



# System-Size Dependence in Grand Canonical and Canonical Ensembles

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## Abstract

The thermodynamics for a system with given temperature, density, and volume is described by the Canonical ensemble. The thermodynamics for a corresponding system with the same temperature, volume, and average density is described by the Grand Canonical ensemble. In general, a chosen thermodynamic potential (e.g., free energy) is different in the two cases. Their relationship is considered here as a function of the system size. Exact expressions relating the fundamental potential for each (free energy and pressure, respectively) are identified for arbitrary system size. A formal asymptotic analysis for large system size gives the expected equivalence, but without any characterization of the intermediate size dependence. More detailed evaluation is provided for the simple case of a homogeneous, non-interacting Fermi gas. In this case, the origin of size dependence arises from only two length scales, the average interparticle distance and quantum length scale (thermal deBroglie or Fermi length). The free energies per particle calculated from each ensemble are compared for particle numbers  $2 \leq N \leq 64$  for a range of temperatures above and below the Fermi temperature. The relevance of these results for applications of density functional theory is discussed briefly.



## 1. INTRODUCTION AND MOTIVATION

Equilibrium statistical mechanics provides the fundamental basis for the thermodynamics of a given system in terms of its Hamiltonian and the characteristics of its environment (e.g., open or closed).<sup>1</sup> The Canonical ensemble applies when the system is in contact with a thermal reservoir, exchanging energy at constant volume and particle number. It is parameterized by the temperature ( $T \equiv 1/k_B\beta$ ), number density ( $n \equiv N/V$ ), and volume ( $V$ ). The fundamental thermodynamic potential associated with this ensemble is the Helmholtz free energy per particle  $f_C(\beta, n, V)$ . The Grand Canonical ensemble applies under the same thermodynamic conditions but with the additional exchange of particle number with its environment. It is parameterized by  $\beta, \mu$ , and  $V$ , where  $\mu$  is the chemical potential. Its thermodynamic potential is the pressure  $p_G(\beta, \mu, V)$ . However, the free energy per particle in the Grand Canonical ensemble  $f_G(\beta, n_G, V)$  can be determined from  $p_G(\beta, \mu, V)$  by a change of variables  $\mu \rightarrow n_G \equiv \partial p_G / \partial \mu$  via a Legendre transform (see below). Here,  $n_G$  is the average density in the Grand Canonical ensemble. Similarly, the pressure can be defined for the Canonical ensemble by the change of variables  $n \rightarrow \mu_C \equiv -\partial f_C / \partial n$  and a corresponding Legendre transform.

For large systems, it is expected on physical grounds that the system becomes extensive, in which case the free energy per particle and pressure become independent of the volume

$$f_C(\beta, n, V) \rightarrow f_C(\beta, n), \quad p_G(\beta, \mu, V) \rightarrow p_G(\beta, \mu). \quad (1)$$

Furthermore, if the two ensembles have the same  $\beta, V$ , and  $\mu$  is chosen such that  $n = n_G(\beta, \mu)$  then the thermodynamics from the two ensembles should be equivalent in this limit, e.g.,

$$f_C(\beta, n) = f_G(\beta, n_G). \quad (2)$$

It is this equivalence that allows one to choose an equilibrium ensemble for convenience of computation or simulation, rather than to fit the actual experimental conditions of interest. For example, most formulations of density functional theory are based in the Grand Canonical ensemble while actual implementations in simulation are for conditions of the Canonical ensemble, specifically for fixed density and volume. This raises the challenge of quantifying the conditions for the validity of (1) and (2), and finding relationships between properties in different ensembles. The objective here is to

formulate this problem more precisely and to provide some answers for the simplest case of a non-interacting Fermi gas.

The large system limit is defined by  $V \rightarrow \infty$  at constant  $n$  or  $n_G$  for the Canonical and Grand Canonical ensembles, respectively. Equivalently, this can be stated as  $N \rightarrow \infty$  at constant  $n$ , or  $N_G \rightarrow \infty$  at constant  $n_G$ . In detail, the shape of the system must be constrained as well, e.g., all dimensions should be of comparable size  $L$  such that  $L/r_0$  is large, where  $r_0$  is the average interparticle spacing defined by  $4\pi n r_0^3/3 = 1$ . The desired limit requires that  $L$  be large compared to all other characteristic length scales as well. One of these is the force range of interaction,  $a$ . For Coulomb systems, this is replaced by the screening length. Another length scale is the thermal de Broglie wavelength  $\lambda$  which becomes large at low temperatures, or the corresponding Fermi length  $\tilde{\lambda}$  at temperatures near zero. There can also be a scale set by the spatial variations of an external potential. Finally, the correlation length is typically of the order of the force range, but becomes large near a critical point so that system-size dependence can be important even for macroscopic systems. In cases for which  $L$  is not the dominant length scale, the system is “small” and, while the thermodynamic formalism is universal, the details must account for the specific environment of the system being described.<sup>2</sup> Here, only the Canonical and Grand Canonical conditions are considered, although many other ensembles for other environments are of experimental interest.<sup>1,2</sup> There is a large literature on the asymptotic evaluation of the difference between properties calculated in different ensembles, e.g., fluctuations in extensive variables.<sup>3</sup> Much less is known away from such asymptotic conditions. However, low temperature thermodynamic properties of interacting fermions in 1D system have also been discussed in the literature (see Ref. 4).

The next section defines the ensembles and their associated thermodynamic potentials. In particular, for comparisons exact relationships between them are identified for arbitrary system size. Generally, the thermodynamic properties for the two cases are not equal. However, in [Section 3](#), an asymptotic analysis for one of these relationships shows their equivalence for large  $V$  (or large  $N$ ) at constant number density. The analysis is formal and does not expose the full dependence on  $V$  nor the cross over to the extensive limit in (1). A more detailed quantitative evaluation is provided in [Section 4](#) for the special case of a homogeneous non-interacting gas. In that case, the only relevant length scales are  $r_0$  and  $\lambda$  (or  $\tilde{\lambda}$ ). Finally, inhomogeneous non-interacting systems with an external potential are discussed in [Section 5](#)

and related to the results of Section 4 using a local density approximation (see below). The relevance for ensemble dependence and system-size corrections to the familiar Thomas–Fermi approximation in density functional theory<sup>5</sup> is discussed.



## 2. CANONICAL AND GRAND CANONICAL ENSEMBLES AND THEIR THERMODYNAMICS

The equilibrium Canonical ensemble for a system of  $N$  particles in a volume  $V$ , coordinates  $\mathbf{q}_i$ , with pairwise interactions and an external single particle potential is defined by the probability density operator

$$\rho_C = e^{-\beta(H_N - Nf_C)}, \quad \beta f_C = -\frac{1}{N} \ln \text{Tr}_N e^{-\beta H_N}. \quad (3)$$

Here,  $H_N$  is the Hamiltonian operator for  $N$  particles

$$H_N = K_N + \Phi_N + \sum_{i=1}^N v(\mathbf{q}_i), \quad (4)$$

where  $K$  and  $\Phi$  are the total kinetic and potential energies, respectively. The specific forms of the pair potential  $\phi(\mathbf{q}_i, \mathbf{q}_j)$  and external potential  $v(\mathbf{q}_i)$  are not required at this point. The equilibrium thermodynamics for this system is defined from the free energy per particle  $f_C(\beta, n, V)$  which is a function of the temperature  $T = 1/k_B\beta$ , the density  $n = N/V$ , and the volume  $V$ . The trace in the definition of  $f_C$  is taken over the  $N$  particle Hilbert space with the appropriate symmetrization (Bosons or Fermions). For large systems (i.e.,  $V \rightarrow \infty$  at fixed finite  $n$ ), it is expected that  $f_C(\beta, n, V)$  becomes independent of  $V$ .

The corresponding Grand Canonical ensemble is defined by the operator

$$\rho_G = e^{-\beta(H_N - \mu N + p_G V)}, \quad \beta p_G V = \ln \sum_{N=0}^{\infty} \text{Tr}_N e^{-\beta(H_N - \mu N)}. \quad (5)$$

The thermodynamics now is defined from the pressure  $p_G(\beta, \mu, V)$ , where the density dependence of the Canonical ensemble is replaced by a dependence on the chemical potential  $\mu$ . For large systems (i.e.,  $V \rightarrow \infty$  at fixed finite  $\mu$ ), it is expected that the pressure becomes independent of  $V$ .

Although the pressure is the fundamentally defined thermodynamic potential in the Grand Canonical ensemble, the corresponding free energy,

$f_G(\beta, n_G, V)$ , is defined in terms of that pressure by a change of variables from  $\mu$  to  $n_G$  using the Legendre transformation

$$f_G n_G = -p_G + \mu n_G. \quad (6)$$

Here, the average number density  $n_G(\beta, \mu, V)$ , is

$$n_G(\beta, \mu, V) \equiv \frac{\partial p_G(\beta, \mu, V)}{\partial \mu}. \quad (7)$$

Similarly, although the free energy is the fundamental potential in the Canonical ensemble, the pressure  $p_C(\beta, \mu_C, V)$  is defined in terms of that free energy by a change of variables from  $n$  to  $\mu_C$  using the Legendre transformation

$$p_C = -f_C n + \mu_C n, \quad (8)$$

where the chemical potential in the Canonical ensemble is

$$\mu_C(\beta, n, V) \equiv -\frac{\partial f_C(\beta, n, V)}{\partial n}. \quad (9)$$

From the forgoing definitions it is seen that the thermodynamics defined by the two ensembles are related exactly by the relation

$$e^{\beta p_G(\beta, \mu, V)V} = \sum_{N=0}^{\infty} e^{\beta \mu N} e^{-\beta f_C(\beta, n, V)N}. \quad (10)$$

The volume is the same for each term in this summation, so the density  $n$  changes accordingly. The inversion of this relationship is obtained in [Appendix A](#):

$$e^{-\beta f_C(\beta, n, V)N} = \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} e^{\beta p_G(\beta, \mu = -i\theta/\beta, V)V} \quad (11)$$

Note that the Grand Canonical pressure must be analytically extended to complex values of the chemical potential.

As noted above, the determination of Canonical ensemble properties from given Grand Canonical ensemble results is relevant for practical applications of density functional theory. The inversion of (10) has been discussed recently<sup>6</sup> where it is proposed to construct  $f_C(\beta, n, V)$  from a set of linear equations obtained from evaluation of  $p_G(\beta, \mu, V)$  at  $M$  discrete values of  $\mu$ . In principle, this requires  $M \rightarrow \infty$  but approximate values for  $f_C(\beta, n, V)$  are obtained for finite  $M$ . More systematic expansions are described in Refs. 7,8. This latter

work has been generalized by Lutsko<sup>9</sup>. Equation (11) appears to be new. A similar complex expression is given in Ref. 3, section 3.2, but under the assumption that the discrete summation over  $N$  in (10) can be replaced by an integration. In that case, it becomes a Laplace transform for which the complex Bromwich integral provides its inversion. The explicit construction of (11) for the actual discrete case is given in Appendix A.



### 3. THERMODYNAMIC EQUIVALENCE FOR LARGE SYSTEMS

In this section, the limit of large systems is considered. For it, the Canonical and Grand Canonical thermodynamics are expected to be equivalent. For the Canonical ensemble, large systems means the limit  $N \rightarrow \infty$  at constant finite density  $n = N/V$  and temperature. For the Grand Canonical ensemble, this limit is  $V \rightarrow \infty$  at constant chemical potential  $\mu$  and temperature. To show this equivalence, consider again (11) written as

$$\beta f_C(\beta, n, V)N = -\ln \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{VA(z=\theta)}, \quad (12)$$

where now  $A(z)$  is a real function of the complex variable  $z$ ,

$$A(z) = izn + \beta p_G(\beta, -iz/\beta, V). \quad (13)$$

It has a stationary saddle point at the value  $z \equiv z_s$  defined by  $dA/dz = 0$ . Using (7) this is

$$\text{Re } n_G(\beta, -iz_s/\beta, V) = n, \quad \text{Im } n_G(\beta, -iz_s/\beta, V) = 0. \quad (14)$$

Since  $n_G(\beta, z, V)$  is a real function of  $z$  the solution is  $z_s = i\beta\mu_s$  with real  $\mu_s$  determined from

$$n_G(\beta, \mu_s, V) = n. \quad (15)$$

Now let  $C$  denote a closed contour in the  $z$  plane including the interval  $[0, 2\pi]$  along the positive real axis and passing through  $i\beta\mu_s$  on the complex axis. Assume that  $A(z)$  is analytic on and within  $C$ , so that the integral of  $\exp(VA(z))$  over the entire contour must vanish. Consequently, the integral of (12) can be replaced by an integration over that part of  $C$  complementary to the interval  $[0, 2\pi]$ . Denoting that part by  $C'$

$$\beta f_C(\beta, n, V)N = -\ln \frac{\beta}{2\pi} \int_{C'} dz e^{VA(z)}, \quad (16)$$

where by definition  $C'$  passes through the stationary point  $\mu_s$  tangent to the complex axis. Since  $A(z)$  is multiplied by  $V$ , the contribution near  $i\beta\mu_s$  gives the dominant contribution for large system size. The usual saddle-point analysis then leads to the asymptotic result

$$\begin{aligned}\beta f_C(\beta, n, V)N &\rightarrow -A(\mu_s)V - \ln \frac{\beta}{2\pi} \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}V|A''|(x-\mu_s)^2} \\ &= -\mu_s\beta N + \beta p_G(\beta, \mu_s, V)V + O(\ln N)\end{aligned}\quad (17)$$

The first two terms are proportional to the free energy of the Grand ensemble evaluated at the value of the chemical potential that ensures  $N_G(\beta, \mu_s, V) = N$ . The free energies are therefore the same up to small corrections of the order  $(\ln N)/N$

$$f_C(\beta, n, V) = f_G(\beta, n_G, V) + O\left(\frac{1}{N} \ln N\right) \quad (18)$$

This is the expected equivalence for large systems. Note, however, that the analysis does not show that the free energy per particle is independent of  $V$ . That question is explored in more detail in the next two sections.



#### 4. NON-INTERACTING, HOMOGENEOUS SYSTEMS AT FINITE SYSTEM SIZE

In this section, the thermodynamics for the Grand Canonical and Canonical ensembles are calculated exactly at arbitrary system size for the simplest case of non-interacting particles without external potential. The Hamiltonian for  $N$  particles is

$$H_N^0 = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m}. \quad (19)$$

For the Canonical ensemble, the particle number and volume are fixed so the boundary conditions chosen here are a cubic box of sides  $L$  with hard walls. Then the momentum components have eigenvalues

$$p_\alpha = \frac{\pi\hbar}{L} k_\alpha, \quad \alpha = x, y, z \quad (20)$$

where  $k_\alpha$  is a positive integer. The Grand Canonical ensemble represents an open system without fixed particle number. However, its derivation represents this as the sum of probabilities for closed systems at the same

volume but different particle number. Hence the same boundary conditions can be used for calculation of components of each  $N$  within the ensemble.

#### 4.1 Grand Canonical Ensemble

The pressure in the Grand Canonical Ensemble is given by (5). Since  $H_N$  is the sum of single-particle operators the summation and trace can be performed directly in occupation number representation with the result for spin 1/2 Fermions<sup>10</sup>

$$\beta p_G = \frac{2}{V} \sum_{\mathbf{k}} \ln \left( 1 + e^{\beta\mu} e^{-\left(\frac{k}{\ell}\right)^2} \right). \quad (21)$$

The three-fold summation is over  $\mathbf{k} = k_x, k_y, k_z$ . Use has been made of

$$\beta \frac{p^2}{2m} = \frac{\beta}{2m} \left( \frac{\pi \hbar}{L} \right)^2 k^2 = \left( \frac{k}{\ell} \right)^2, \quad \ell^2 = \frac{4}{\pi} \left( \frac{L}{\lambda} \right)^2, \quad (22)$$

where  $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$  is the thermal de Broglie wavelength. Similarly, the average number density  $n_G$  is

$$n_G = \frac{2}{V} \sum_{\mathbf{k}} \left( e^{-\beta\mu} e^{(k/\ell)^2} + 1 \right)^{-1}. \quad (23)$$

It is tempting at this point to represent the summations over  $\mathbf{k}$  as integrals, i.e.,

$$\sum_{k_x} F(k/\ell) = \ell \sum_x \Delta x F(x) \stackrel{?}{\rightarrow} \ell \int dx F(x) \quad (24)$$

Indeed this replacement leads to the familiar textbook results in terms of Fermi integrals. However,  $\Delta x = \Delta k_x/\ell = 1/\ell$  is small only for  $L/\lambda \gg 1$ . This is not the case for low temperatures or small system sizes. Hence for the purposes here the discrete summation must be evaluated directly.

At this point, all properties will be given a corresponding dimensionless form. The dimensionless temperature  $t$  is

$$t = \frac{1}{\beta\epsilon_F}, \quad \epsilon_F = \frac{1}{2m} \hbar^2 (3\pi^2 n_G)^{2/3}. \quad (25)$$

where  $\epsilon_F$  is the Fermi energy. It follows that



$$n_G \lambda^3 = \frac{8}{3\sqrt{\pi}} t^{-3/2}, \quad (26)$$

so that (23) becomes

$$t^{-3/2} = \frac{6}{\pi \ell^3} \sum_{\mathbf{k}} \left( e^{-\beta \mu} e^{(k/\ell)^2} + 1 \right)^{-1}, \quad (27)$$

and

$$\ell = \left( \frac{3}{\pi} N_G t^{3/2} \right)^{1/3}. \quad (28)$$

An appropriate dimensionless pressure is

$$p_G^*(t, N_G) = \frac{\beta p_G}{n_G} = \frac{2}{N_G} \sum_{\mathbf{k}} \ln \left( 1 + e^{\beta \mu} e^{-(\frac{k}{\ell})^2} \right). \quad (29)$$

Here, it is understood that  $\beta \mu = \beta \mu(t, N_G)$  as determined from (27). Finally, the dimensionless free energy per particle is obtained from the Legendre transformation as described in (6).

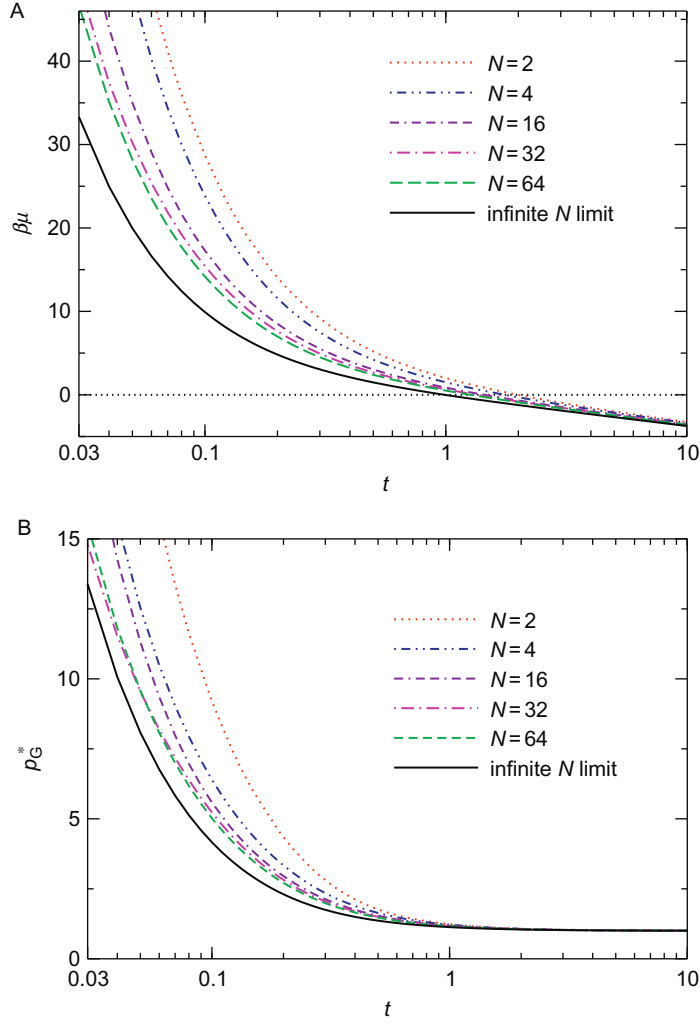
$$f_G^*(t, N_G) \equiv -p_G^*(t, N_G) + \beta \mu(t, N_G). \quad (30)$$

The dimensionless system-size parameter is now  $N_G$ . The analysis proceeds as follows: (1) choose a value for  $N_G$  and calculate  $\beta \mu(t, N_G)$  as a function of  $t$  from (27). Repeat for different values of  $N_G$ . The results are shown in Fig. 1A. Also shown is the limiting value for  $N_G \rightarrow \infty$  obtained from the continuum limit (i.e., 24); (2) calculate  $p_G^*(t, N_G)$  from (29) as a function of  $t$  for the same set of values for  $N_G$ . The results are shown in Fig. 1B; and (3) calculate the dimensionless free energy  $f_G^*(t, N_G)$  as a function of  $t$  for the same set of  $N_G$  from (30). The results are shown in Fig. 2.

These figures show that the system-size dependence is small for  $N_G \geq 16$  at  $t = 10$ , but is more significant as the temperature is lowered. This is expected since that dependence is controlled by  $\ell = \left( \frac{3}{\pi} N_G t^{3/2} \right)^{1/3}$  and vanishes only for large  $\ell$ . Below  $t = 1$ , larger values of  $N_G$  are required to approach system-size independence.

## 4.2 Canonical Ensemble

Equation (11) shows that the Canonical ensemble free energy per particle can be obtained from the Grand Canonical pressure, extended to complex values for the chemical potential. It is written as

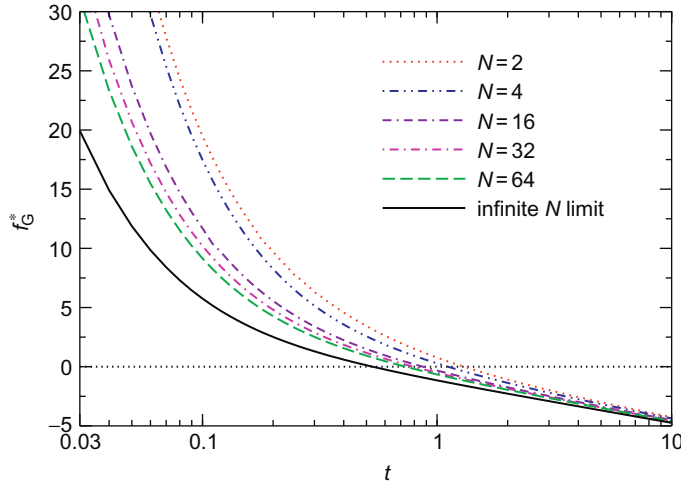


**Figure 1** (A) Plot of  $\beta\mu(t, N_G)$  as a function of the dimensionless temperature  $t$  for several values of  $N_G = N$ . Also shown is the large system-size limit. (B) Plot of the dimensionless pressure  $p_G^*(t, N_G)$  as a function of the dimensionless temperature  $t$  for several values of  $N_G = N$ .

$$\beta f_C(\beta, n, V) = -\frac{1}{N} \ln \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{(i\theta + g(\theta, t, N))N}, \quad (31)$$

with

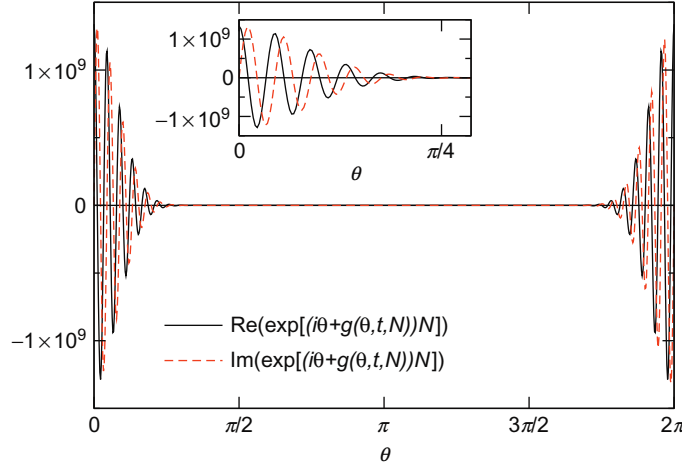
$$g(\theta, t, N) \equiv \frac{\beta p_G(\beta, \mu = -i\theta/\beta, V)}{n} = \frac{2}{N} \sum_{\mathbf{k}} \ln \left( 1 + e^{-i\theta} e^{-\left(\frac{k}{t}\right)^2} \right). \quad (32)$$



**Figure 2** Plot of the dimensionless free energy per particle,  $f_G^*(t, N_G) = \beta f_G(\beta, n_G, V)$ , as a function of the dimensionless temperature  $t$  for several values of  $N_G = N$ .

The definitions of  $t$  and  $\ell$  are the same as in (25) and (28) except with  $n_G$  and  $N_G$  replaced by  $n$  and  $N$ . The calculation of  $g(\theta, t, N)$  is similar to that of  $p_G^*(t, N_G)$  in (29), except that it has both real and imaginary parts. Their numerical calculation is straightforward but the final  $\theta$  integration of (31) is now problematical. Due to the complex integral, it has an oscillatory integrand whose variation increases as  $N$ , and whose modulation varies between values of the order  $\exp(\pm N)$ . Figure 3 illustrates the problem for  $N = 64$ ,  $t = 0.63$ . This is a precursor for the cross-over to the asymptotic analysis of Section 3. The first difficulty of a rapidly oscillating integrand can be overcome by increasing the density of mesh points. That works in principle for both very large  $N$  and  $t$ . The second problem of huge cancellations when the integral is evaluated numerically as a sum over mesh points does not have a simple solution because of the finite precision of floating point numbers. As can be seen from the Fig. 3, the highest magnitude of the integrand is  $\sim 10^9$  while the final value of the real part of the integral is  $\sim 10^{-10}$ . Quadruple precision is required for adequate accuracy within the restricted domain  $0.1 < t < 10$  and  $N \leq 64$ .

Figure 4A–D shows the dimensionless Canonical ensemble free energy per particle in comparison with the corresponding Grand Canonical ensemble results of the last section. Generally, for  $N > 16$  there is good agreement between the results of the two ensembles, although significant system-size



**Figure 3** Illustration of the strong variation with  $\theta$  for the integrand of (31), for  $N = 64$ ,  $t = 0.63$ .

dependence relative to the large system-size limit remains. At smaller values of  $N$ , the discrepancies between the two ensembles decreases at lower  $t$ . On the contrary, the difference for both ensemble from the large system limit increases with smaller  $N$  and  $t$ .

For  $t = 0$ , the free energy for both Canonical and Grand Canonical ensembles are the same for given  $N$  as it is the sum of discrete energies up to the Fermi energy for  $N$  particles. This, however, is still different from the infinite system limit which is an integral over the density of states.



## 5. RELATIONSHIP TO DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) describes the thermodynamics of an equilibrium, inhomogeneous system whose Hamiltonian has the form (4).<sup>5</sup> The external potential implies that the local density is non-uniform. DFT has a variational principle that states that the thermodynamic properties are obtained from a functional of this density at its extremum. The definition of the functional can be given as follows. First, the Grand Canonical ensemble pressure and density are computed as functionals of the external potential as in (5)

$$\beta p_G V = \ln \sum_{N=0}^{\infty} T r_N e^{-\beta(H_N - \mu N)}, \quad n_G(\mathbf{r}) \equiv -\frac{\partial p_G(\beta, \mu, V)}{\partial v(\mathbf{r})}. \quad (33)$$

Next, the external potential is eliminated by inverting the second equation to give  $\beta p_G V$  as a functional of the density and finally, the density functional of DFT is then given by<sup>5</sup>

$$F_{\text{DFT}} \equiv -p_G V + \int d\mathbf{r} (\mu - v(\mathbf{r})) n_G(\mathbf{r}), \quad (34)$$

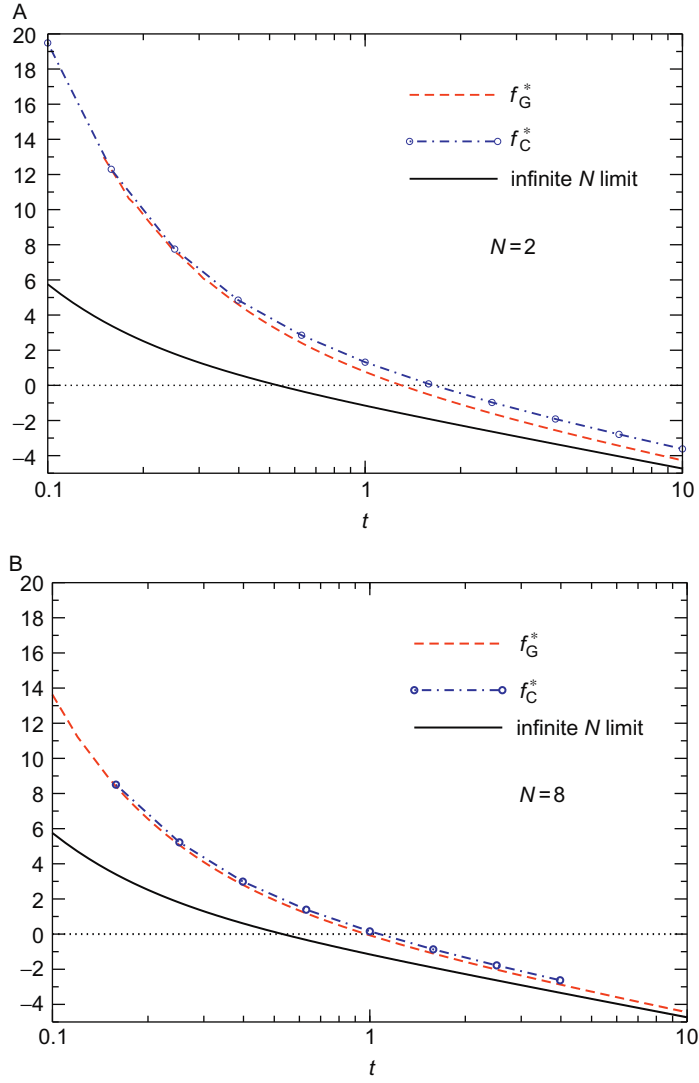
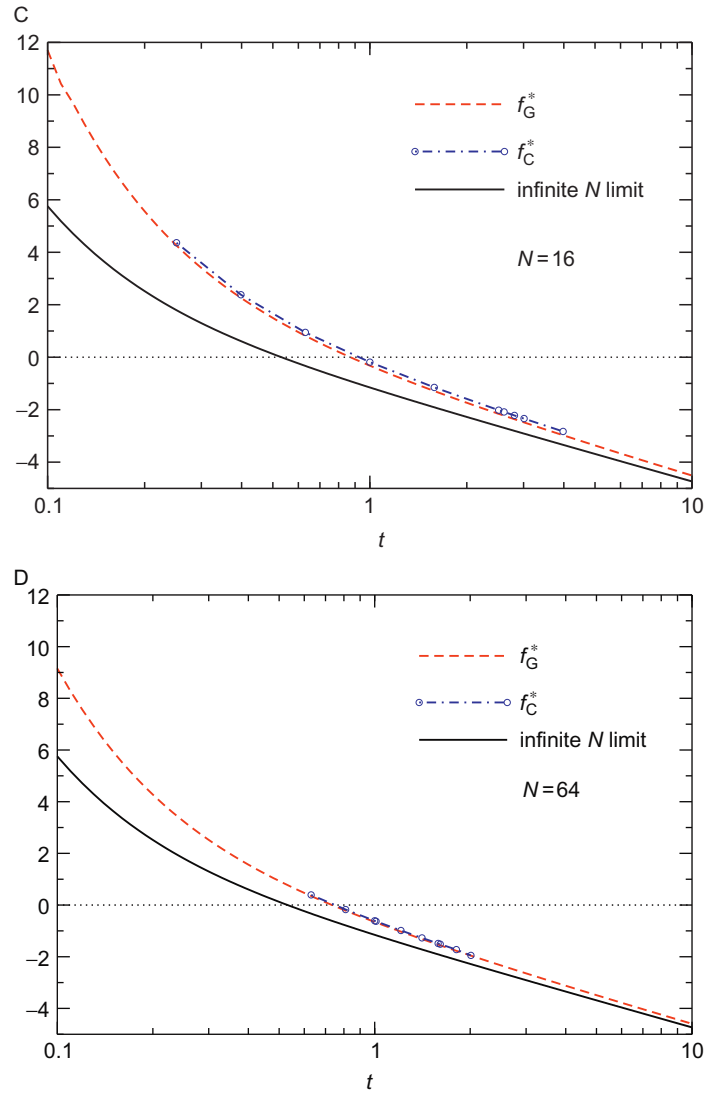


Figure 4—Cont'd



**Figure 4—Cont'd** Panel (A) compares the dimensionless free energy per particle for Canonical and Grand Canonical ensemble ( $f_G^*(t, N_G)$ ,  $f_C^*(t, N)$ ) as a function of the dimensionless temperature  $t$  for  $N = 2$ . Also shown is the large system-size limit. Panels (B)–(D) show the same comparison for  $N = 8$ ,  $N = 16$ , and  $N = 64$ , respectively.

It is understood that the density and external potential in the second term are now independent functions. They become related by the extremum condition that provides the equilibrium density in terms of the external potential. Finally, with that relationship established, evaluation of  $F_{\text{DFT}}$  at its extremum gives the Legendre transform (6) (extended to the inhomogeneous case) and hence the equilibrium Grand Canonical free energy.

It is clear from this brief description of DFT that its theoretical formulation is tied to the Grand Canonical ensemble. However, in practice construction of approximate functionals often presumes the large system-size limit (e.g., Thomas–Fermi and local density approximations). Calculations almost always fix the total number of particles,  $N$ , as in the Canonical ensemble. Consequently, system-size corrections and ensemble dependencies are overlooked or ignored. The analysis of the previous sections is therefore quite relevant for current problems of DFT.

To illustrate this, consider the non-interacting part of the DFT functional constructed as above

$$\beta p_{\text{G}}^{(0)} V = \int d\mathbf{r} \left\langle \mathbf{r} \left| \ln \left( 1 + e^{\beta\mu} e^{-\beta(\frac{\hat{p}^2}{2m} + \nu(\hat{\mathbf{q}}))} \right) \right| \mathbf{r} \right\rangle \quad (35)$$

$$n_{\text{GC}}^{(0)}(\mathbf{r}) = \left\langle \mathbf{r} \left| \left( e^{-\beta\mu} e^{\beta(\frac{\hat{p}^2}{2m} + \nu(\hat{\mathbf{q}}))} + 1 \right)^{-1} \right| \mathbf{r} \right\rangle \quad (36)$$

$$\begin{aligned} \beta F_{\text{DFT}}^{(0)} = & - \int d\mathbf{r} \left\langle \mathbf{r} \left| \ln \left( 1 + e^{\beta\mu} e^{-\beta(\frac{\hat{p}^2}{2m} + \nu^{(0)}(\hat{\mathbf{q}} n_{\text{GC}}))} \right) \right| \mathbf{r} \right\rangle \\ & + \int d\mathbf{r} \beta(\mu - \nu(\mathbf{r})) n_{\text{GC}}^{(0)}(\mathbf{r}). \end{aligned} \quad (37)$$

On the right side of (36)  $\nu^{(0)}(\hat{\mathbf{q}} | n_{\text{GC}}^{(0)})$  denotes the inversion of (35) to obtain  $\nu(\mathbf{r})$  as a functional of  $n_{\text{GC}}^{(0)}(\mathbf{r})$ . Further construction of  $\beta F_{\text{DFT}}^{(0)}$  is nontrivial for general external potential and entails diagonalization of the single particle Hamiltonian  $\hat{p}^2/2m + \nu(\hat{\mathbf{q}})$  and self-consistent inversion of the expression for  $n_{\text{GC}}^{(0)}(\mathbf{r})$  (the Kohn–Sham approach).<sup>11,12</sup> A simpler method is the local density approximation that replaces the operator dependence of the external potential by its value at the point of interest,  $(\nu(\hat{\mathbf{q}})) \rightarrow \nu(\mathbf{r})$ . Then for instance the density equation can be evaluated in momentum representation using the same boundary conditions as above

$$n_{\text{GC}}^{(0)}(\mathbf{r}) \rightarrow \frac{2}{V} \sum_{\mathbf{k}} \left( e^{-\beta(\mu-\nu(r))} e^{(k/\ell)^2} + 1 \right)^{-1} |\psi_{\mathbf{k}}(\mathbf{r})|^2 \quad (38)$$

In the large system-size limit, the summation can be represented as an integration and becomes the familiar finite temperature Thomas–Fermi approximation

$$n_{\text{TF}}^{(0)}(\mathbf{r}) \rightarrow h^{-3} \int d\mathbf{p} \left( e^{-\beta(\mu-\nu(r))} e^{\beta \frac{p^2}{2m}} + 1 \right)^{-1}. \quad (39)$$

Equations (38) and (39) are the same results as for the homogenous system analysis of the last section, with only the replacement  $\mu \rightarrow \mu - \nu(r)$ . Hence the system-size corrections found there for small  $N, t$  apply here as well, and those corrections for the free energy per particle identified in Figs. 2 and 4A–D are required for the DFT functional as well. Notwithstanding those corrections, it is expected that differences between the results for the two ensembles are small for  $N = N_G > 16$ . Further discussion of system-size and ensemble dependence of the DFT functional will be given elsewhere.

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## A. APPENDIX

### A.1 Determination of $f_{\text{C}}(\beta, n, V)$ from $p_{\text{G}}(\beta, \mu, V)$

The definition of  $f_{\text{C}}(\beta, n, V)$  in (3) can be written in the equivalent form

$$\beta f_{\text{C}} = -\frac{1}{N} \ln \text{Tr}_N e^{-\beta H_N} = -\frac{1}{N} \ln \sum_{M=0}^{\infty} \text{Tr}_M \delta_{N,M} e^{-\beta H_M}, \quad (\text{A.1})$$

with a representation for the Kronecker delta  $\delta_{N,M}$  to get

$$\begin{aligned} \beta f_{\text{C}}(\beta, n, V) &= -\frac{1}{N} \ln \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} \sum_{M=0}^{\infty} \text{Tr}_M e^{-i\theta M} e^{-\beta H_M} \\ &= -\frac{1}{N} \ln \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} e^{\beta p_{\text{G}}(\beta, \mu = -i\theta/\beta, V) V}. \end{aligned} \quad (\text{A.2})$$



The last line follows from the definition of  $p_G$  in (5). This gives the relationship (11) quoted in the text

$$e^{-\beta f_C(\beta, n, V)N} = \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} e^{\beta p_G(\beta, \mu = -i\theta/\beta, V)V}. \quad (\text{A.3})$$

The consistency of this result with its inverse (10) can be demonstrated by substituting the latter into the right side of (11)

$$\begin{aligned} e^{-\beta f_C(\beta, n, V)N} &= \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta N} \sum_{M=0}^{\infty} e^{-i\theta M} e^{-\beta f_C(\beta, n=M/V, V)M} \\ &= \sum_{M=0}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} d\theta e^{i\theta(N-M)} e^{-\beta f_C(\beta, n=M/V, V)M} \\ &= e^{-\beta f_C(\beta, n, V)N}. \end{aligned} \quad (\text{A.4})$$

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