a spherical trap with oscillation frequency $\nu = 150$ Hz and $N = 4\times10^4$, fairly typical conditions for original experiments with Rb atoms,[16–18] Eq. (101) gives $T_c = 6.77$ nK$\times N^{1/3} = 232$ nK. Note that $\hbar\omega/k_{\rm B} = 7.20$ nK $\ll T_c$, so that a large number of oscillator states are excited at T_c, and the use of the integral approximation to the sum over states is legitimate.

The number of particles in excited states for $T < T_c$, $\mu = 0$ is $N_{\rm excited} = N(T/T_c)^3$, and the number in the ground state is therefore

$$N_0 = N[1 - (T/T_c)^3], \quad (T < T_c), \quad (102)$$

with $N_0 = 0$ for $T > T_c$. These calculations illuminate the conditions under which a real Bose–Einstein condensate can be formed in a gas, and make good homework problems.

The number density in a spherical trap follows from Eq. (99),

$$n(r) = N_0(T) |\psi_0(r)|^2 + \frac{1}{h^3}$$

$$\times \int d^3p (e^{\beta(p^2/2m + m\omega^2 r^2/2)} - 1)^{-1}, \quad (103)$$

for $T < T_c$, where $r = \sqrt{\boldsymbol{x}^2}$, and

$$\psi_0(r) = \frac{1}{\pi^{3/2} r_0^3} e^{-r^2/r_0^2}, \quad r_0 = \sqrt{\hbar/m\omega}. \quad (104)$$

The actual evaluation of the local number density in the trap from Eq. (103) requires some numerical calculation, but gives a striking illustration of the emergence of the condensate. It is useful to scale r by r_0, $n(r) = d^3N/d^3r$ by N, and T by T_c, and change to $t = p^2/2m$ as the variable in the final momentum integration. Then, if I use Eqs. (101), (102), and (104), I obtain

$$\frac{1}{N} \frac{d^3N}{d^3(r/r_0)} = \frac{1}{\pi^{3/2}} \left[1 - \left(\frac{T}{T_0}\right)^3\right] e^{-r^2/r_0^2}$$

$$+ \frac{1}{\sqrt{2}\pi^2\zeta(3)} \left(\frac{\hbar\omega}{k_{\rm B}T_c}\right)^{3/2} \left(\frac{T}{T_c}\right)^{3/2} \int dt\,\sqrt{t}$$

$$\times (e^{t + 1/2(\hbar\omega/k_{\rm B}T_c)(T_c/T)(r^2/r_0^2)} - 1)^{-1}. \quad (105)$$

The original number distribution at T_c has a characteristic width $\approx \sqrt{k_{\rm B}T_c/m\langle\omega^2\rangle}$. A very sharp ground-state peak appears in the number distribution as T is lowered below T_c. A comparison of the calculation with the number distribution observed in the original experiments on Bose–Einstein condensation in Refs. 16–18 shows qualitative agreement, and gives a real feeling for how the theory describes to the observed emergence of a condensate.

The pressure in the trapped system can be calculated using similar methods, and balances the force from the confining oscillator potentials. However, because of the long mean free path for particle intractions, it is not relevant for the expansion of the condensate when the confining interactions are suddenly removed.

V. COMMENTS

The main objective of this paper has been to give direct derivations of the pressures in Fermi and Bose systems using the relation of pressure to momentum flow and the quantum stress tensor. This quantum kinetic theory approach is simple conceptually, and shows that the pressure is naturally defined locally, a point of interest for particles in external fields. It leads also to a direct understanding of the difference in Fermi and Bose pressures at fixed particle number and temperature in terms of the different momentum states excited, a point often argued qualitatively. A bonus of the analysis was the appearance of the simple examples of the use of boundary perturbation theory to establish the connection of the usual thermodynamic arguments for particles and fields to the results obtained directly in a stress-tensor approach.

I also discussed the properties of extensive, quasi-continuous systems, showed the role of excitations high on the scale of $k_{\rm B}T$ in obtaining isotropic pressures in intrinsically anisotropic systems, and illustrated the appearance of anisotropies and the effective reduction of the dimension of a system at low enough temperatures. Finally, I gave an explicit WKB derivation of the usual expressions for the number density and pressure of particles in an external field, and presented several examples that illustrate the use of the stress-tensor method in real physical problems. I have found these examples to make good homework problems in a graduate course on statistical mechanics.

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