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Excess Grand Potential for a System under an External Field: Effects of External Field Driven Nonextensivity

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We report that an external field can drive inherently extensive systems into nonextensive ones. For the correct grand canonical description of nonextensive systems, it is necessary to take into account the excess grand potential, X, in addition to the conventional grand potential proportional to the thermodynamic pressure, which has long been overlooked in the literature in this field. We present the statistical mechanical expression for X of a system as a functional of the external field imposed on the system, from which we establish the criterion for the external field that drives an inherently extensive macroscopic system into a nonextensive one.

The grand canonical ensemble (GCE) is one of the most fundamental ensembles for statistical mechanical description of an open system in which both the energy and the number of particles fluctuate.[1,2] Since GCE was firmly established by Tolman,[3] it has been exploited to solve a variety of problems encountered in physics and chemistry.[4−9]

The conventional formula that connects the grand canonical ensemble to thermodynamics, originally due to Fowler,[10,11] is given by

$$P_{\mathrm{G}} = kT\frac{1}{V}\ln \Xi(\mu, V, T) \tag{1}$$

where P_G, T, V, and μ denote the conventional grand canonical pressure, the temperature, the volume, and the chemical potential of the system, respectively.[5,7,12−17] k denotes the Boltzmann constant. A long time ago, Yang pointed out that the conventional grand canonical pressure P_G in eq 1 is not the grand canonical average $\langle P\rangle$ of the canonical pressure

$$\langle P\rangle = kT\frac{\partial}{\partial V}\ln \Xi(\mu, V, T) \tag{2}$$

but P_G is the second average of $\langle P\rangle$ over all volumes from zero to the actual volume of the system.[18,19] However, later, Lewis showed that conventional grand canonical pressure, P_G, becomes identical to $\langle P\rangle$ given in eq 2 in the limit of infinite systems, whenever P_G exists.[20] Presented in ref 20 is a direct proof for the equivalence between P_G in eq 1 and $\langle P\rangle$ in eq 2 for an extensive macroscopic system. On the other hand, it is established that, in the macroscopic limit, the effects of fluctuation in particle number become negligible so that $\langle P\rangle$ defined in eq 2 becomes identical to the canonical pressure, $\langle P\rangle_c$,

$$\langle P\rangle_{\mathrm{c}} = kT\frac{\partial}{\partial V}\ln Q(N, V, T) \tag{3}$$

where $Q(N,V,T)$ is the canonical partition function of the system of N particles in volume V in equilibrium with a heat bath with temperature T.

However, it is not necessarily well-known that an external field can make an inherently extensive system nonextensive so that eq 1 may not hold for the system under an external field unlike the thermodynamic connection formulas for other popular statistical ensembles such as microcanonical ensemble and canonical ensemble. Percus, Pozhar, and Gubbins once noted that an intuitive generalization of eq 1 does not provide the correct hydrodynamic description of strongly inhomogeneous fluids;[21] however, the external field driven nonextensivity and its contribution to grand potential have never been yet recognized to the best of our knowledge. In this Letter, we introduce the notion of external field driven nonextensivity, and quantify the previously neglected contribution of the nonextensivity to the grand potential on the bases of simple and exact analyses. In addition, we present the quantitative criterion for the external field that drives an inherently extensive macroscopic system into a nonextensive one. We also note that, even in descriptions of homogeneous systems, eq 1 has been used out of its application range in literatures.[7,13−17,22] For example, an ideal homogeneous Bose−Einstein gas system is a nonextensive system as long as it is finite and does not obey eq 1, which has long been overlooked in textbooks in this field.[13−17] To such nonextensive systems, whether or not induced by an external field, care must be taken in applying such thermodynamic equations as the Gibbs−Duhem equation and the compressibility equation,[23,24] which are correct only for extensive systems.

In the beginning of this Letter, we present exact model analyses to demonstrate that the grand canonical pressure P_G defined in eq 1 can be much different from the canonical pressure $\langle P\rangle_c$ in eq 3 for a system under external potential even in the macroscopic limit.[25] We will then show that the

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discrepancy between P_G defined in eq 1 and $\langle P\rangle_c$ in eq 3 occurs because an external field drives an inherently extensive system into a nonextensive one to which eq 1 is inapplicable. For the correct grand canonical description of a nonextensive system, it is necessary to introduce the excess grand potential X defined by $G - \mu N$ with G and μ being the Gibbs free energy and the chemical potential, in addition to the conventional grand potential given by $-PV$. We obtain a simple statistical mechanical expression for X as a functional of external field, from which we establish the criterion for the external potential that can generate the nonextensivity on macroscopic systems. We note here that Lewis's mathematical proof in ref 20 may be free of error, but it is proved for an extensive system whose canonical partition function Q satisfies the following properties: $\lim_{N\to\infty} N^{-1} \ln Q(N,V,T)$ exists and is a function of density N/V and temperature T only,[26] which may not always be the case for a system under an external field.

Let us first consider a system of N mutually noninteracting gas particles confined in a volume V under an external potential, $U_{ext}(\mathbf{r})$. The canonical partition function $Q_{gas}(N,V,T)$ of the system is given by $Q_{gas}(N,V,T) = q(V,T)^N/N!$, where $q(V,T)$ denotes the molecular partition function defined by $q(V,T) = [1/\Lambda(T)^3]\int_V d\mathbf{r} \exp[-\beta U_{ext}(\mathbf{r})]$, with $\Lambda(T)$ and β being the thermal de Broglie wavelength of the gas particle and $(kT)^{-1}$, respectively. The corresponding grand canonical system is the gas system in the same volume V but with a permeable boundary in which the chemical potential μ is fixed so that the number of gas particles fluctuates around the average value $\bar{N}$ given by N. For the latter grand canonical system, eq 1 yields the equation of state of an ideal gas:

$$P_G = \beta^{-1}\bar{N}/V \equiv P_{id} \tag{4}$$

where $\bar{N}$ is given by $\bar{N} = \exp(\beta\mu)q(V,\beta)$. Note that eq 4 results from eq 1 for the mutually noninteracting gas system irrespective of the functional form of the external field, $U_{ext}(\mathbf{r})$ imposed on the system.

In comparison, the canonical pressure $\langle P\rangle_c$ defined in eq 3 can deviate from the ideal gas law or eq 4, depending on the external potential imposed on the gas system. For example, consider the gas system under external potential U_g defined by $U_g(\mathbf{r}) \to \infty$ for $|\mathbf{r}| < \sigma$ and $U_g(\mathbf{r}) = -C/|\mathbf{r}|$ for $|\mathbf{r}| > \sigma$, with C and σ being positive constants. From eq 3, the canonical pressure $\langle P\rangle_c^{(g)}$ of this system on the surface defined by $|\mathbf{r}| = R(>\sigma)$ can be obtained as

$$\langle P\rangle_c^{(g)} = P_{id}\frac{(R'^3 - \sigma'^3)\exp(1/R')}{\psi(R') - \psi(\sigma')} \tag{5}$$

where R', σ', and ψ are respectively defined by $R' = R/\beta C$, $\sigma' = \sigma/\beta C$, and $\psi(x) = 2^{-1}[e^{1/x}x(1 + x + 2x^2) - \mathrm{Ei}(1/x)]$, with Ei denoting the exponential integral function.

Although $\langle P\rangle_c^{(g)}$ given in eq 5 deviates significantly from P_G, the discrepancy between $\langle P\rangle_c^{(g)}$ and P_G becomes smaller as R' increases; as the value of R' increases, $\langle P\rangle_c^{(g)}$ approaches P_{id} as follows:

$$\langle P\rangle_c^{(g)} = P_{id}\{1 - (2R')^{-1} - (2R')^{-2} + O(R'^{-3})\} \qquad (R \gg \beta C) \tag{6}$$

That is to say, in the macroscopic limit, the canonical pressure $\langle P\rangle_c^{(g)}$ calculated by eq 3 for this model is identical to the grand canonical pressure P_G predicted by eq 1.

However, the equivalence between eqs 1 and 3 in the macroscopic limit is not universal. For example, the prediction, $\langle P\rangle_c^{(h)}$, of eq 3 for the pressure at the surface defined by $|\mathbf{r}| = R$ for the gas system under the isotropic harmonic potential, $U_h(\mathbf{r})(\equiv 2^{-1}\kappa|\mathbf{r}|^2)$, with κ being the force constant, is given by

$$\langle P\rangle_c^{(h)} = P_{id}\frac{\xi^3}{\phi(\xi)} \tag{7}$$

Here, ξ and $\phi(\xi)$ are given by $\xi = (\beta\kappa/2)^{1/2}R$ and $\phi(\xi) = (3/4)[\sqrt{\pi}\exp(\xi^2)\,\mathrm{Erf}(\xi) - 2\xi]$, respectively. $\langle P\rangle_c^{(h)}$ given in eq 7 does not reduce to P_{id} in the macroscopic limit; instead, it obeys the following nonideal asymptotic behavior:

$$\langle P\rangle_c^{(h)} \cong P_{id}\frac{4}{3\sqrt{\pi}}\left(\sqrt{\frac{\beta\kappa}{2}}R\right)^3 \exp\left(-\frac{\beta\kappa}{2}R^2\right), \qquad (R \gg \sqrt{\beta\kappa/2}) \tag{8}$$

Note that, in this case, the discrepancy between $\langle P\rangle_c^{(h)}$ and P_G increases with R. In other words, even in the macroscopic limit, the canonical pressure defined in eq 3 is not identical to the grand canonical pressure P_G defined in eq 1 for the gas system under the isotropic harmonic potential. Physically, the pressure of the gas system under the isotropic harmonic potential, U_h, is expected to be smaller than that of the ideal gas system without any external field. The physical intuition is consistent with the expression for the canonical pressure $\langle P\rangle_c^{(h)}$ in eq 8 but not with that of the conventional grand canonical pressure P_G in eq 4. This example shows that, in the presence of external potential, the conventional thermodynamic connection formula, eq 1, of the grand canonical ensemble may not be always correct.

The discrepancy between the conventional grand canonical pressure P_G in eq 1 and the averaged mechanical pressure given in eq 2 or eq 3 can emerge for a nonextensive system only. Since the grand potential Ω, defined by $F - \mu N$ with F being the Helmholtz free energy, is related to the grand canonical partition function as $\Omega = -kT \ln \Xi$,[12−17] eq 1 is obviously correct for an extensive system of which Gibbs free energy, $G(\equiv F + PV)$, can be written as

$$G = \mu N \tag{9}$$

Note that, throughout this work, μ denotes the chemical potential with the following standard definition, i.e., $\mu \equiv (\partial U/\partial N)_{S,V} = (\partial F/\partial N)_{T,V} = (\partial G/\partial N)_{T,P}$,[27] not generalized chemical potentials with different definitions.[28,29] One can easily show that eq 9 holds if the canonical partition function Q satisfies the property assumed by Lewis:[20] $\lim_{N\to\infty} N^{-1} \ln Q(N,V,T)$ is a function of N/V and T only.[26] Note that the latter condition for the canonical partition function is satisfied if and only if the Helmholtz free energy F satisfies $\lim_{N\to\infty} F(\lambda N,\lambda V,T)/(\lambda N) = \lim_{N\to\infty} F(N,V,T)/N$ for arbitrary λ, or

$$F(\lambda N, \lambda V, T) = \lambda F(N, V, T) \tag{10}$$

in the macroscopic limit. Equation 9, on which eq 1 is based, can be derived from eq 10 by application of Euler's theorem,[30] i.e., by taking the partial derivative on both sides of eq 10 with respect to λ and setting the value of λ equal to 1. This simple proof shows that eq 1 holds under the above-mentioned assumption for the canonical partition function, in accordance with Lewis's more direct proof.[20] Equation 1 holds also for a finite system as long as the system is an extensive system for which eq 9 or 10 holds. As shown here, however, application of eq 1 to a nonextensive system, which has become routine in the literature,[7,13−17,22] is not justifiable regardless of whether the system is under an external field or not.

To quantify the nonextensivity of a system, we introduce the excess grand potential X with the following definition: $X \equiv G - \mu N$. The grand canonical expression for X is given by

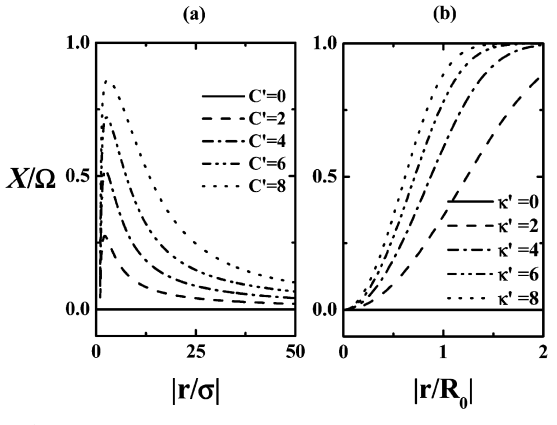

Figure 1. Contribution of the excess grand potential X resulting from external field driven nonextensivity to the grand potential Ω for a classical perfect gas system (a) under potential U_g defined by $U_g(\mathbf{r}) \to \infty$ for $|\mathbf{r}| < \sigma$ and $U_g(\mathbf{r}) = -C/|\mathbf{r}|$ for $|\mathbf{r}| > \sigma$, with C and σ being positive constants, and (b) under isotropic harmonic potential U_h, defined by $U_h = 2^{-1}\kappa|\mathbf{r}|^2$. C' and κ' are unitless variables defined by $C' = \beta C/\sigma$ and $\kappa' = 2^{-1}\beta\kappa R_0^2$, with R_0 being an arbitrary unit of length. X/Ω is equal to $1 - \langle P\rangle/P_G$, where P_G is the conventional grand canonical pressure defined in eq 1 and $\langle P\rangle$ is the ensemble average of the mechanical pressure given in eq 2 or, equivalently, eq 3.

$$X = kTV\left[\frac{\partial(V^{-1}\ln\Xi(\mu, V, T))}{\partial \ln V}\right]_{\mu,T} \tag{11}$$

which can be readily obtained by substituting eq 2 into the definition of grand potential

$$\Omega \equiv X - PV = -kT\ln\Xi \tag{12}$$

Equations 11 and 12 indicate that eq 1 does not hold unless $V^{-1}\ln\Xi$ is constant in V and the excess grand potential X resulting from the nonextensivity vanishes. In Figure 1, we plot the relative contribution of the excess grand potential X to the total grand potential Ω for the classical gas system under the external potentials considered above. Note that X/Ω vanishes for the gas system under external potential U_g in the macroscopic limit but not for the gas system under harmonic external potential U_h.

Let us now establish the criterion for the external field that drives the inherently extensive gas system into a nonextensive one. For the classical gas system, eq 11 reduces to

$$X_{\text{ext}} = kT\bar{N}\left(\frac{\partial \ln \chi_{\text{ext}}(V)}{\partial \ln V}\right)_T \tag{13}$$

where $\bar{N}$ denotes the average number given by $e^{\beta\mu}\chi_{\text{ext}}(V)V/\Lambda^3$, with $\chi_{\text{ext}}(V) \equiv V^{-1}\int_V d\mathbf{r}\exp[-\beta U_{\text{ext}}(\mathbf{r})]$. Equation 13 tells us that the nonextensivity of the mutually noninteracting gas system can be induced by external potential U_{ext} whenever $\chi_{\text{ext}}(V)$ is not a finite constant in V. Furthermore, eqs 4, 12, and 13 tell us that, for the mutually noninteracting gas system under external potential U_{ext}, eq 1 is incorrect even in the macroscopic limit unless $\gamma_\infty[\equiv\lim_{V\to\infty}((\partial \ln \chi_{\text{ext}}(V))/(\partial \ln V))_T]$ of the external potential U_{ext} vanishes. Note that γ_∞ is zero for the gas system under external potential U_g, for which eq 1 is correct in the macroscopic limit, but is -1 for the system under U_h, for which eq 1 does not hold.

Note that eqs 11 and 12 are correct in quantum statistics as well. As such, eq 1, valid for an extensive system only, should not be applied to a finite ideal Bose–Einstein (BE) gas system, since the latter system is an inherently nonextensive system whose excess grand potential X is given by $kT\ln[1 - \exp(\beta\mu)]$. The latter excess grand potential has long been misinterpreted as the ground-state contribution to PV for a finite ideal Bose–Einstein gas system due to the inappropriate application of eq 1.[13−17]

The canonical expression for X is given by

$$X = kT\left[-\ln Q + \left(\frac{\partial \ln Q}{\partial \ln V}\right)_{N,\beta} + \left(\frac{\partial \ln Q}{\partial \ln N}\right)_{V,\beta}\right] \tag{14}$$

One can show that the grand canonical expression for X in eq 12 becomes identical to eq 14 for a macroscopic open system in which the fluctuation in particle number around the mean is negligible. For the mutually noninteracting gas system, eq 14 reduces to eq 13 with $\bar{N}$ replaced by the constant particle number, N, in the canonical ensemble. For a fluid system composed of N indistinguishable particles under an arbitrary potential, $U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, the canonical partition function Q can be written as $Q = (1/N!)[V\chi_N(V)/\Lambda^3]^N$, where $\chi_N(V)$ is given by $\chi_N(V) = V^{-1}\{Z_N(V,T)\}^{1/N}$, with $Z_N(V,T)$ being the configurational integral defined by $\int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \ldots \int_V d\mathbf{r}_N \exp[-\beta U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)]$. For the fluid system, eq 14 becomes

$$X = N\beta^{-1}\left[\left(\frac{\partial \ln \chi_N(V)}{\partial \ln V}\right)_{N,\beta} + \left(\frac{\partial \ln \chi_N(V)}{\partial \ln N}\right)_{V,\beta}\right] \tag{15}$$

One can show that the excess grand potential X in eq 15 is identically zero when $\chi_N(V)$ is a function of density, N/V, and temperature, T, only. For example, X vanishes for van der Waals fluid, for which $\chi_N(V)$ is given by $\chi_N^{\text{VDW}}(V) = (1 - Nb/V)\exp(\beta aN/V)$ in the absence of any external potential. When there is only external potential U_{ext} but not any mutual interaction between particles, i.e., when $U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{j=1}^N U_{\text{ext}}(\mathbf{r}_j)$, $\chi_N(V)$ reduces to $\chi_{\text{ext}}(V)$ so that eq 15 correctly reduces to the canonical equivalent of eq 13. In the general case where $U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the sum of the interparticle potential $U_{\text{int}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and the external potential, $\sum_{j=1}^N U_{\text{ext}}(\mathbf{r}_j)$, $\chi_N(V)$ can be approximated as $\chi_N(V) \cong \chi_N^{\circ}(V)\tilde{\chi}_{\text{ext}}(V)$ for a macroscopic system, where $\chi_N^{\circ}(V)$ denotes $\chi_N(V)$ of the system in the absence of the external potential and $\tilde{\chi}_{\text{ext}}(V)$ is given by $\tilde{\chi}_{\text{ext}}(V) = \exp[\lim_{N\to\infty} N^{-1}\ln\langle\prod_{i=1}^N \exp[-\beta U_{\text{ext}}(\mathbf{r}_i)]\rangle_{\circ}$, with $\langle f(\mathbf{r}^N)\rangle_{\circ}$ being the average of f over the equilibrium distribution of the system in the absence of any external potential. For the inherently extensive macroscopic system of which $\chi_N^{\circ}(V)$ is a function of density and temperature only, X given in eq 15 again reduces to eq 13, but with $\bar{N}$ and $\chi_{\text{ext}}(V)$ being replaced by N and $\tilde{\chi}_{\text{ext}}(V)$, respectively. In other words, the external potential can induce nonextensivity to the inherently extensive interacting fluid system as well unless $\tilde{\chi}_{\text{ext}}(V)$ is a finite constant in V. To such nonextensive systems, whether or not the nonextensivity is induced by an external field, care must be taken in applying such thermodynamic equations as the Gibbs–Duhem equation and the compressibility equation,[23,24] which are correct only for extensive systems for which X or $G - \mu N$ is identically zero.

In the present Letter, we report that an external field makes an inherently extensive system nonextensive and that it is necessary to take into account the excess grand potential X ($\equiv G - \mu N$), in addition to the conventional grand potential $-PV$, for correct grand canonical description of a nonextensive system, which has been overlooked in the literature in this field. We have presented the statistical mechanical relationship between X and an external potential. From the result, we have established the criterion for the external field capable of inducing nonextensivity on extensive macroscopic systems.

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Supporting Information Available: We present a detailed proof of the equivalence between the mean mechanical pressure at a surface of a system and the thermodynamic pressure given in eq 2 of the system in the presence of an inhomogeneous external field, according to an anonymous reviewer's request. This material is available free of charge via the Internet at http://pubs.acs.org.

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