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2006 J. Phys. A: Math. Gen. 39 L499

(http://iopscience.iop.org/0305-4470/39/30/L03)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **39** (2006) L499–L505 doi:10.1088/0305-4470/39/30/L03

LETTER TO THE EDITOR

Statistical mean-field theory of finite quantum systems: canonical ensemble formulation

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Received 7 March 2006, in final form 8 March 2006
Published 12 July 2006
Online at stacks.iop.org/JPhysA/39/L499

Abstract

We develop a statistical mean-field theory of finite quantum systems in thermal equilibrium. Our formulation employs the canonical ensemble of statistical mechanics, and it enables us to analytically determine the occupation number distributions of interacting particles obeying Bose–Einstein or Fermi–Dirac statistics. We have also developed a numerical procedure that enables us to obtain a universal scaled occupation number distribution that, for a given total number of interacting particles in a finite system, makes it possible to determine the occupation number distribution for any temperature. The developed mean-field theory is applicable to a wide range of atomic, nuclear and condensed matter systems for which finite-size effects can play an important role. In particular, the present approach makes it possible to formulate a finite temperature mean-field theory for a specific ion in a dense plasma.

PACS numbers: 05.30.−d, 05.30.Ch, 05.30.Fk, 05.30.Jp

Recently, there has been a growing interest in the statistical properties of mesoscopic quantum systems, composed of finite numbers of interacting particles. Such finite many-body systems are ubiquitous in nature, and they can often be realized in laboratory experiments. The examples include, but are by no means limited to, ultracold Bose and Fermi gases confined in atomic traps [1–8], multi-nucleon nuclei [9–11], electrons embedded into small metallic particles [12], one-dimensional mesoscopic rings [13], and multi-electron atoms and ions in plasmas [14–19]. The number of interacting particles in such mesoscopic systems can vary from a few, as is the case with the bound electrons in low-Z atoms or ions, to hundreds of thousands for the case of trapped neutral alkali atoms. The range of relevant thermodynamic conditions is also very broad: from ultra-low temperatures and densities in the case of trapped Bose and Fermi gases to very high temperatures and densities in the case of some plasmas.

Hence the development of a unified statistical theory of such systems, capable of taking into account finite-size effects, is quite timely, and it can have a broad spectrum of potential applications. Since the number of particles is finite and fixed, we have to work with the canonical ensemble, which usually presents formidable difficulties.

Some progress along these lines has however been made to date. In particular, several variants of a statistical theory of an ideal cold, trapped Bose gas were formulated using the canonical ensemble of statistical mechanics [1–5]. Later, the theory was generalized to incorporate two-body atomic interactions as well [6]. The mean-field canonical ensemble description of interacting nucleons has been developed in [9–11]. More recently, different versions of the canonical ensemble treatment of intermediate to high-Z ions in hot dense plasmas have been advanced with the help of the so-called superconfiguration approach [15–19]. Further, the statistical approach employing the canonical ensemble to model classical liquids as collections of finite numbers of impenetrable spheres has also been recently presented [20, 21]. Unfortunately, many of these approaches suffer from significant drawbacks. In particular, some authors only consider either systems with relatively large numbers of particles [1–6, 16–19], or those at low temperatures [1–6], or else they neglect the inter-particle interactions [1–5, 7, 8]. Some alternative versions of the theory require an extensive amount of numerical work to obtain results for realistic systems [9–11]. Moreover, many of the proposed theories are only concerned with Bose [1–6] or Fermi [9–13, 15–19] particles, or else with those obeying classical statistics [20, 21]. Thus the formulation of a self-consistent statistical theory of finite systems, free of the just mentioned flaws, remains an open problem.

The purpose of this letter is to outline such a theory. We follow the path integral approach to the generation of a statistical mean-field theory, previously formulated for very large nuclear systems whose statistical behaviour is specified by the grand canonical ensemble [22, 23]. We generalize this method to treat finite-size systems described by the canonical ensemble. We develop the simplest variant of the mean-field theory, which does not take into account exchange effects, and we provide for the first time, to our knowledge, a closed form analytical expression for the occupation number distribution of particles in finite interacting quantum systems under the mean-field approximation. Moreover, we have developed a numerical procedure that enables us to obtain a universal scaled occupation number distribution that, for a given total number of interacting particles in a finite system, makes it possible to determine the occupation number distribution for any temperature. Our results can be straightforwardly generalized to include exchange effects, extending the approach of [23] to the case of finite systems. Not only does our theory enable us to derive the canonical occupation number distribution in a self-consistent manner, but it treats Bose and Fermi systems on equal footing as well.

To begin, we consider a finite many-body quantum system described by the Hamiltonian

$$\hat{H} = \int \mathrm{d}^3 r\, \hat{h}(\mathbf{r})\hat{\rho}(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \hat{\rho}(\mathbf{r}) V(\mathbf{r}-\mathbf{r}')\hat{\rho}(\mathbf{r}'). \tag{1}$$

Here $\hat{h}$ is the kernel of a single-particle Hamiltonian, given by the expression

$$\hat{h} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}), \tag{2}$$

where $U(\mathbf{r})$ is a generic external potential. Further, $V(\mathbf{r}-\mathbf{r}')$ is a two-body interaction potential, and the single-particle density operator is defined as

$$\hat{\rho}(\mathbf{r}) = \sum_{j=1}^{N_t} \delta(\mathbf{r}-\mathbf{r}_j). \tag{3}$$

The first step in solving the statistical problem is to calculate a partition function. For the canonical ensemble of our finite quantum systems, the latter quantity is defined as

$$Z_C \equiv \sum_{\{n_i|N_t\}} \exp\bigl(-\beta E_{\{n_i|N_t\}}\bigr) = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \mathrm{e}^{-\beta E_{\{n_i\}}} \delta_{N_t N}. \tag{4}$$

Here $\beta = 1/kT$, and the notation $\{n_i|N_t\}$ implies the summation over all possible energy configurations $\{n_i\}$ with the fixed total number of particles N_t in the system. To be able to maintain this constraint and sum over the states of the system with any number of particles, we use the following integral representation for the constraint

$$\delta_{N_t N} = \int_0^{2\pi} \frac{\mathrm{d}\phi}{2\pi} \mathrm{e}^{-\mathrm{i}\phi(N_t - N)}. \tag{5}$$

Using this identity on the right-hand side of equation (4) and interchanging the orders of the summation and integration we obtain the expression

$$Z_C = \frac{1}{2\pi\mathrm{i}} \oint \frac{\mathrm{d}\zeta}{\zeta^{N_t+1}} \mathrm{Tr}[\zeta^{\hat{N}} \mathrm{e}^{-\beta\hat{H}}]. \tag{6}$$

Here we have converted the integral to the contour one along the circle $|\zeta| = 1$ by the change of variables $\zeta = \mathrm{e}^{\mathrm{i}\phi}$. The trace is assumed to be taken over the complete set of the eigenstates of $\hat{H}$ and $\hat{N}$, $[\hat{H}, \hat{N}] = 0$. It can be seen from equation (6) that the second term in the integrand can be thought of as a grand canonical partition function with a fictitious complex-valued chemical potential. Consequently, we can adopt to our case the powerful path integral technique which was developed in [22–24] to calculate the grand canonical partition function of large statistical systems. In particular, we can represent expression (6) as a path integral over an auxiliary classical field in the form

$$Z_C = \int \mathcal{D}[\sigma] \exp\{-\beta\Omega[\sigma, \beta, \zeta]\}, \tag{7}$$

where σ is the auxiliary field, and Ω is given by

$$\Omega[\sigma, \beta, \zeta] = -\frac{1}{2}(\sigma, V\sigma) - \frac{1}{\beta} \ln\left\{\frac{1}{2\pi\mathrm{i}} \oint \frac{\mathrm{d}\zeta}{\zeta^{N_t+1}} \mathrm{Tr}[\zeta^{\hat{N}} \hat{U}_\sigma(\beta)]\right\}. \tag{8}$$

Here

$$\hat{U}_\sigma(\beta) = T_\tau \exp\{-\beta[(\hat{h}, \hat{\rho}) + (\hat{\rho}, V\sigma)]\}, \tag{9}$$

with T_τ being the ordering operator in dimensionless imaginary time τ, $-\mathrm{i}/2 \leqslant \tau \leqslant \mathrm{i}/2$, and we have introduced the notation

$$(\hat{\rho}, V\sigma) \equiv \int_{-\mathrm{i}/2}^{\mathrm{i}/2} \mathrm{d}\tau \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \hat{\rho}(\mathbf{r}, \tau) V(\mathbf{r} - \mathbf{r}') \sigma(\mathbf{r}', \tau), \tag{10}$$

with the similar definition for $(\hat{h}, \hat{\rho})$.

The introduction of the path integration over the auxiliary field was necessary to reduce the original system to the one of effectively independent particles moving in the time-dependent external potential $\sigma(\mathbf{r}, \tau)$. The next step is to apply the saddle point method to evaluate the path integral in equation (7), with the saddle point assumed to be given by a static mean field $\sigma_0(\mathbf{r})$ which is determined from the condition

$$\delta\Omega = 0. \tag{11}$$

The leading contribution to the path integral in equation (7) gives a canonical partition function of the mean-field theory:

$$Z_{\mathrm{CMF}} \simeq \exp\{-\beta\Omega_{\mathrm{CMF}}[\sigma_0, \beta, N_t]\}. \tag{12}$$

The trace in equation (8) can then be calculated in the basis of the eigenstates of $\hat{U}$, specified by the equation [22, 23]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) + \int \mathrm{d}^3 r' \sigma_0(\mathbf{r}') V(\mathbf{r}-\mathbf{r}')\right]\psi_j = \epsilon_j \psi_j. \tag{13}$$

Assuming further that we can solve this equation, we proceed to evaluating the partition function in terms of the orbital energies.

Recalling that in the mean-field approximation, the particles are treated as independent and moving in the static mean field $\sigma_0(\mathbf{r})$, we can evaluate the trace in equation (8) ignoring the time ordering. Performing the summation over the single particle states of bosons or fermions, similar to the case of noninteracting Fermi and Bose gases [25], we can represent the final result as

$$\Omega_{\mathrm{CMF}} = -\frac{1}{2}(\sigma_0, V\sigma_0) - \frac{1}{\beta}\ln\left\{\frac{1}{2\pi \mathrm{i}}\oint \frac{\mathrm{d}\zeta}{\zeta^{N_t+1}} \exp\left[\mp \sum_k \ln(1 \mp \zeta\, \mathrm{e}^{-\beta\epsilon_k})\right]\right\}. \tag{14}$$

Hereafter the upper sign will always correspond to bosons and the lower one to fermions. We now substitute from equation (14) into equation (11) to find, after some algebra, the expression for the mean field:

$$\sigma_0(\mathbf{r}) = \sum_j f(\epsilon_j)|\psi_j(\mathbf{r})|^2. \tag{15}$$

It follows from equation (15) that σ_0 plays the role of a particle density, and $f(\epsilon_j)$ is the occupation number distribution, which is found to be given by

$$f(\epsilon_j) = \frac{\partial}{\partial(-\beta\epsilon_j)}\ln\left\{\oint \frac{\mathrm{d}\zeta}{\zeta^{N_t+1}} \exp\left[\mp \sum_k \ln(1 \mp \zeta\, \mathrm{e}^{-\beta\epsilon_k})\right]\right\}. \tag{16}$$

The analysis indicates that the only pole inside the contour $|\zeta| = 1$ of the integrand in equation (16) is at $\zeta = 0$. Consequently, using the residue theorem to evaluate the integral in equation (16), we obtain, after somewhat lengthy algebra, the following analytical expression for the occupation number distribution:

$$f(\epsilon_j) = \frac{\sum_{M=1}^{N_t} \frac{N_t!}{(N_t-M)!}(\pm)^{M+1}\, \mathrm{e}^{-M\beta\epsilon_j} \frac{\mathrm{d}^{(N_t-M)}}{\mathrm{d}\zeta^{(N_t-M)}} \exp\left[\mp \sum_k \ln(1 \mp \zeta\, \mathrm{e}^{-\beta\epsilon_k})\right]\Big|_{\zeta=0}}{\frac{\mathrm{d}^{N_t}}{\mathrm{d}\zeta^{N_t}} \exp\left[\mp \sum_k \ln(1 \mp \zeta\, \mathrm{e}^{-\beta\epsilon_k})\right]\Big|_{\zeta=0}}. \tag{17}$$

Equations (13), (15) and (17) form the self-consistent mean-field equations of finite interacting systems. Once they have been solved, one can use the expression for the partition function, equation (12), to determine all the thermodynamic properties of such systems in the mean-field approximation. Interestingly, the evaluation of the right-hand side of equation (17) for $N_t = 1$ leads to the Maxwell–Boltzmann distribution, $f(\epsilon_j) = \mathrm{e}^{-\beta\epsilon_j} \big/ \sum_k \mathrm{e}^{-\beta\epsilon_k}$. However, the expression for $f(\epsilon_j)$ becomes progressively more complicated as N_t increases.

To demonstrate how finite-size effects influence the particle occupation number distribution, we consider a simple example of a collection of uncoupled one-dimensional harmonic oscillators with the energies $\epsilon_j = \hbar\omega j$, $(j = 0, 1, 2, \ldots)$, obeying Fermi statistics. We compare the canonical occupation number distribution of such a system, obtained from equation (17) for a given total number of particles $N_t = 3$, with the usual Fermi–Dirac distribution function with the same average number of particles, $\langle N\rangle = N_t$. The results are displayed in figure 1 for the two cases: (*a*) $\beta\hbar\omega = 2$ and (*b*) $\beta\hbar\omega = 4$. It is seen from the figure that the canonical occupation number distribution is steeper than the Fermi–Dirac one. This behaviour is quite general and can be explained by the following qualitative argument. The number of particles in representations corresponding to a grand canonical ensemble can

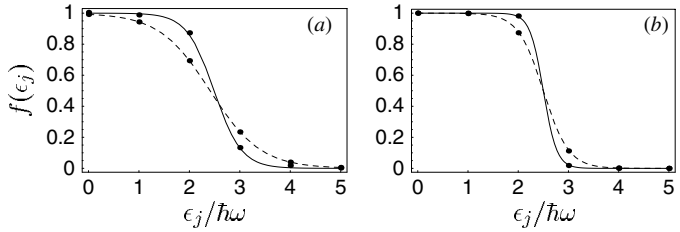

Figure 1. Canonical (solid line) versus grand canonical (dashed line) occupation number distributions for $N_t = 3$ uncoupled 1D harmonic oscillators obeying Fermi–Dirac statistics; the temperature is chosen such that $(a)\,\hbar\omega/kT = 2$ and $(b)\,\hbar\omega/kT = 4$.

fluctuate around the average. The number of representations with the total numbers of particles below the average is bounded by the zero particle limit, while the number of representations with numbers of particles above the average is unlimited. For sufficiently low but finite temperatures, the additional particles above the average will have to occupy the next available energy levels due to the Pauli exclusion principle, resulting in higher energy level occupancies than those for the canonical ensemble representations. On the other hand, to maintain the equality, $\langle N\rangle = N_t$, the occupancies of the grand canonical ensemble representations with numbers of particles below the average are smaller than those of the corresponding canonical ensemble representations[4].

Returning to the case of finite interacting systems, we notice that the canonical occupation number distribution, equation (17), depends only on the ratio of a single orbital energy to the thermal energy. Such a scaling dependence enables us to work out a universal scaled distribution that, for a given total number of particles in the system, will make it possible to determine particle occupation numbers for any temperature. To this end, we first consider the occupation number distribution as a function of continuous energy, ϵ. Second, we introduce a fine mesh breaking the continuous energy line into a number of very small equidistant intervals of length $\Delta\epsilon$ such that $\Delta\epsilon/kT \ll 1$ and $N_{\max}\Delta\epsilon/kT \gg 1$, where $N_{\max}$ is the total number of such energy intervals, which provides a cut-off for the evaluation of the sums in equation (17). Provided the mesh is sufficiently fine, the actual orbital energies ϵ_j which are determined by self-consistently solving mean-field equations (13), (15) and (17), can be well approximated by some values on the mesh.

Next, we use MATHEMATICA to symbolically evaluate the derivatives in equation (17) to any necessary order, which is followed by a numerical evaluation of the sums. The results are presented in figures 2 and 3 where we exhibited the canonical occupation number distributions for the systems of $N_t = 10$ and $N_t = 20$ particles, respectively, obeying Fermi–Dirac or Bose–Einstein statistics. It follows by comparing the corresponding distributions of Bose and Fermi particles that with the increase of the total number of interacting particles, there is a dramatic enhancement of the difference in the behaviour of Fermi and Bose particle distributions. Indeed, even for systems with such a moderate number of particles as $N_t = 20$, the canonical distribution of Fermi particles is much broader than its counterpart for Bose particles which tend to cluster around a relatively few low energy states.

Finally, we have compared the scaled canonical occupation number distribution for $N_t = 20$ Fermi particles with the scaled Fermi–Dirac distribution and found them to be indistinguishable. Consequently, the grand canonical ensemble is expected to reliably describe

[4] As the temperature goes to zero the two distributions become indistinguishable.

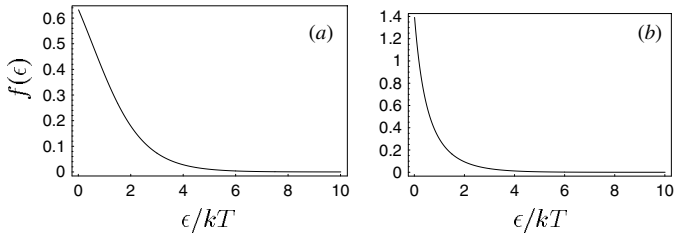

Figure 2. Canonical occupation number distribution for a system of interacting Fermi (a) or Bose (b) particles as a function of the scaled energy, ϵ/kT. The number of particles is taken to be $N_t = 10$, and the mesh is chosen such that $N_{\max} = 100$, $\Delta\epsilon/kT = 0.1$.

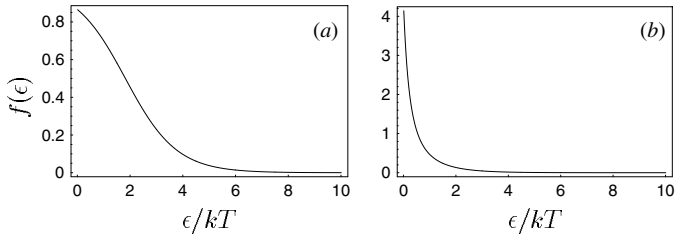

Figure 3. Same as in figure 2, but for $N_t = 20$ particles.

systems of $N_t \geqslant 20$ Fermi particles at any temperature. Unfortunately, a similar comparison for Bose systems cannot be carried out because the Bose–Einstein distribution diverges at zero energy, below the critical temperature at which the Bose–Einstein condensation takes place [25]. Hence a comparison between the canonical occupation number distribution and the Bose–Einstein distribution requires a special consideration which goes beyond the scope of this letter[5]. We will only remark here that the canonical ensemble treatment of Bose systems with small numbers of particles has two significant advantages over the usual grand canonical ensemble approach: first, the canonical ensemble theory avoids the divergence issue at zero energy, and second, such a theory circumvents the need to compute the chemical potential.

In conclusion, we have formulated a statistical mean-field theory of finite quantum systems described by the canonical ensemble of statistical mechanics. We derived the mean-field equations for such systems as well as the occupation number distribution for particles obeying Fermi–Dirac or Bose–Einstein statistics. We illustrated the behaviour of the particle occupation number distribution by examples. Our results may find numerous applications to mesoscopic systems in atomic, molecular, nuclear and condensed matter physics. In particular, the developed mean-field theory for finite quantum systems can be successfully employed to describe ions embedded in dense plasmas. Typically, the so-called average atom model is used to describe a characteristic (average) ion in such plasmas [26]. This description entirely lacks information about characteristics of a specific plasma ion, one with a fixed number of electrons. Our theory makes it possible to provide a more physically accurate statistical description of a specific ion in such plasmas.

[5] We plan to address this issue in a future publication.

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