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Exchange symmetry, fluctuation-compressibility relation, and thermodynamic potentials of quantum liquids

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Liquid helium does not obey the Gibbs fluctuation-compressibility relation, which was noted more than six decades ago. However, still missing is a clear explanation of the reason for the deviation or the correct fluctuation-compressibility relation for the quantum liquid. Here we present the fluctuation-compressibility relation valid for any grand canonical system. Our result shows that the deviation from the Gibbs formula arises from a nonextensive part of thermodynamic potentials. The particle-exchange symmetry of many-body wave function of a strongly degenerate quantum gas is related to the thermodynamic extensivity of the system; a Bose gas does not always obey the Gibbs formula, while a Fermi gas does. Our fluctuation-compressibility relation works for classical systems as well as quantum systems. This work demonstrates that the application range of the Gibbs-Boltzmann statistical thermodynamics can be extended to encompass nonextensive open systems without introducing any postulate other than the principle of equal *a priori* probability.

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I. INTRODUCTION

The Gibbs fluctuation-compressibility formula provides the general relationship of the mean-scaled particle number fluctuation $\langle \delta N^2 \rangle / \bar{N}$ to the isothermal compressibility κ_T of a fluid system [1,2]:

$$\frac{\langle \delta N^2 \rangle}{\bar{N}} = \bar{\rho} k T \kappa_T, \tag{1}$$

where $\bar{\rho}$ and kT denote the mean density of the fluid and the thermal energy, respectively. Equation (1) is used to show the equivalence between canonical ensemble and grand canonical ensemble of a macroscopic system with finite compressibility [3]. It also serves as the starting point for the derivation of the compressibility equation, the well-known integral equation relating the particle pair correlation to the compressibility in a fluid system and the relationship of the integrated intensity of the radiation scattered by a fluid or the static structure factor to the compressibility of the fluid [4,5]. As a general statistical mechanical equation, Eq. (1) has been used in various fields of physical science [6–21].

More than six decades ago, however, Price pointed out that liquid helium does not obey Eq. (1) [22,23]. This issue has been neither well known nor carefully examined, so Eq. (1) has been applied to quantum liquids without caution in the literature [3,16,20,21,24,25]. There have been a few papers in which Price's work was noted [26,27]. A deviation from Eq. (1) was directly observed in the two-dimensional Bose gas of cesium [28]. However, so far, the correct form of the fluctuation-compressibility relation has remained unknown for general quantum liquids and there has not been yet a clear explanation of why the Gibbs fluctuation formula does not hold for liquid helium.

In this work we present a universal form of the fluctuation-compressibility relation, which holds exactly for any open system at grand canonical equilibrium states. As will be shown shortly, Eq. (1) exactly holds only for an extensive system whose thermodynamic potentials, such as the internal energy and free energies, are strictly linear with respect to the system size [3,29]. It was previously shown that a homogeneous classical mechanical system becomes an extensive system in the macroscopic limit [30]. However, many systems of interest in modern science are so small that they may not be extensive systems due to surface interactions with the surrounding environment [31]. Even for a macroscopic system, nonextensivity can be developed by a spatially inhomogeneous external potential imposed on the system [32]. Quantum mechanical nature of a system can be another cause of nonextensivity. The universal fluctuation-compressibility relation reported in the present work holds for those nonextensive systems as well and it reduces to the Gibbs fluctuation formula for extensive systems.

We find that the particle-exchange symmetry of the many-body wave function is fundamentally related to thermodynamic extensivity of an ideal quantum gas system at low temperature; a strongly degenerate Bose gas does not satisfy the Gibbs fluctuation-compressibility relation because of a nonextensive part of the grand potential even in the macroscopic limit, whereas a Fermi gas does satisfy Eq. (1) at all accessible temperatures [33]. The correctness of the present fluctuation-compressibility relation could be confirmed for ideal quantum gas systems and also for the classical ideal gas system under a constant force field that does not obey the Gibbs fluctuation formula. Our result is obtained by considering the standard grand canonical ensemble and it demonstrates that the application range of the Gibbs-Boltzmann statistical thermodynamics can be extended to encompass nonextensive open systems without introducing any fundamental assumption other than the principle of equal *a priori* probability.

II. UNIVERSAL FLUCTUATION FORMULA

To begin, we introduce a thermodynamic potential X that is defined by $X \equiv G - \mu \bar{N}$, where G, μ, and $\bar{N}$ denote the Gibbs free energy, the chemical potential, and the average

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number of particles in our grand canonical system. Euler's theorem dictates that X of extensive systems be identically equal to zero [29], so it does not play any role in thermodynamics of extensive systems. However, thermodynamic potential X is indispensable for the thermodynamic description of nonextensive open systems within Gibbs-Boltzmann statistical mechanics.

In terms of the thermodynamic potential X, the grand potential Ω ($\equiv G - \mu\bar{N} - PV$) of an open system at the grand canonical equilibrium state defined by chemical potential μ, temperature T, and volume V is given by

$$\Omega \equiv X - PV = -kT \ln \Xi(\mu,T,V), \tag{2}$$

where Ξ denotes the grand partition function of the system. In Eq. (2), the thermodynamic potential X is a part of the grand potential Ω, which emerges for a nonextensive system only. For an extensive system of which X is identically equal to zero, the thermodynamic pressure P in Eq. (2) is given by $P = -\Omega/V = kT \ln \Xi(\mu,T,V)/V$ [29], which is the textbook result. However, for a system with nonvanishing X, P is no longer given by $-\Omega/V$; instead, it is given by $P = kT[\partial \ln \Xi(\mu,V,T)/\partial V]_{\mu,T}$ [32,34,35] (see Appendix A). Substituting the latter equation into Eq. (2), one obtains the statistical mechanical expression of thermodynamic potential X:

$$X = kTV\left[\frac{\partial[V^{-1}\ln \Xi(\mu,V,T)]}{\partial \ln V}\right]_{\mu,T}. \tag{3}$$

On the other hand, the remaining part $-PV$ of the grand potential Ω is given by $-PV = kT[\partial \ln \Xi(\mu,V,T)/\partial \ln V]_{\mu,T}$. Note that X does not vanish unless $\ln \Xi(\mu,V,T)$ or $-\Omega/kT$ is linearly proportional to V [32].

For a system with a thermodynamic potential X, we could obtain the relation between the mean-scaled variance $\langle \delta N^2\rangle/\bar{N}$ of the particle number fluctuation and the isothermal compressibility κ_T [$\equiv -V^{-1}(\partial V/\partial P)_{T,\bar{N}}$] as

$$\frac{\langle \delta N^2\rangle}{\bar{N}} = \bar{\rho}kT\kappa_T\left[1+\frac{1}{\bar{N}}\left(\frac{\partial X}{\partial \mu}\right)_{T,\bar{N}}\right]\left[1+\frac{1}{\bar{N}}\left(\frac{\partial X}{\partial \mu}\right)_{T,V}\right]. \tag{4}$$

A detailed derivation of Eq. (4), the key result of the present work, is given in Appendix B. Note that Eq. (4) reduces to the Gibbs fluctuation formula, Eq. (1), if our system is an extensive system of which X is identically equal to zero. Because the derivation of Eq. (4) was made by considering the standard grand canonical ensemble without using any approximation, it is the general fluctuation formula applicable to any system in the grand canonical equilibrium state. Below, the correctness of Eq. (4) is confirmed for a few exactly solvable models.

III. IDEAL BOSE GAS SYSTEM

For an ideal Bose gas system with a macroscopic volume, the analytic expression of the grand partition function Ξ_{BE} is given by [3,29,36]

$$\begin{aligned} -\Omega_{BE}/kT &= \ln \Xi_{BE}(\mu,V,T) \\ &= Vg_{5/2}(z)/\Lambda^3(T) - \ln(1-z) \quad (0 < z < 1), \end{aligned} \tag{5}$$

where z and $\Lambda(T)$ denote $\exp(\mu/kT)$ and the thermal de Broglie wavelength, respectively. In Eq. (5), $g_\nu(z)$ is defined by $g_\nu(z) \equiv \sum_{n=1}^{\infty} z^n/n^\nu$. By substituting Eq. (5) into Eq. (3), we obtain the expression of the thermodynamic potential X for an ideal Bose gas system as

$$X = kT\ln(1-z)(\equiv X_{BE}). \tag{6}$$

Note that X_{BE} is nothing but the ground-state contribution to the grand potential Ω_{BE}, which corresponds to the last term on the right-hand side of Eq. (5). Substituting Eq. (6), in turn, into Eq. (4), we obtain the fluctuation formula of an ideal Bose gas system as

$$\frac{\langle \delta N^2\rangle}{\bar{N}} = \bar{\rho}kT\kappa_T(1-f_0)^2, \tag{7}$$

where f_0 denotes the ground-state fraction defined by $\bar{n}_0/\bar{N}$, with $\bar{n}_0$ being the average number of particles in the ground quantum state, i.e., $\bar{n}_0 = z/(1-z)$ [3,29,36]. Because the mean particle number $\bar{N}$ is given by $\bar{N} = Vg_{3/2}(z)/\Lambda(T)^3 + \bar{n}_0$ for an ideal Bose gas system [3,29,36], f_0 [$=1-(\bar{N}-\bar{n}_0)/\bar{N}$] can be written as

$$f_0 = 1 - \frac{g_{3/2}(z)}{\bar{\rho}\Lambda^3(T)} = 1 - \frac{g_{3/2}(z)}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2}, \tag{8}$$

where T_0 denotes the condensation temperature defined by $\bar{\rho}\Lambda^3(T_0) \equiv g_{3/2}(1) \cong 2.612$. A positivity of f_0 enforces the range of z to decrease with temperature T for an ideal Bose gas system (see Appendix C).

Let us now test the correctness of Eq. (7). For the ideal Bose gas system, the exact expression of $\langle \delta N^2\rangle/\bar{N}$ can be obtained from the general relation $\langle \delta N^2\rangle/\bar{N} = (\partial \ln \bar{N}/\partial \ln z)_{T,V}$ [3,29,36]:

$$\frac{\langle \delta N^2\rangle}{\bar{N}} = \frac{g_{1/2}(z)}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2} + \frac{f_0}{1-z}. \tag{9}$$

On the other hand, the exact expression of κ_T can be obtained from the equation of state of the Bose gas system (see Appendix D):

$$\kappa_T = \frac{1}{\bar{\rho}kT}\frac{1}{(1-f_0)^2}\left[\frac{g_{1/2}(z)}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2} + \frac{f_0}{1-z}\right]. \tag{10}$$

With Eqs. (9) and (10) at hand, one can easily verify the correctness of Eq. (7) or (4) for an ideal Bose gas system.

In the macroscopic limit where $\bar{N} \to \infty$, $V \to \infty$, and $\bar{N}/V = \bar{\rho} = \text{const}$, f_0 can be approximated by $f_0 \cong 0$ when $T > T_0$ and $f_0 \cong 1 - (T/T_0)^{3/2}$ when $T < T_0$ [3,29,36]. Consequently, in the macroscopic limit, Eq. (7) reads as

$$\frac{\langle \delta N^2\rangle}{\bar{N}} \cong \begin{cases} \bar{\rho}kT\kappa_T(T/T_0)^3 & (T < T_0) \\ \bar{\rho}kT\kappa_T & (T > T_0). \end{cases} \tag{11}$$

Note that the Gibbs fluctuation formula is approximately valid when $T > T_0$, but it is not when $T < T_0$, even in the macroscopic limit.

The isothermal compressibility κ_T of an ideal Bose gas, given in Eq. (10), has a phase transition at $T = T_0$. In Fig. 1(a) we show the dependence of κ_T on temperature T for various values of $\bar{N}$ with a phase transition at $T = T_0$. In the high-temperature limit, κ_T of the ideal Bose gas reduces to the

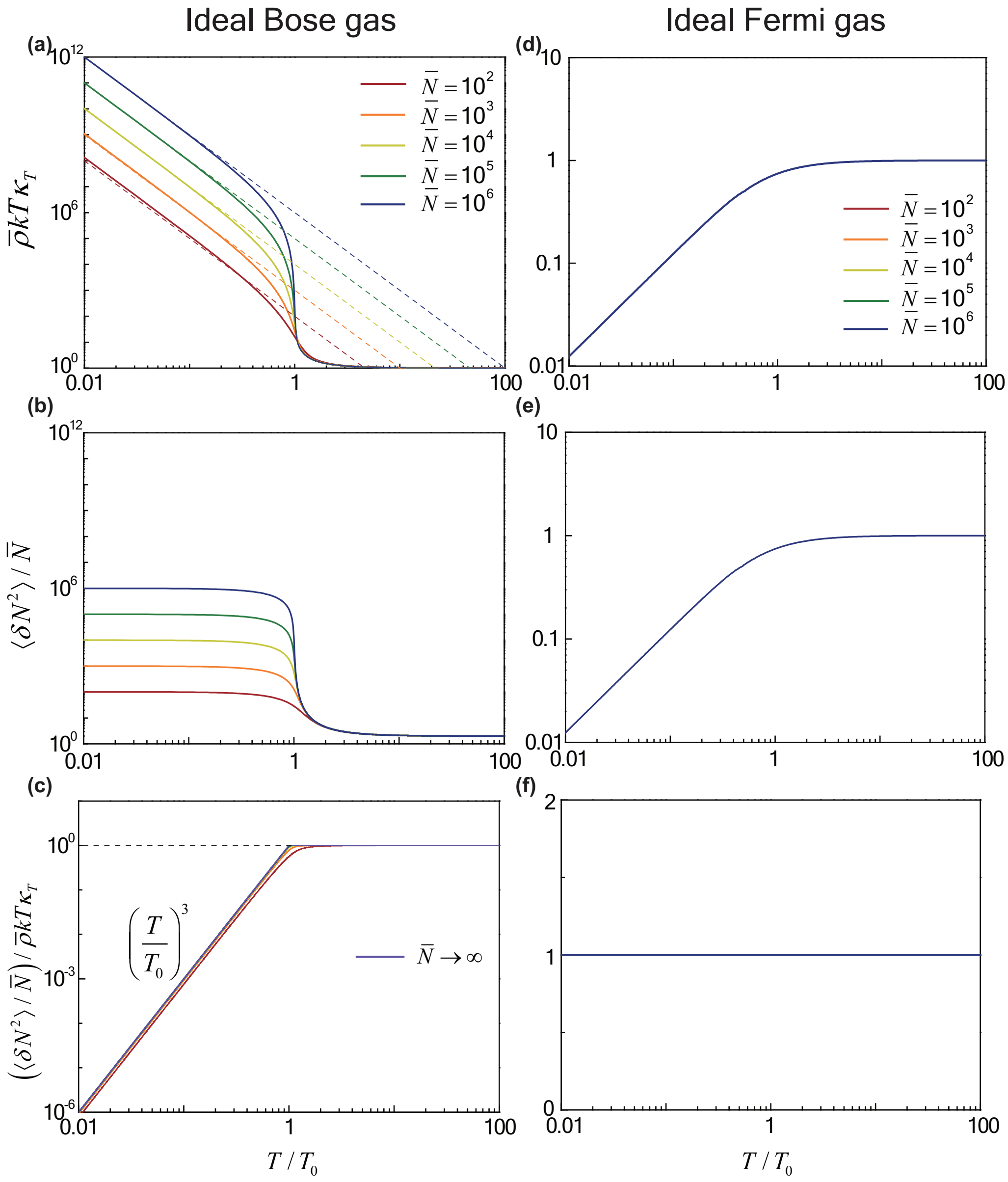

FIG. 1. (Color online) Temperature dependence of the scaled isothermal compressibility $\bar{\rho}kT\kappa_T$, the mean scaled number fluctuation $\langle\delta N^2\rangle/\bar{N}$, and the ratio of $\bar{\rho}kT\kappa_T$ to $\langle\delta N^2\rangle/\bar{N}$ for (a)–(c) an ideal quantum gas with the positive exchange symmetry (Bose gas) and for (d)–(f) an ideal quantum gas with the negative exchange symmetry (Fermi gas). An ideal Bose gas does not obey the Gibbs fluctuation-compressibility relation, Eq. (1), below the condensation temperature T_0, whereas an ideal Fermi gas does at all accessible temperature. Both an ideal Bose gas system and an ideal Fermi gas system obey our fluctuation-compressibility relation, Eq. (4). For an ideal Bose gas system, $\bar{\rho}kT\kappa_T$ and $\langle\delta N^2\rangle/\bar{N}$ are not the same and dependent on the size of system, in contrast with those for usual extensive systems including an ideal Fermi gas system. The discrepancy between $\bar{\rho}kT\kappa_T$ and $\langle\delta N^2\rangle/\bar{N}$ of an ideal Bose gas system persists in the macroscopic limit below the condensation temperature.

isothermal compressibility of a classical ideal gas system

$$\kappa_T \cong \frac{1}{\bar{\rho}kT} = \kappa_T^{id} \quad (T/T_0 \gg 1). \tag{12a}$$

In comparison, in the low-temperature limit, the approximate expression of κ_T is found to be

$$\kappa_T \cong \frac{\bar{N}}{\bar{\rho}kT}\left(\frac{T_0}{T}\right)^3 \quad (T/T_0 \ll 1) \tag{12b}$$

(see Appendix E). As shown in Fig. 1(a), Eq. (12) provides an excellent approximation of the exact κ_T given in Eq. (10). Note that the isothermal compressibility of the strongly degenerate Bose gas is dependent on the system size $\bar{N}$. This reflects that an ideal Bose gas system is not a usual extensive system when $T < T_0$. Note also that $\bar{\rho}kT\kappa_T$ of a strongly degenerate ideal Bose gas is proportional to $(T/T_0)^{-3}$, divergent as T/T_0 approaches zero.

Substituting Eq. (12) into Eq. (11), one obtains the asymptotic behavior of $\langle\delta N^2\rangle/\bar{N}$ for an ideal Bose gas system in the grand canonical equilibrium state:

$$\frac{\langle\delta N^2\rangle}{\bar{N}} \cong \begin{cases} \bar{N} & (T \ll T_0) \\ 1 & (T \gg T_0). \end{cases} \tag{13}$$

Equation (13) can also be obtained directly from Eq. (9) by using the method in Appendix E. Note that, in the low-temperature limit, the standard deviation of the number fluctuation in a strongly degenerate ideal Bose gas system does not vanish even in the macroscopic limit, i.e., $\lim_{\bar{N}\to\infty}\sqrt{\langle\delta N^2\rangle}/\bar{N} \cong 1$. For this reason, the equivalence between the grand canonical ensemble and the canonical ensemble cannot be guaranteed for a strongly degenerate ideal Bose gas system [37]. However, when $T > T_0$, the particle number distribution is given by the classic Poisson statistics of which the mean scaled standard deviation is small in the macroscopic limit, i.e., $\sqrt{\langle\delta N^2\rangle}/\bar{N} = 1/\sqrt{\bar{N}}$. Recently, the transition of the photon number distribution between the large fluctuation regime of an ideal Bose condensate and the small fluctuation regime of Poisson statistics was directly observed for a photon gas system in a dye microcavity [37]. A brief review of the particle number fluctuation in the grand canonical system and other statistical ensembles of the ideal Bose gas system is presented in Appendix F.

IV. IDEAL FERMI GAS SYSTEM

The grand potential or logarithm of the grand partition function of an ideal Fermi gas system with a macroscopic volume is linearly proportional to the volume of the system [3,29,36]

$$-\Omega_{FD}/kT = \ln \Xi_{FD}(\mu,V,T) = V h_{5/2}(z)/\Lambda^3(T), \tag{14}$$

with $h_\nu(z) = \sum_{n=1}^{\infty}(-1)^{n+1}z^n/n^\nu$. For the macroscopic ideal Fermi gas system, the thermodynamic potential X defined in Eq. (3) vanishes; consequently, Eq. (4) reduces to the Gibbs fluctuation formula and it should be correct. This prediction could be confirmed by substituting the exact expressions of $\langle\delta N^2\rangle/\bar{N}$ and κ_T of an ideal Fermi gas system into Eq. (1) (see Appendix G):

$$\langle\delta N^2\rangle/\bar{N} = \bar{\rho}kT\kappa_T = \frac{h_{1/2}(z)}{\bar{\rho}\Lambda^3(T)}. \tag{15}$$

As shown in Figs. 1(d) and 1(e), $\langle\delta N^2\rangle/\bar{N}$ or $\bar{\rho}kT\kappa_T$ of an ideal Fermi gas system is independent of the system size at all temperatures, in contrast to that of an ideal Bose gas system below the condensation temperature.

V. PARTICLE EXCHANGE SYMMETRY AND THERMODYNAMIC EXTENSIVITY

Our results suggest that the particle-exchange (PE) symmetry of many-body wave function of an ideal quantum gas system is fundamentally related to thermodynamic extensivity of the system at low temperature. An ideal gas system with the positive PE symmetry (Bose gas) switches from an extensive system to a nonextensive system as the system cools down below the condensation temperature; in contrast, an ideal gas system with the negative PE symmetry (Fermi gas) is an extensive system in the macroscopic limit at all accessible temperatures [33].

To explain why the PE symmetry plays an essential role here, let us recall that the PE symmetry of many-body wave function of an ideal quantum gas system is related to the thermodynamics of the system; the grand potential Ω of an ideal quantum gas system is given by

$$-\Omega/kT = \pm\sum_k \ln[1 \pm z\exp(-\varepsilon_k/kT)], \tag{16}$$

with the minus sign for bosons and the plus sign for fermions, where ε_k denotes the quantum mechanical energy of the kth quantum state of a single gas particle [3,29,36]. For an ideal quantum gas system with a macroscopic volume, the grand potential given in Eq. (16) reduces to Eq. (5) for bosons and to Eq. (14) for fermions. As shown in Secs. III and IV, the thermodynamic potential X associated with the latter vanishes at all accessible temperatures, whereas that associated with the former does not. This is because only the grand potential (5) of bosons contains the nonextensive part arising from the ground-state contribution, which is not negligible below the condensation temperature.

The PE symmetry-dependent thermodynamics emerges because the number of ideal gas particles occupying a single quantum state depends on the PE symmetry. Let us recall that the grand potential (16) of an ideal quantum gas system can be written as

$$-\Omega/kT = \sum_k \ln \sum_{n_k=0}^{n_k^{\max}} [z\exp(-\varepsilon_k/kT)]^{n_k},$$

where $n_k^{\max}$ denotes the maximum number of ideal gas particles in the kth quantum state [3,29,36]. The negative PE symmetry inherent to the many-body wave function of an ideal Fermi gas system forbids more than one fermion from being in the same quantum state, so we have $n_k^{\max} = 1$ for the ideal Fermi gas system. For this reason, the contribution of a single quantum state to the grand potential is always negligible for the macroscopic Fermi gas system. On the other hand, for an ideal Bose gas system, there is no restriction on the occupancy of each quantum state and $n_k^{\max}$ should read as infinity, so the contribution of the ground state to the grand potential, which is the nonextensive part of the grand potential, can be significant below the condensation temperature. This explains why the thermodynamic extensivity of an ideal quantum gas system depends on the PE symmetry of the many-body wave function of the system.

Let us compare the entropy of an ideal Bose gas system with that of an ideal Fermi gas system, which can be calculated by $S = -(\partial\Omega/\partial T)_{\mu,V}$ with $\Omega = -kT\ln\Xi$. If a system is an extensive system, the entropy per particle $S/\bar{N}$ of the system should be independent of the system size. As shown in Fig. 2(a), $S/\bar{N}$ of an ideal Bose gas system is independent of the system size when $T > T_0$, but it becomes dependent on the system size when $T < T_0$; in contrast, $S/\bar{N}$ of an ideal Fermi gas system is independent of the system size at any temperature. In Fig. 2(b) we also display the relative contribution X/Ω of thermodynamic potential X to the grand potential Ω for the ideal quantum gas systems. Note that, for an ideal Bose gas system with any finite size, the thermodynamic

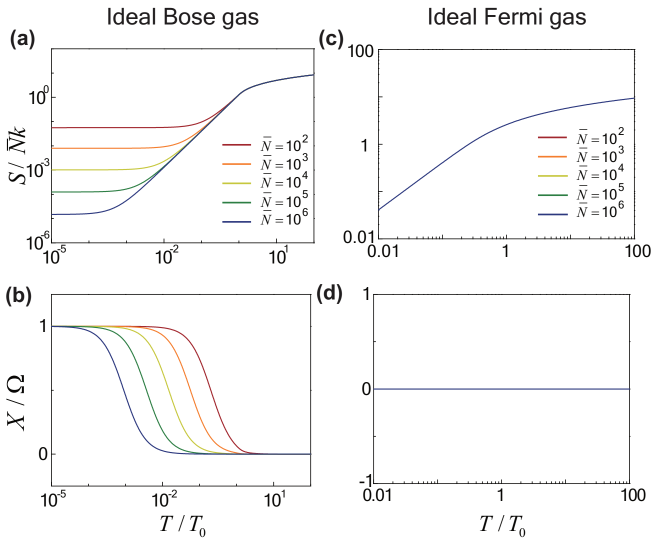

FIG. 2. (Color online) Temperature dependence of entropy and thermodynamic potential X for (a,b) an ideal Bose gas system and for (c,d) an ideal Fermi gas system with various sizes. For an ideal Bose gas system, the entropy is not strictly linear with respect to the system size so that entropy per particle $S/\bar{N}$ is dependent on the system size, and thermodynamic potential X makes the dominant contribution to the total grand potential Ω when $T \ll T_0$. For an ideal Fermi gas system, in contrast, the entropy is strictly linear with respect to the system size and X/Ω is zero at all accessible temperatures.

potential X makes the dominant contribution to the total grand potential Ω in the low-temperature regime, where the entropy is no longer an extensive variable, but it vanishes in the high-temperature regime where the entropy of the system is an extensive variable. In contrast, $X/\Omega = 0$ at any temperature for an ideal Fermi gas system.

We note that, at any finite temperature, X/Ω actually vanishes in the thermodynamic limit where $\bar{N} \to \infty$, $V \to \infty$, and $\bar{N}/V = \bar{\rho} =$ const for a strongly degenerate Bose gas system as well as for a Fermi gas system [29]. This is because X, given in Eq. (6), is proportional to $\ln V$, whereas Ω, given in Eq. (5), is proportional to V. However, this does not mean that $\bar{n}_0 = -(\partial X/\partial \mu)_{V,T}$ is always negligible compared to $\bar{N} = -(\partial \Omega/\partial \mu)_{V,T}$ in the thermodynamic limit. Similarly, the effect of thermodynamic potential X on the fluctuation formula, Eq. (4) or (7), is not negligible at all for the strongly degenerate Bose gas system in the thermodynamic limit. In the sense that a strongly degenerate Bose gas system does not obey the Gibbs fluctuation formula that is exact for any extensive system whose thermodynamic potential X is identically equal to zero, the strongly degenerate Bose gas system is a nonextensive system.

VI. OTHER MODELS

For an ideal Bose gas system, the thermodynamic potential X defined in Eq. (3) comes from the last term on the right-hand side (RHS) of Eq. (5), the ground-state contribution to $\ln \Xi_{BE}$. Its effect on the fluctuation formula is negligible when $T > T_0$, but it is not when $T < T_0$, as shown in Eq. (11). The similar phase transition is expected for other Bose gas systems with the following form of grand partition function:

$$\ln \Xi(\mu,V,T) = V\phi(\mu,T) - \ln(1-z). \tag{17}$$

Here $\phi(\mu,T)$ can be a general function of μ and T. A representative example is an ideal Bose gas system trapped in a harmonic potential $U(\mathbf{r}) = 2^{-1}m\omega^2|\mathbf{r}|^2$, with m and $m\omega^2$ denoting the mass of the gas particle and the force constant, respectively. The grand partition function of this system conforms to Eq. (17), given that the volume V is identified by $(kT_0/m\omega^2)^{3/2}$, and the thermodynamic potential X and the fluctuation formula are given by Eqs. (3) and (4) (see Appendix H).

Equation (7) tells us that the population condensation of ideal Bose particles to the single-particle ground state makes an ideal Bose gas system deviate from the Gibbs fluctuation formula. This result suggests that a similar deviation from the Gibbs fluctuation formula would occur for an imperfect Bose gas system below the condensation temperature at which the population condensation to the ground state or to a small number of low-energy quantum states occurs [38–41] (see Appendix I). Recently, an experimental estimation for the dependence of κ_T on temperature was made in the three-dimensional Bose gas of ^{87}Rb within the temperature interval $(T_0, 2T_0)$ [5]. The experimental data clearly exhibit the temperature-dependent phase transition of κ_T, which is qualitatively the same as that shown in Fig. 2 as T approaches T_0 from above. The authors' experimental analysis was made effectively on the basis of the Gibbs fluctuation formula, Eq. (1), but it does not introduce a serious error as Eq. (1) is approximately valid when $T > T_0$, as shown in Eq. (11). The experimental data of κ_T at temperature below T_0 are yet to be reported, but we note here that care must be taken in the analysis of the experimental data at temperature below T_0 where neither the Gibbs fluctuation formula nor the assumption of the equivalence between different ensembles is valid.

Note that the first term on the RHS of Eq. (5), the contribution of the excited states, to $\ln \Xi$ is linear in volume V, which makes the Bose gas system an extensive system at high temperatures at which condensation to the ground quantum state is negligible. However, the contribution of the excited states to $\ln \Xi$ may not be always linear with respect to volume V under the presence of an inhomogeneous external field, which can be a separate source of the nonextensivity leading to the deviation from the Gibbs fluctuation formula. For example, let us consider a system of mutually noninteracting particles in a cylinder with a fixed basement area A and variable height l under the inhomogeneous external field producing a downward external force f_d [Fig. 3(a)]. The grand partition function of the system is given by

$$-\beta\Omega = \ln \Xi = z\,[V/\Lambda^3(T)][1-\exp(-V/V^*)](V/V^*) \tag{18}$$

in the classical limit, which is nonlinear with respect to volume V ($\equiv Al$). In Eq. (18), V^* denotes a characteristic volume defined by $V^* = kTA/f_d$. For this system, thermodynamic potential X defined in Eq. (3) can be easily obtained as

$$X = kT\bar{N}\left(\frac{V/V^*}{\exp(V/V^*)-1} - 1\right). \tag{19}$$

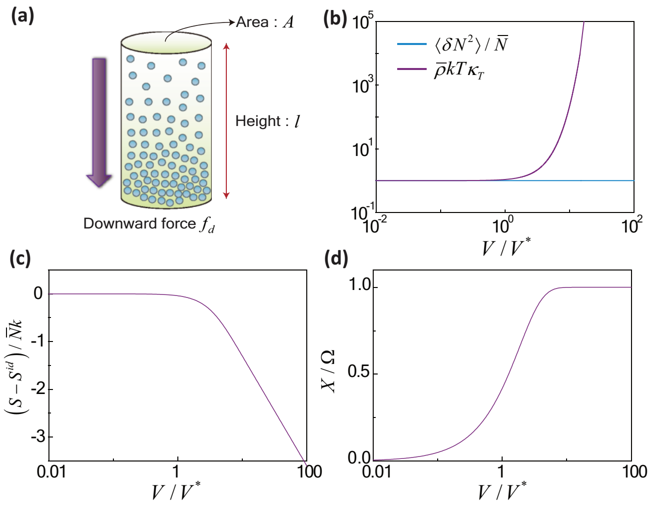

FIG. 3. (Color online) Fluctuation-compressibility, entropy, and thermodynamic potential X of a classical ideal gas system under constant downward force f_d. (a) Schematic representation of the mutually noninteracting gas system under constant downward force f_d. (b) Comparison between the mean-scaled fluctuation $\langle \delta N^2\rangle/\bar{N}$ (=1) and the scaled isothermal compressibility $\bar{\rho}kT\kappa_T$. Here V ($=Ah$) denotes the volume of the system and V^* denotes the characteristic volume defined by $V^* \equiv AkT/f_d$. (c) The entropy per each particle becomes dependent on the system size when $V/V^* > 1$. Here S^{id} denotes the entropy of the classical ideal gas system in the absence of an external field. (d) The relative contribution of X to Ω becomes dominant when $V \gg V^*$, where the entropy per each particle is significantly dependent on the system volume.

The corresponding fluctuation formula (4) reads as

$$\frac{\langle \delta N^2\rangle}{\bar{N}} = \bar{\rho}kT\kappa_T \left\{\frac{V/2V^*}{\sinh(V/2V^*)}\right\}^2. \quad (20)$$

A detailed derivation of Eqs. (18)–(20) is presented in Appendix J. Note that, unless the external force f_d vanishes, Eq. (20) deviates from the Gibbs fluctuation relation, Eq. (1). The correctness of Eq. (20) can be confirmed with the exact expressions $\langle \delta N^2\rangle/\bar{N} = 1$ and $\bar{\rho}kT\kappa_T = \sinh^2(x)/x^2$ with $x = V/2V^*$, available for this system, which are displayed in Fig. 3(b). A detailed derivation of the exact expressions for $\langle \delta N^2\rangle/\bar{N}$ and κ_T of this system is also presented in Appendix L. The deviation from the Gibbs fluctuation formula implies that this system is a nonextensive system. Indeed, the entropy per each particle in this system is found to be dependent on the size of the system especially when $V > V^*$, where the relative contribution of nonextensive part X to the total grand potential becomes dominant [see Fig. 3(c) and Appendix L].

VII. CONCLUSION

To conclude, starting from the standard grand canonical ensemble, we obtain a universal fluctuation-compressibility relation, Eq. (4), which is a generalization of the Gibbs fluctuation formula for nonextensive open systems. This work demonstrates that the application range of Gibbs-Boltzmann statistical thermodynamics can be extended to nonextensive open systems without introducing an additional postulate other than the principle of equal *a priori* probability by introducing thermodynamic potential X ($\equiv G - \mu N$). The Gibbs-Duhem equation, the compressibility equation, and other related statistical thermodynamic equations, which are exact only for extensive open systems, can be extended to general nonextensive open systems with use of the thermodynamic potential X. The thermodynamic potential X would play a crucial role also in the thermostatistical description of small open systems of which properties are dependent on their surface interactions with the surrounding environment. More research should be directed toward the development of statistical thermodynamics of a small nonextensive system interacting with its environment, which has a number of practical applications.

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APPENDIX A: RELATIONSHIP BETWEEN GRAND CANONICAL PRESSURE AND CANONICAL PRESSURE

We note here that the grand canonical pressure $P = kT[\partial \ln \Xi(\mu,V,T)/\partial V]_{\mu,T}$ is nothing but the grand canonical average of the canonical pressure [32,35]. Given that (N,j) denotes the jth microscopic state of a grand canonical system containing N particles, the probability $p(N,j)$ that the grand canonical system is at a microstate (N,j) is given by

$$p(N,j) = \exp\{\beta[\mu N - \varepsilon_{(N,j)}(V)]\}/\Xi, \quad (A1)$$

where μ, β, and $\varepsilon_{(N,j)}$ denote the chemical potential, the inverse temperature, and the quantum mechanical energy of the system in state (N,j) and Ξ denotes the grand canonical partition function defined by $\Xi = \sum_{N,j}\exp\{\beta[\mu N - \varepsilon_{(N,j)}(V)]\}$. The grand canonical pressure is given by

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{\mu,T} = kT\left(\frac{\partial \ln \Xi(\mu,V,T)}{\partial V}\right)_{\mu,T}. \quad (A2)$$

Noting that Ξ can be expressed as $\sum_N z^N Q(N,V,T)$ with z defined by $z = \exp(\beta\mu)$ and $Q(N,V,T)$, the canonical partition function, defined by $Q(N,V,T) = \sum_j \exp[-\beta\varepsilon_{(N,j)}(V)]$, Eq. (A2) can be rewritten as

$$\begin{aligned} P &= kT\sum_{N=0}^{\infty} p(N)\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_T \\ &= \sum_{N=0}^{\infty} p(N)\left(-\frac{\partial F}{\partial V}\right)_{N,T}, \end{aligned} \quad (A3)$$

where

$$p(N) = \sum_j p(N,j) = z^N Q(N,V,T)/\Xi(\mu,V,T)$$

and F represents the Helmholtz free energy defined by $F = -kT \ln Q(N,V,T)$. Equation (A3) shows that the grand canonical pressure is the particle number average of the canonical pressure $P^{(C)}$ $[\equiv -(\partial F/\partial V)_{N,T}]$.

APPENDIX B: DERIVATION OF EQ. (4)

For a grand canonical system, $\langle N^2\rangle$ is given by [3,4,6]

$$\langle N^2\rangle = \sum_N \sum_j N^2 p(N,j) = \bar{N}^2 + kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}, \tag{B1}$$

where $\bar{N}$ denotes the average particle number defined by $\bar{N} = \sum_N \sum_j N p(N,j)$. Equation (B1) can be easily obtained from Eq. (A1). For an extensive system, it is well known that

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = \frac{\bar{N}^2}{V}\kappa_T, \tag{B2}$$

with κ_T the isothermal compressibility defined by $\kappa_T = -V^{-1}(\partial V/\partial P)_{T,\bar{N}}$ [3,4,6]. The derivation of Eq. (B2) relies on the Gibbs-Duhem equation that is correct only when $G = \mu N$ or $X = 0$. Substituting Eq. (B2) into Eq. (B1), we obtain the conventional fluctuation-compressibility equation, Eq. (1).

For a nonextensive system of which thermodynamic potential X $(\equiv G - \mu\bar{N})$ does not vanish, Eq. (B1) yields Eq. (4). To show this, we rewrite $(\partial \bar{N}/\partial \mu)_{T,V}$ in Eq. (B1) as

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial V}{\partial \mu}\right)_{T,\bar{N}}\left(\frac{\partial \bar{N}}{\partial V}\right)_{T,\mu}. \tag{B3}$$

Here $(\partial V/\partial \mu)_{T,\bar{N}}$ can be related to the isothermal compressibility as

$$\left(\frac{\partial V}{\partial \mu}\right)_{T,\bar{N}} = \left(\frac{\partial P}{\partial \mu}\right)_{T,\bar{N}}\left(\frac{\partial V}{\partial P}\right)_{T,\bar{N}} = -\kappa_T V\left(\frac{\partial P}{\partial \mu}\right)_{T,\bar{N}}. \tag{B4}$$

One can relate $(\partial P/\partial \mu)_{T,\bar{N}}$ appearing in Eq. (B4), in turn, to $(\partial X/\partial \mu)_{T,\bar{N}}$ by using the well-known thermodynamic equation, $dG = d(\mu\bar{N} + X) = VdP - SdT + \mu d\bar{N}$:

$$V\left(\frac{\partial P}{\partial \mu}\right)_{T,\bar{N}} = \bar{N} + \left(\frac{\partial X}{\partial \mu}\right)_{T,\bar{N}}. \tag{B5}$$

With Eqs. (B4) and (B5) at hand, we can rewrite Eq. (B3) as follows:

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = \kappa_T\left[\bar{N} + \left(\frac{\partial X}{\partial \mu}\right)_{T,\bar{N}}\right]\left(\frac{\partial \bar{N}}{\partial V}\right)_{T,\mu}. \tag{B6}$$

The remaining task is to relate $(\partial \bar{N}/\partial V)_{T,\mu}$ to the derivative of the thermodynamic potential X with respect to the chemical potential μ. By noting that

$$d\Omega = d(F - \mu\bar{N}) = -SdT - PdV - \bar{N}d\mu, \tag{B7}$$

we obtain

$$\left(\frac{\partial \bar{N}}{\partial V}\right)_{T,\mu} = \left(\frac{\partial P}{\partial \mu}\right)_{T,V}. \tag{B8}$$

Here $(\partial P/\partial \mu)_{T,V}$ can be related to $(\partial X/\partial \mu)_{T,V}$. Substituting $F = G - PV$ into Eq. (B7), we obtain

$$d(PV) = dX + SdT + PdV + \bar{N}d\mu, \tag{B9}$$

from which we can get

$$\left[\frac{\partial (PV)}{\partial \mu}\right]_{T,V} = V\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = \bar{N} + \left(\frac{\partial X}{\partial \mu}\right)_{T,V}. \tag{B10}$$

Substituting Eq. (B10) into Eq. (B8) and plugging the resultant expression for $(\partial \bar{N}/\partial V)_{T,\mu}$ into Eq. (B6), we obtain

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = \frac{\kappa_T}{V}\left[\bar{N} + \left(\frac{\partial X}{\partial \mu}\right)_{T,\bar{N}}\right]\left[\bar{N} + \left(\frac{\partial X}{\partial \mu}\right)_{T,V}\right]. \tag{B11}$$

Finally, substituting the latter equation into Eq. (B1), we obtain

$$\langle \delta N^2\rangle = \langle N^2\rangle - \bar{N}^2 = \frac{\bar{N}^2 kT\kappa_T}{V}\left[1 + \frac{1}{\bar{N}}\left(\frac{\partial X}{\partial \mu}\right)_{T,\bar{N}}\right] \times \left[1 + \frac{1}{\bar{N}}\left(\frac{\partial X}{\partial \mu}\right)_{T,V}\right], \tag{B12}$$

which can be easily rearranged to Eq. (4) in the main text.

APPENDIX C: DEPENDENCE OF THE RANGE OF ACTIVITY *z* [≡exp(*μ*/*kT*)] ON TEMPERATURE *T*

As the fraction f_0 of the ground-state population given in Eq. (8) is non-negative, the following inequality should be satisfied: $g_{3/2}(z) \leqslant g_{3/2}(1)(T_0/T)^{3/2} = \bar{\rho}\Lambda^3(T)$, where $\Lambda(T) = h/\sqrt{2\pi mkT}$. At temperatures below T_0, the latter inequality is satisfied for any value of z $[=\exp(\mu/kT)]$ in the interval (0,1). To satisfy the inequality at temperatures above T_0, however, values of z must be in the interval $0 < z < g_{3/2}^{-1}[g_{3/2}(1)(T_0/T)^{3/2}]$ $(\equiv z_{\max})$, where $g_{3/2}^{-1}$ denotes the inverse function of $g_{3/2}$. In the small-z limit, we have $g_{3/2}(z) = \sum_{n=1}^{\infty} z^n/n^{3/2} \cong z$, so $g_{3/2}^{-1}(z) \cong z$. Because of the latter equation, the upper bound $z_{\max}$ of z is approximately given by $z_{\max} \cong g_{3/2}(1)(T_0/T)^{3/2}$ when $T \gg T_0$. Since z should be positive and smaller than $z_{\max}$, the value of z should approach zero in the high-temperature limit. As such, an ideal Bose gas system in such limit as $T \to \infty$ and $z \to 1$ does not exist [13].

APPENDIX D: DERIVATION OF THE EXACT EXPRESSION (10) OF κ_T FOR AN IDEAL BOSE GAS

Here we derive Eq. (10) starting from the definition of the isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_{T,\bar{N}}$ and the equation of state of the ideal Bose gas. The thermodynamic pressure of the ideal Bose gas can be obtained by substituting

$$\ln \Xi_{BE}(\mu,V,T) = -\int_{\varepsilon>0}^{\infty} D(\varepsilon)\ln(1 - ze^{-\beta\varepsilon})d\varepsilon - \ln(1 - z)$$

into Eq. (A2) [3,4,6]:

$$P = \frac{kT}{\Lambda^3} g_{5/2}(z). \tag{D1}$$

Noting that $dg_\nu(z)/dz = z^{-1}g_{\nu-1}(z)$, we obtain

$$\left(\frac{\partial P}{\partial V}\right)_{T,\bar{N}} = \frac{kT}{\Lambda^3}\left(\frac{\partial z}{\partial V}\right)_{T,\bar{N}}\frac{g_{3/2}(z)}{z}, \tag{D2}$$

where $(\partial z/\partial V)_{T,\bar{N}}$ can be written as

$$\left(\frac{\partial z}{\partial V}\right)_{T,\bar{N}} = -\frac{\left(\frac{\partial \bar{N}}{\partial V}\right)_{T,z}}{\left(\frac{\partial \bar{N}}{\partial z}\right)_{T,V}} = -\frac{\frac{g_{3/2}(z)}{\Lambda^3}}{\frac{V}{\Lambda^3}\frac{g_{1/2}(z)}{z} + \frac{1}{(1-z)^2}}. \tag{D3}$$

For the derivation of the second equality in Eq. (D3), we make use of the textbook expression of $\bar{N}$, given by $\bar{N} = Vg_{3/2}(z)/\Lambda^3 + \bar{n}_0$ with $\bar{n}_0 = z/(1-z)$. Substituting Eq. (D3) into Eq. (D2), we obtain

$$\kappa_T^{-1} = -V\left(\frac{\partial P}{\partial V}\right)_{T,\bar{N}} = \frac{kT}{V}\frac{\left[\frac{V}{\Lambda^3}g_{3/2}(z)\right]^2}{\frac{V}{\Lambda^3}g_{1/2}(z) + \frac{z}{(1-z)^2}}. \tag{D4}$$

Noting that $Vg_{3/2}(z)/\Lambda^3$ is nothing but the number of particles in the excited states, i.e., $\bar{N} - \bar{n}_0$, one can rearrange Eq. (D4) as

$$\kappa_T = \frac{1}{\bar{\rho}kT}\frac{1}{[1-(\bar{n}_0/\bar{N})]^2}\frac{g_{1/2}(z) + \frac{\Lambda^3}{V}\frac{z}{(1-z)^2}}{\bar{\rho}\Lambda^3}. \tag{D5}$$

From the expression of $\bar{N}$ given above Eq. (D4), one can obtain the well-known expression for $\bar{\rho}\Lambda^3$:

$$\bar{\rho}\Lambda^3 = g_{3/2}(z) + \frac{\Lambda^3}{V}\frac{z}{1-z}. \tag{D6}$$

Substituting Eq. (D6) into Eq. (D5), we obtain

$$\kappa_T = \frac{1}{\bar{\rho}kT}\frac{1}{[1-(\bar{n}_0/\bar{N})]^2}\frac{g_{1/2}(z) + \frac{\Lambda^3}{V}\frac{z}{(1-z)^2}}{g_{3/2}(z) + \frac{\Lambda^3}{V}\frac{z}{1-z}}. \tag{D7}$$

We can get an alternative expression for κ_T by noting that

$$\bar{\rho}\Lambda^3 = \bar{\rho}\Lambda_0^3(\Lambda/\Lambda_0)^3 = g_{3/2}(1)(T_0/T)^{3/2}. \tag{D8}$$

Substituting Eq. (D8) into Eq. (D5), we obtain

$$\kappa_T = \frac{1}{\bar{\rho}kT}\frac{1}{[1-(\bar{n}_0/\bar{N})]^2}\left[\frac{g_{1/2}(z)}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2} + \frac{\frac{\Lambda^3}{V}\frac{z}{(1-z)^2}}{\bar{\rho}\Lambda^3}\right]. \tag{D9}$$

Noting that $\bar{n}_0 = z/(1-z)$ and that $\bar{\rho}V = \bar{N}$, we obtain Eq. (10) from Eq. (D9).

APPENDIX E: DERIVATION OF EQS. (12a) AND (12b) FROM EQ. (10)

In the high-temperature limit, z approaches zero (Appendix C), so both $\bar{n}_0$ [$=z/(1-z)$] and $f_0 = \bar{n}_0/\bar{N}$ approach zero as well. In this limit, we can approximate $g_\nu(z)$ by $g_\nu(z) = \sum_{n=1}^{\infty} z^n/n^\nu \cong z$. Therefore, Eqs. (8) and (10) become

$$f_0 \cong 1 - \frac{z}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2} \quad (T/T_0 \gg 1) \tag{E1}$$

and

$$\kappa_T \cong (\bar{\rho}kT)^{-1}\frac{z}{g_{3/2}(1)}\left(\frac{T}{T_0}\right)^{3/2} \quad (T/T_0 \gg 1) \tag{E2}$$

when the temperature is high enough. From Eq. (E1) we have $z(T/T_0)^{3/2}/g_{3/2}(1) \cong 1$. Substituting the latter into (E2), we obtain Eq. (12a) in the main text.

On the other hand, when $T/T_0 \ll 1$, z approaches unity [3,29] and f_0 given in Eq. (8) becomes

$$f_0 = \bar{n}_0/\bar{N} \cong 1 - (T/T_0)^{3/2}. \tag{E3}$$

From the latter equation and $\bar{n}_0 = z/(1-z)$, one can obtain the following approximate expression of z:

$$z \cong 1 - \frac{1}{1+\bar{N}[1-(T/T_0)^{3/2}]} \cong 1 - \frac{1}{1+\bar{N}} \quad (T/T_0 \ll 1). \tag{E4}$$

If $\bar{N}$ is a large number, z is close to unity where $g_{1/2}(z)$ has the following asymptotic behavior:

$$g_{1/2}(z) \cong \sqrt{\pi\bar{N}f_0} \cong \sqrt{\pi\bar{N}} \quad (T/T_0 \ll 1). \tag{E5}$$

Substituting Eqs. (E3)–(E5) into Eq. (10), we obtain

$$\kappa_T \cong \frac{(T_0/T)^3}{\bar{\rho}kT}\left[\frac{\sqrt{\pi\bar{N}}}{g_{3/2}(1)} + \bar{N}\right] \quad (T/T_0 \ll 1), \tag{E6}$$

which reduces to Eq. (12b) when $\bar{N}$ is a large number.

APPENDIX F: PARTICLE NUMBER FLUCTUATION OF AN IDEAL BOSE GAS SYSTEM IN A GRAND CANONICAL ENSEMBLE AND OTHER STATISTICAL ENSEMBLES

In the grand canonical ensemble of an ideal Bose gas system, the anomalously large fluctuation in the particle number in the low-temperature limit is caused by the condensation of the entire population of the gas particles to the ground quantum state of a single gas particle. It is known that the variance $\langle\delta n_k^2\rangle$ of the number n_k of gas particles in the kth quantum state is given by $\bar{n}_k^2 + \bar{n}_k$ for a grand canonical ideal Bose gas system [36]. In the low-temperature limit, the number n_0 of Bose gas particles in the ground state becomes effectively the same as N, so the statistics of N become the same as those of n_0, i.e., $\lim_{T\to 0}\langle\delta N^2\rangle = \bar{N}^2 + \bar{N}$.

In the low-temperature limit, the probability $p(N)$ of the number N of ideal boson particles in the system is given by

$$\lim_{T\to 0} p(N) = z^N(1-z), \tag{F1}$$

where the mechanical energy of the ground quantum state is set equal to zero. Following the notation of the main text, z denotes the activity defined by $\exp(\mu/kT)$. Equation (F1) follows from the general statistical mechanical equation

$$p(N) = \frac{z^N Q(N,V,T)}{\Xi}, \tag{F2}$$

where $Q(N,V,T)$ denotes the canonical partition function of the system and Ξ denotes the grand partition function given by $\Xi = \sum_{N=0}^{\infty} z^n Q(N,V,T)$. In the low-temperature limit, $Q(N,V,T) = \exp(N\varepsilon_0/kT)$ for the ideal boson gas system. If we set the energy ε_0 of the ground quantum state equal to zero, we have $\lim_{T\to 0} Q(N,V,T) = 1$, so Eq. (F2) reduces to Eq. (F1) in the low-temperature limit. The mean and variance of the distribution given in Eq. (F1) are given by

$$\lim_{T\to 0} \bar{N} = \frac{z}{1-z} \tag{F3}$$

and

$$\lim_{T\to 0} \langle \delta N^2 \rangle = \bar{N}^2 + \bar{N}, \tag{F4}$$

respectively. In the macroscopic limit where $\bar{N} \gg 1$, Eq. (F4) reduces to the low-temperature limit result of Eq. (13) in the main text.

On the other hand, in the high-temperature limit, Eq. (F2) reduces to the Poisson distribution

$$\lim_{T\to\infty} p(N) = \frac{(zq)^N}{N!} \exp(-zq), \tag{F5}$$

where q is the partition function of the single gas particle [29,36]. As is well known, the variance of the Poisson distribution is identically equal to the mean value:

$$\lim_{T\to\infty} \langle \delta N^2 \rangle = \bar{N} = zq. \tag{F6}$$

Equation (F6) is the same as the high-temperature limit result of Eq. (13) in the main text.

In a microcanonical or canonical ensemble of an ideal Bose gas system, the ratio of the variance $\langle \delta n_0^2 \rangle_c$ to the mean $\langle n_0 \rangle_c$ of the number n_0 of particles in the ground state vanishes in the low-temperature limit [13,42,43]. This can be easily understood because the variance $\langle \delta N^2 \rangle$ of the total number N of particles is zero for a microcanonical or canonical system and because N becomes approximately equal to n_0 in the low-temperature limit for the ideal Bose gas system. Similar results were reported also for a canonical ensemble of a nonideal Bose gas system [44].

APPENDIX G: DERIVATION OF $\langle \delta N^2 \rangle/\bar{N}$ AND κ_T FOR AN IDEAL FERMI GAS SYSTEM

For an ideal Fermi gas system, the grand canonical partition function is well known as $\Xi_{FD} = \prod_{\mathbf{p}} [1 + z\exp(-\beta\varepsilon_{\mathbf{p}})]$. Here $\mathbf{p}$ ($=2\pi\hbar\mathbf{n}/V^{1/3}$) denotes the momentum eigenvalue, where $\mathbf{n}$ is a vector whose components are integers. With the latter at hand, one can derive the expression of the mean number $\bar{N}$ of the Fermi gas particle by means of the standard statistical mechanical relation, i.e., $\bar{N} = kT(\partial \ln \Xi/\partial\mu)_{T,V}$. The result reads as

$$\bar{N} = \frac{V}{\Lambda^3} h_{3/2}(z), \tag{G1}$$

where $h_\nu(z) = \sum_{n=1}^{\infty} (-1)^{n+1} z^n/n^\nu$. Furthermore, one can easily get the expression of $\langle \delta N^2 \rangle$ by taking advantage of the identity $\langle \delta N^2 \rangle = kT(\partial\bar{N}/\partial\mu)_{T,V} = z(\partial\bar{N}/\partial z)_{T,V}$:

$$\langle \delta N^2 \rangle = \frac{V}{\Lambda^3} h_{1/2}(z). \tag{G2}$$

In derivation of Eq. (G2), we make use of $dh_\nu(z)/dz = h_{\nu-1}(z)/z$.

On the other hand, we can derive the exact expression of κ_T for an ideal Fermi gas system from the equation of states of the system and the definition of κ_T, i.e., $\kappa_T = -V^{-1}(\partial V/\partial P)_{T,\bar{N}}$. For an ideal Fermi gas system, the equation of state is well known as [29]

$$P = \frac{kT}{\Lambda^3} h_{5/2}(z). \tag{G3}$$

To obtain the expression of κ_T, we first obtain the expression for $(\partial P/\partial V)_{T,\bar{N}}$:

$$\left(\frac{\partial P}{\partial V}\right)_{T,\bar{N}} = \left(\frac{\partial z}{\partial V}\frac{\partial P}{\partial z}\right)_{T,\bar{N}} = \frac{kT}{z\Lambda^3} h_{3/2}(z) \left(\frac{\partial z}{\partial V}\right)_{T,\bar{N}}. \tag{G4}$$

Here we again take advantage of the identity $dh_\nu(z)/dz = z^{-1}h_{\nu-1}(z)$. In Eq. (G4), $(\partial z/\partial V)_{T,\bar{N}}$ can be rewritten as

$$\left(\frac{\partial z}{\partial V}\right)_{T,\bar{N}} = -\left(\frac{\partial \bar{N}}{\partial V}\right)_{T,z} \Bigg/ \left(\frac{\partial \bar{N}}{\partial z}\right)_{T,V}, \tag{G5}$$

which follows directly from the mathematical identity

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.$$

The expressions of the denominator and numerator on the right-hand side of Eq. (G5) can be written in terms of $h_\nu(z)$; from (G1), one obtains $(\partial\bar{N}/\partial V)_{T,z} = h_{3/2}(z)/\Lambda^3$ and $(\partial\bar{N}/\partial z)_{T,V} = Vh_{1/2}(z)/z\Lambda^3$. Substituting the latter equations into Eq. (G5), we get

$$\left(\frac{\partial z}{\partial V}\right)_{T,\bar{N}} = -\frac{z}{V}\frac{h_{3/2}(z)}{h_{1/2}(z)}. \tag{G6}$$

Substitution of Eq. (G6) into Eq. (G4) results in

$$\left(\frac{\partial P}{\partial V}\right)_{T,\bar{N}} = -\frac{kT}{\Lambda^3 V}\frac{h_{3/2}^2(z)}{h_{1/2}(z)}. \tag{G7}$$

From the definition of the isothermal compressibility, we finally get

$$\kappa_T \equiv -V^{-1}\left(\frac{\partial V}{\partial P}\right)_{T,\bar{N}} = \frac{\Lambda^3}{kT}\frac{h_{1/2}(z)}{h_{3/2}^2(z)}. \tag{G8}$$

From Eq. (G1), one can easily obtain $h_{3/2}(z) = \bar{\rho}\Lambda^3$. Substituting the latter into Eq. (G8), we finally obtain

$$\kappa_T = \frac{1}{\bar{\rho}kT}\frac{h_{1/2}(z)}{\bar{\rho}\Lambda^3}. \tag{G9}$$

Note that $\langle \delta N^2 \rangle/\bar{N}$ given in Eq. (G2) and κ_T given in Eq. (G9) obey the Gibbs fluctuation formula, in accordance with our prediction for the ideal Fermi gas system.

APPENDIX H: IDEAL BOSE GAS TRAPPED BY AN ISTOTROPIC HARMONIC POTENTIAL

For a mutually noninteracting Bose gas system, the logarithm of the grand canonical partition function is given by

$$\ln \Xi_{BE}(\mu, V, T) = -\int_{\varepsilon>0}^{\infty} D(\varepsilon)\ln(1 - ze^{-\beta\varepsilon})d\varepsilon - \ln(1-z), \tag{H1}$$

where the density of states $D(\varepsilon)$ is dependent on the external field imposed on the system. When mutually noninteracting bosons are trapped in the d-dimensional isotropic harmonic potential $U(\mathbf{r}) = \frac{1}{2}m\omega^2|\mathbf{r}|^2$, the corresponding density of states is given by

$$D(\varepsilon) \cong \frac{\varepsilon^{d-1}}{\Gamma(d)(\hbar\omega)^d}. \tag{H2}$$

Substitution of Eq. (H2) into Eq. (H1) yields

$$\ln \Xi_{BE}(\mu,V,T) \cong \frac{1}{(\beta\hbar\omega)^d} g_{d+1}(z) - \ln(1-z). \tag{H3}$$

In Eq. (H3) we can identify the effective spatial extension of the harmonically trapped system $(kT^*/m\omega^2)^{d/2}$ as V, where T^* is a certain constant temperature employed to convert the unit of ω^{-d} to that of volume and ω^{-d} is an extensive thermodynamic variable of the system as mentioned in Ref. [45]. Equation (H3) then conforms to Eq. (17) with $\phi(\mu,T)$ identified by

$$\phi(\mu,T) = \frac{(2\pi)^{d/2}}{\Lambda^d}\left(\frac{T}{T^*}\right)^{d/2} g_{d+1}(z). \tag{H4}$$

In the main text, T^* is chosen as the condensation temperature T_0, which is given by $T_0 = (\hbar\omega/k)[\bar{N}/g_d(1)]^{1/d}$.

APPENDIX I: THERMODYNAMIC POTENTIAL X OF AN INTERACTING BOSE GAS SYSTEM

Equation (7) of the present work shows that the population condensation of ideal Bose particles to the single-particle ground state makes the system deviate from the Gibbs fluctuation formula even in the macroscopic limit when the temperature of the system is below the condensation temperature. This result suggests that a similar deviation from the Gibbs fluctuation formula would occur for an imperfect *BE* system below the condensation temperature at which the population condensation to the ground state or to a small number of low-energy quantum states occurs [38–41]. Not to mention, the nonextensive free energy does not vanish for a finite-size Bose gas model either. As is the case for any finite-size system, the free energy of a finite-size imperfect Bose gas system is not strictly linear with respect to the size of the system due to the surface contribution. For example, we refer the grand potential of a hard-sphere Bose gas system with a finite size in Ref. [46].

Here we briefly examine the effect of interparticle hard-core repulsion on the grand potential $\Omega_{BE} = -kT \ln \Xi_{BE}$ and thermodynamic potential X defined in Eq. (3) using the model system considered by Huang *et al.* [38]. In the model, a/Λ (with a the s-wave scattering length) is a small parameter and the first-order expansion of $-\Omega_{BE}/kT$ with respect to a/Λ can be obtained as

$$\begin{aligned} -\Omega_{BE}/kT &= \ln \Xi_{BE}(\mu,V,T) \\ &\cong \frac{V}{\Lambda^3} g_{5/2}(z)\left[1 - \frac{2a}{\Lambda}\frac{g_{3/2}(z)^2}{g_{5/2}(z)}\right] \\ &\quad - \ln(1-z) - \frac{2a}{\Lambda}\left(\frac{z}{1-z}\right) \\ &\quad \times \left[2g_{3/2}(z) + \frac{\Lambda^3}{V}\left(\frac{z}{1-z}\right)\right] + O(a^2/\Lambda^2). \end{aligned} \tag{I1}$$

Substituting Eq. (I1) into Eq. (3), we obtain the expression of X_{BE} for the interacting Bose gas system as follows:

$$\begin{aligned} X_{BE}/kT &\cong \ln(1-z) + \frac{4a}{\Lambda}\left(\frac{z}{1-z}\right) \\ &\quad \times \left[g_{3/2}(z) + \frac{\Lambda^3}{V}\left(\frac{z}{1-z}\right)\right] + O(a^2/\Lambda^2). \end{aligned} \tag{I2}$$

Since

$$\bar{N} \cong \frac{V}{\Lambda^3} g_{3/2}(z) + \frac{z}{1-z} + O(a/\Lambda),$$

Eq. (I2) can be rewritten as

$$X_{BE}/kT \cong \ln(1-z) + \frac{4a}{\Lambda}\left(\frac{z}{1-z}\right)\bar{\rho}\Lambda^3 + O(a^2/\Lambda^2). \tag{I3}$$

Substituting Eq. (I3) into Eq. (4), we can obtain the fluctuation-compressibility relation for this system. The explicit expression of the relation, which is rather involved, will be omitted here, but the leading-order expression is the same as Eq. (7) in the main text, i.e.,

$$\frac{\langle \delta N^2 \rangle}{\bar{N}} \cong \bar{\rho} kT \kappa_T (1-f_0)^2 + O(a/\Lambda). \tag{I4}$$

Equation (I4) tells us that the effect of the thermodynamic potential X on the fluctuation-compressibility relation does not go away in the nonideal Bose gas system either, so it also deviates from the Gibbs fluctuation formula when the fraction f_0 $(\equiv \bar{n}_0/\bar{N})$ of particles in the ground quantum state is nonzero.

APPENDIX J: DERIVATION OF EQS. (19) AND (20)

Let us consider a system of mutually noninteracting classical particles in a cylinder with a fixed basement area A and a variable height l under the external potential, the expression of which is given by $U(x,y,z) = f_d z$ in Cartesian coordinate system. The grand canonical partition function of the system is given by

$$\ln \Xi = \exp(\beta\mu) q(\beta), \tag{J1}$$

where $q(\beta)$ denotes the molecular partition function given by

$$\begin{aligned} q &= \frac{1}{h^3}\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp(-\beta|\mathbf{p}|^2/2m)A \\ &\quad \times \int_0^l dz' \exp(-\beta f_d z') \\ &= \frac{Al}{\Lambda^3}\frac{1-\exp(-\beta f_d l)}{\beta f_d l}. \end{aligned} \tag{J2}$$

Substituting Eq. (J1) into Eq. (3), we obtain the expression of thermodynamic potential X $(\equiv G - \mu N)$ as

$$\begin{aligned} X &= kTAl\left(\frac{\partial(zq/Al)}{\partial \ln l}\right)_{\mu,T} = zkTl\left(\frac{\partial(q/l)}{\partial \ln l}\right)_T \\ &= \bar{N}kT\left(\frac{\partial \ln(q/l)}{\partial \ln l}\right)_T, \end{aligned} \tag{J3}$$

where z and $\bar{N}$ denote the absolute activity and the average number of particles in the system, given by $z = \exp(\beta\mu)$ and $\bar{N} = zq$ [3,4,6].

To obtain the explicit fluctuation-compressibility relation for the system [Eq. (4)], we must obtain the expression for $(\partial X/\partial\mu)_{T,V}$ and $(\partial X/\partial\mu)_{T,\bar{N}}$. From Eq. (J3) we obtain the following expression of $(\partial X/\partial\mu)_{T,V}$:

$$\begin{aligned}\left(\frac{\partial X}{\partial\mu}\right)_{T,V} &= \left(\frac{\partial z}{\partial\mu}\right)_{T} kTq\left(\frac{\partial\ \ln(q/l)}{\partial\ \ln l}\right)_{T}\\ &= \bar{N}\left(\frac{\partial\ \ln(q/l)}{\partial\ \ln l}\right)_{T}.\end{aligned} \tag{J4}$$

The derivation of the expression for $(\partial X/\partial\mu)_{T,\bar{N}}$ is a bit more involved. Using the chain rule, we get

$$\left(\frac{\partial X}{\partial\mu}\right)_{T,\bar{N}} = \left(\frac{\partial l}{\partial\mu}\right)_{T,\bar{N}}\left(\frac{\partial X}{\partial l}\right)_{T,\bar{N}}. \tag{J5}$$

Here $(\partial l/\partial\mu)_{T,\bar{N}}$ is given by the inverse of $(\partial\mu/\partial l)_{T,\bar{N}}$, the expression of which can be obtained as

$$\left(\frac{\partial\mu}{\partial l}\right)_{T,\bar{N}} = -kT\left(\frac{\partial\ \ln q}{\partial l}\right)_{T}. \tag{J6}$$

Equation (J6) follows from

$$\ln\bar{N} = \beta\mu + \ln q. \tag{J7}$$

On the other hand, the expression of $(\partial X/\partial l)_{T,\bar{N}}$ on the RHS of Eq. (J5) is given by

$$\begin{aligned}\left(\frac{\partial X}{\partial l}\right)_{T,\bar{N}} &= \bar{N}kT\frac{\partial}{\partial l}\left(l\frac{\partial\ \ln(q/l)}{\partial l}\right)_{T}\\ &= \bar{N}kT\left[\left(\frac{\partial\ \ln q}{\partial l}\right)_{T} + l\left(\frac{\partial^2\ln q}{\partial l^2}\right)_{T}\right],\end{aligned} \tag{J8}$$

which can be obtained by taking the partial derivatives of X given in Eq. (J3). Substituting Eqs. (J6) and (J8) into Eq. (J5), we obtain

$$\left(\frac{\partial X}{\partial\mu}\right)_{T,\bar{N}} = -\bar{N}\left\{1 + l\frac{\partial}{\partial l}\left[\ln\left(\frac{\partial\ln q}{\partial l}\right)_{T}\right]_{T}\right\}. \tag{J9}$$

Substituting the explicit expression (J2) of q into Eqs. (J4) and (J9), we get

$$\left(\frac{\partial X}{\partial\mu}\right)_{T,V} = \bar{N}\left(\frac{\beta f_d l}{\exp(\beta f_d l) - 1} - 1\right) \tag{J10}$$

and

$$\left(\frac{\partial X}{\partial\mu}\right)_{T,\bar{N}} = \bar{N}\left(\frac{\beta f_d l}{1 - \exp(-\beta f_d l)} - 1\right). \tag{J11}$$

Substituting Eqs. (J10) and (J11) into Eq. (4), we finally obtain

$$\frac{\langle\delta\rho^2\rangle}{\bar{\rho}^2} = \frac{\bar{\rho}kT\kappa_T}{\bar{N}}\frac{(\beta f_d l)^2\exp(-\beta f_d l)}{[1 - \exp(-\beta f_d l)]^2}, \tag{J12}$$

which is the same as Eq. (20) in the main text.

APPENDIX K: DENSITY FLUCTUATION AND ISTOTHERMAL COMPRESSIBILITY OF A CLASSICAL IDEAL GAS SYSTEM UNDER CONSTANT FORCE FIELD

The probability $p(N)$ that a grand canonical system contains N particles is well known as [3,4,6]

$$p(N) = z^N Q(N,V,T)/\Xi. \tag{K1}$$

Here $Q(N,V,T)$ denotes the canonical partition function given by $Q(N,V,T) = q^N/N!$ for the mutually noninteracting particles. Substituting the latter into Eq. (J7), we get the Poisson distribution

$$p(N) = (zq)^N\exp(-zq)/N!. \tag{K2}$$

It is well known that the variance $\langle\delta N^2\rangle$ of Poisson distribution is the same as its mean $\bar{N}$, i.e.,

$$\langle\delta N^2\rangle/\bar{N} = 1. \tag{K3}$$

Now let us derive the expression for the isothermal compressibility κ_T of the system from the definition of the isothermal compressibility and the equation of state of the system. Note that the pressure of the system of which grand canonical partition function is given in Eq. (J1) is given by

$$\begin{aligned}P &= kT\left(\frac{\partial\ \ln\Xi}{\partial V}\right)_{\mu,T} = kT\left[\frac{\partial(zq)}{\partial V}\right]_{\mu,T}\\ &= \frac{kTz}{A}\left(\frac{\partial q}{\partial l}\right)_{T} = \frac{kT}{A}\bar{N}\left(\frac{\partial\ \ln q}{\partial l}\right)_{T}.\end{aligned} \tag{K4}$$

From Eq. (K4) one can obtain the following expression of the isothermal compressibility κ_T defined by $\kappa_T = -V^{-1}(\partial V/\partial P)_{T,\bar{N}}$:

$$\begin{aligned}\kappa_T^{-1} &= -V\left(\frac{\partial P}{\partial V}\right)_{T,\bar{N}} = -l\left(\frac{\partial P}{\partial l}\right)_{T,\bar{N}}\\ &= -l\frac{kT}{A}\bar{N}\left(\frac{\partial^2\ln q}{\partial l^2}\right)_{T}.\end{aligned} \tag{K5}$$

Substituting Eq. (J2) into Eq. (K5), we get

$$\kappa_T^{-1} = \frac{kT}{Al}\bar{N}\frac{(\beta f_d l)^2\exp(\beta f_d l)}{[\exp(\beta f_d l) - 1]^2}. \tag{K6}$$

With Eqs. (K3) and (K6) at hand, one can confirm the correctness of Eq. (20).

APPENDIX L: DERIVATION OF THE EXACT EXPRESSIONS FOR $S/\bar{N}k$ AND X/Ω FOR THE SYSTEM IN FIG. 3(a)

When we want to know the expression for $S/\bar{N}k$, we can start from the general identity $\Omega = -kT\ln\Xi$. From $d\Omega = -SdT - PdV + Nd\mu$, S can be expressed as $S = -(\partial\Omega/\partial T)_{V,\mu}$. For the classical ideal gas under a constant force field, the grand canonical partition function is given by (see Appendix J)

$$\ln\Xi = \exp(\beta\mu)q(\beta) = \exp(\beta\mu)\frac{V}{\Lambda^3(T)}\frac{1 - \exp(-\beta f_d l)}{\beta f_d l}. \tag{L1}$$

By using Eq. (L1), we can get the entropy expression as

$$\frac{S}{\bar{N}k} = \frac{7}{2} - \beta\mu - \frac{\beta f_d l}{\exp(\beta f_d l) - 1}, \tag{L2}$$

where Eq. (J7) has been used.

Using the entropy expression, S^{id} in the case of a zero force field, which is given by

$$\frac{S^{id}}{\bar{N}k} = \ln \frac{V}{\Lambda^3}\frac{e^{5/2}}{\bar{N}}, \tag{L3}$$

and Eqs. (J2) and (J7), Eq. (L2) can be rewritten as

$$\frac{S}{\bar{N}k} = \frac{S^{id}}{\bar{N}k} + 1 + \ln \frac{1 - \exp(-\beta f_d l)}{\beta f_d l} - \frac{\beta f_d l}{\exp(\beta f_d l) - 1}, \tag{L4}$$

which is used in Fig. 3(c). The expression of X/Ω used in Fig. 3(d) is simply given by

$$\frac{X}{\Omega} = 1 - \frac{V/V^*}{\exp(V/V^*) - 1} \tag{L5}$$

using Eqs. (19), (J1), and (J7).

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[1] L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) **17**, 793 (1914).

[2] L. S. Ornstein and F. Zernike, *The Equilibrium Theory of Classical Fluids* (Benjamin, New York, 1964).

[3] K. Huang, *Statistical Mechanics* (Wiley, New York, 1987).

[4] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).

[5] A. Blumkin, S. Rinott, R. Schley, A. Berkovitz, I. Shammass, and J. Steinhauer, Phys. Rev. Lett. **110**, 265301 (2013).

[6] J. Luttinger and P. Nozieres, Phys. Rev. **127**, 1423 (1962).

[7] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 4714 (1967).

[8] J. Barker and D. Henderson, Annu. Rev. Phys. Chem. **23**, 439 (1972).

[9] J. Lin and P. W. Schmidt, Phys. Rev. A **10**, 2290 (1974).

[10] D. Tripathy and S. Mandal, Phys. Rev. B **16**, 231 (1977).

[11] T. Sota and K. Suzuki, Phys. Rev. B **40**, 2464 (1989).

[12] J. Lemmich, K. Mortensen, J. H. Ipsen, T. Hønger, R. Bauer, and O. G. Mouritsen, Phys. Rev. E **53**, 5169 (1996).

[13] M. Gajda and K. Rzazewski, Phys. Rev. Lett. **78**, 2686 (1997).

[14] G. G. Batrouni, V. Rousseau, R. T. Scalettar, M. Rigol, A. Muramatsu, P. J. H. Denteneer, and M. Troyer, Phys. Rev. Lett. **89**, 117203 (2002).

[15] M. Iskin and C. A. R. Sá de Melo, Phys. Rev. Lett. **97**, 100404 (2006).

[16] C.-H. Zhang, Phys. Rev. A **73**, 023601 (2006).

[17] G. E. Astrakharchik, J. Boronat, I. L. Kurbakov, and Yu. E. Lozovik, Phys. Rev. Lett. **98**, 060405 (2007).

[18] B.-J. Schaefer and J. Wambach, Phys. Rev. D **75**, 085015 (2007).

[19] A. Adare *et al.*, Phys. Rev. Lett. **101**, 232301 (2008).

[20] M. Rigol, G. G. Batrouni, V. G. Rousseau, and R. T. Scalettar, Phys. Rev. A **79**, 053605 (2009).

[21] V. I. Yukalov, Phys. Rev. A **72**, 033608 (2005).

[22] P. J. Price, Phys. Rev. **86**, 495 (1952).

[23] P. J. Price, Phys. Rev. **94**, 257 (1954).

[24] I. Fujiwara, D. Ter Haar, and H. Wergeland, J. Stat. Phys. **2**, 329 (1970).

[25] R. M. Ziff, G. E. Uhlenbeck, and M. Kac, Phys. Rep. **32**, 169 (1977).

[26] M. H. Lee and M. Long, Phys. Rev. E **52**, 189 (1995).

[27] G. E. Astrakharchik, R. Combescot, and L. P. Pitaevskii, Phys. Rev. A **76**, 063616 (2007).

[28] C.-L. Hung, X. Zhang, N. Gemelke, and C. Chin, Nature (London) **470**, 236 (2011).

[29] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1973).

[30] L. van Hove, Physica **15**, 951 (1949).

[31] T. L. Hill, J. Chem. Phys. **36**, 3182 (1962).

[32] Y. R. Lim, W. Jung, J. H. Bae, B. J. Park, J. Jang, and J. Sung, J. Phys. Chem. B **113**, 7982 (2009).

[33] J. Dunkel and S. Hilbert, Nat. Phys. **10**, 67 (2014).

[34] C. N. Yang, *Special Problems of Statistical Mechanics* (University of Washington, Seattle, 1952).

[35] M. B. Lewis and A. J. F. Siegert, Phys. Rev. **101**, 1227 (1956).

[36] R. Pathria, *Statistical Mechanics* (Pergamon, Oxford, 1996).

[37] J. Schmitt, T. Damm, D. Dung, F. Vewinger, J. Klaers, and M. Weitz, Phys. Rev. Lett. **112**, 030401 (2014).

[38] K. Huang, C. Yang, and J. Luttinger, Phys. Rev. **105**, 776 (1957).

[39] D. S. Jin, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Phys. Rev. Lett. **77**, 420 (1996).

[40] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Science **269**, 198 (1995).

[41] G. Su, L. Chen, and J. Chen, Phys. Lett. A **326**, 252 (2004).

[42] S. Grossmann and M. Holthaus, Phys. Rev. E **54**, 3495 (1996).

[43] H. D. Politzer, Phys. Rev. A **54**, 5048 (1996).

[44] Z. Idziaszek, M. Gajda, P. Navez, M. Wilkens, and K. Rzazewski, Phys. Rev. Lett. **82**, 4376 (1999).

[45] V. Romero-Rochín and V. S. Bagnato, Braz. J. Phys. **35**, 607 (2005).

[46] W.-S. Dai and M. Xie, J. Math. Phys. **48**, 123302 (2007).