

Full quantum theory of nonequilibrium phonon condensation and phase transitionXuanhua Wang ^{1,*} and Jin Wang ^{1,2,3,†}¹*Center for Theoretical Interdisciplinary Sciences, Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325001, China*²*Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794, USA*³*Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, USA*

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Fröhlich condensation is a room-temperature nonequilibrium phenomenon which is expected to occur in many physical and biological systems. Although predicted theoretically a half century ago, the nature of such condensation remains elusive. In this Letter, we derive a full quantum theory of Fröhlich condensation from the Wu-Austin Hamiltonian and present an analytical proof that a second-order phase transition induced by nonequilibrium and nonlinearity emerges in the large- D limit with and without decorrelation approximation. This critical behavior cannot be witnessed if external sources are treated classically. We show that the phase transition is accompanied by large fluctuations in the statistical distribution of condensate phonons and that the Mandel- Q factor which characterizes fluctuations becomes negative in the limit of excessive external energy input. In contrast with the cold atom equilibrium Bose-Einstein condensation (BEC), the Fröhlich condensate is a result of the nonequilibrium driving where the pump plays a role of setting the number of particles, and the medium plays a role of setting the temperature. Hence, BEC can either arise by reducing the medium temperature at fixed pump (equilibrium case), or by increasing the pump at fixed medium temperature (nonequilibrium case).

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Introduction. In biological systems, a driven nonequilibrium condensation phenomenon which is often compared with the Bose-Einstein condensation (BEC) was hypothesized by Fröhlich in the late 1960s [1–4]. Although BEC is a low-temperature equilibrium phenomenon whose discovery was only recently realized as the cooling technology advances [5,6], the Fröhlich condensate is intrinsically an out-of-equilibrium condensation of collective vibrations at the lowest mode driven by an external energy supply and is expected to occur at much higher temperatures. The proposal has stimulated a wide range of studies on the collective modes in nonequilibrium systems, such as quasiequilibrium magnon condensation at room temperature [7–9], polariton condensation in photonic systems [10–14] as well as nonequilibrium phase transitions [15,16]. Recently, due to the rapid progress of terahertz technology, many experimental and analytical works have been carried out in this direction and signals of the long-anticipated nonequilibrium condensation were finally observed [17–21]. Further experimental investigations in both biological and nonbiological systems have been proposed, such as spectroscopic studies using lysozymes and the bovine serum albumin (BSA) proteins, and optomechanical experiments using an array of membranes coupled with a cavity [22,23].

The essential piece in Fröhlich’s conjecture is the rate equations of the vibrational modes. The rate equations in

Fröhlich’s reasoning were constructed heuristically by requiring a Bose-Einstein distribution of the phonons in the absence of energy sources [1,2]. A rigorous derivation of the rate equations was provided by Wu and Austin from a quantum Hamiltonian, now known as the Wu-Austin Hamiltonian [24–27]. The Hamiltonian is composed of three parts: the oscillating dipoles, the heat bath that interacts nonlinearly with the system dipoles, and the external energy supply. The microscopic theory was formulated based on the Hamiltonian and finite-temperature Green’s functions and confirmed the possibility of detecting the phonon condensation in biological systems even at room temperature [24–27]. The rate equations suggest the emergence of the cooperative self-organization when the input energy is strong and the chemical potential approaches the lowest energy in the branch of vibrational modes [26,28].

Although the theory of Fröhlich condensation dates back half a century ago, little was known regarding its quantum and statistical properties near the transition. The common lore for predicting the feature of Fröhlich condensate is to make an analogy of the atomic BEC [1–4]. However, this *a priori* assumption should be carefully scrutinized as Fröhlich condensation is intrinsically an out-of-equilibrium phenomenon whose mechanism is more suitably compared to that of a single-mode maser of which the quantum properties and phase transitions are intensively studied [22,29–35]. The first investigation of the quantum statistics of the condensate was performed in Ref. [22] where the system and the bath are modeled by quantum oscillators and the external pump is treated classically. The calculation in Ref. [22] shows a continuous crossover between the two phases—the normal phase with

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almost no condensate and the condensate phase. Although some critical pump strength can be defined artificially as a reference scale at which the external input is roughly strong enough to generate the condensate, there is no qualitative distinction across the two phases. On the other hand, recent experiments using BSA proteins have indicated not only the existence of the collective oscillations of the biomolecules, but also a sign of a sharp transition when the control parameter exceeds certain critical threshold value [18,21]. Like many studies on the Fröhlich condensate, the analysis in Ref. [21] adopts a semiclassical method [28,36]. They proceeded by dequantizing the Wu-Austin Hamiltonian to obtain the classical equations of motion. However, such treatment renders the analysis nearly intractable and difficult to retrieve further information beyond the dynamics of mean values [36].

In this Letter, we derive a full quantum theory of the nonequilibrium condensation from the Wu-Austin Hamiltonian. In contrast with Ref. [22], both the surrounding solvents and the external source are treated quantum mechanically in our Letter, which results in crucial differences in the critical behaviors near the condensation point from what was reported in Ref. [22], such as the emergence of nonequilibrium phase transitions. We provide an analytical proof that the transition from the nonequilibrium steady state (NESS) with no condensate to the condensate state is similar to a second-order phase transition in the large- D limit regardless of certain approximations used in the precedent research. Moreover, the finite-size effects of the system on the transition and statistics are investigated. Unlike BEC, the condensation process does not require extremely low temperature but a high-temperature energy input. We demonstrate that such transition is accompanied by large fluctuations in its statistics and that excessive energy input promotes the system to the regime with a negative Mandel- Q parameter.

Driven dissipative system. The appearance of the Fröhlich condensate is believed to be a general consequence of the following three conditions: dissipation to the thermal bath, external energy source, and nonlinearity. For the terahertz vibrations inside protein molecules, such as phonon modes in DNA or BSA proteins, the surrounding solvents function approximately as a thermal bath. The nonlinear coupling between the system vibration modes and the surrounding medium in the second quantization form gives rise to the Hamiltonian formulized by Wu and Austin [24–27]. The system we consider is modeled by a collection of oscillators in a narrow bandwidth $\omega_i \in \mathcal{I}_{\text{sys}}$ which corresponds to D -normal modes of the oscillation. The vibrational modes are annihilated by operator a_i . The normal modes interact with the surrounding biological system with the excitation energies $\bar{\Omega}_k$ and the associated annihilation operator b_k as well as the external source with frequency Ω_i and annihilation operator p_i . The interaction Hamiltonian can be written as

$$\begin{aligned} V_{\text{int}}(t) = & \hbar \sum_i \sum_k f_{i,k} a_i^\dagger b_k e^{i(\omega_i - \bar{\Omega}_k)t} \\ & + \hbar \sum_{i,j} \sum_k g_{i,j,k} a_i^\dagger a_j b_k e^{i(\omega_i - \omega_j - \bar{\Omega}_k)t} \\ & + \hbar \sum_i \sum_k \lambda_{i,k} a_i^\dagger p_k e^{i(\omega_i - \Omega_k)t} + \text{H.c.}, \quad (1) \end{aligned}$$

where $f_{i,k}$ and $g_{i,j,k}$ are the coupling constants between the molecular vibrations and the solvent, and $\lambda_{i,k}$ is the coupling between the external source field and the system. ω_i , $\bar{\Omega}_k$, and Ω_k denote the frequencies associated with the i th vibrational mode of molecules, the solvent modes, and of the energy source. The Hamiltonian has been criticized for the unbounded potential energy from below [37]. This does not concern us here as the Hamiltonian is only used as an effective approximation in the interested energy domain rather than a fundamental description.

The rate equation of the condensate can be derived directly from the above interaction Hamiltonian. The details of the derivation can be found in the Supplemental Material [38]. We use the standard techniques of the full quantum master equation with Born and Markov approximations which returns formally the equations of motion for the whole system [39–41]. We then reduce the equations of motion of the density operator to only the l th state. After rearranging and contracting the repeated indices, we obtain the rate equation of phonons at mode ω_l in reminiscence of the heuristic equation given by Fröhlich,

$$\begin{aligned} \langle \dot{n}_l \rangle = & \phi [\bar{n}_{\omega_l} - \langle n_l \rangle] + \Lambda [n_{\omega_l} - \langle n_l \rangle] \\ & + \chi \left\{ \sum_{j>l} [\bar{n}_{\omega_j} \langle n_j - n_l \rangle + \langle n_j n_l + n_j \rangle] \right. \\ & \left. + \sum_{j<l} [\bar{n}_{\omega_j} \langle n_j - n_l \rangle - \langle n_j n_l + n_l \rangle] \right\}, \quad (2) \end{aligned}$$

where $\phi = 2\pi f_\omega^2 \mathcal{D}(\omega)$, $\Lambda = 2\pi \lambda_\omega^2 \mathcal{D}(\omega)$, $\chi = 2\pi g_\omega^2 \mathcal{D}(\omega)$ are the rates of dissipation, energy input, and energy redistribution, respectively. $\mathcal{D}(\omega)$ is the density of states of the surrounding environment. Since the bandwidth of the oscillations \mathcal{I}_{sys} is assumed to be narrow, the variation of the bath density and the couplings within the frequency range is slow, thus, the rates can be well approximated to be the same for each mode. As such, $\mathcal{D}(\omega)$, f_ω , λ_ω , and g_ω can all be evaluated at a typical value of ω_0 , the lowest of the vibrational modes. The rate equation of the total number of phonons $\hat{N} = \sum_{s=0}^D a_s^\dagger a_s$ can be further calculated to be the following: $\langle \dot{\hat{N}} \rangle = (D+1)(\phi \bar{n}_s + \Lambda n_{ex}) - (\phi + \Lambda)\langle N \rangle$. In the NESS, the solution of the total number of phonons is

$$\langle N \rangle \simeq \frac{(D+1)(\phi \bar{n}_s + \Lambda n_{ex})}{\phi + \Lambda}, \quad (3)$$

where \bar{n}_s is the occupation of the solvent at frequency ω_0 , n_{ex} is the occupation of the external source at ω_0 , and D is the total number of modes. Note that the nonlinear term does not contribute to the total phonon number and only contributes to the energy redistribution. At the steady state, the phonon number at mode ω_0 can be formally expressed as

$$\langle n_0 \rangle = \frac{\phi \bar{n}_s + \chi(\bar{n}_s + 1)(\langle N \rangle - \langle n_0 \rangle) + \Lambda n_{ex}}{\phi + \Lambda - \chi(\langle N \rangle - \langle n_0 \rangle - D\bar{n}_s)}. \quad (4)$$

It is easy to check that by setting the nonlinear coupling $\chi = 0$, the mean value of phonon number at mode ω_0 becomes the weighted average of thermal distributions due to the solvent and the external source: $\langle n_0 \rangle = \frac{\phi \bar{n}_s + \Lambda n_{ex}}{\phi + \Lambda}$. This is expected

from the secular approximation used in the equations of motion which ignores the off-diagonal subdominant contribution [39–43]. To obtain Eq. (4), we have assumed the decorrelation approximation between n_0 and n_l , namely, $\langle n_0 n_l \rangle \simeq \langle n_0 \rangle \langle n_l \rangle$ and $\langle n_0^2 \rangle \simeq \langle n_0 \rangle^2$. In the case of large molecule numbers, the total number of vibrational modes D is large, and the solution for the mean condensate number is approximately,

$$\langle n_0 \rangle \simeq \frac{\langle N \rangle - D\bar{n}_s}{2} + \frac{1}{2} \sqrt{(\langle N \rangle - D\bar{n}_s)^2 + 4(\bar{n}_s + 1)\langle N \rangle}. \quad (5)$$

It is easy to see that in the limit of large total number of modes D , the fraction of the condensate becomes $\langle n_0 \rangle / \langle N \rangle \xrightarrow{D \rightarrow \infty} 0$ for $n_{ex} \leq \bar{n}_s$. When $n_{ex} > \bar{n}_s$, we have

$$\langle n_0 \rangle / \langle N \rangle \simeq \frac{\Lambda}{\phi\bar{n}_s + \Lambda n_{ex}} (n_{ex} - \bar{n}_s), \quad (6)$$

which suggests a continuous phase transition at $n_{ex} = \bar{n}_s$ and gives the critical exponent $\beta = 1$. The fraction approaches to one in the limit of large n_{ex} .

Condensate statistics and fluctuations without decorrelation approximation. The above approach to solve for the approximate mean value of condensate phonons is a reminiscence of Fröhlich's equation. However, one can argue that the decorrelation approximation used in obtaining the formula is heavily invalidated by the nonlinear term in the Hamiltonian as well as by the coherence in the vibrational modes and fluctuations in each mode [29,35]. Therefore, in situations with strong coherence or near the transition point, such approximations are not applicable, and new approaches need to be considered. To gain insight into the transition phenomenon, we study the quantum statistics of condensate phonons assuming only the decorrelation between the total number of phonons $\langle N \rangle$ and the condensate phonon number $\langle n_0 \rangle$, namely, $\langle n_0 N \rangle \simeq \langle n_0 \rangle \langle N \rangle$. The total phonon number $\langle N \rangle$ has a much smaller relative fluctuation due to the central limit theorem and is conserved under the nonlinear two-phonon interaction which correlates two individual modes. The statistics of the condensate contains not only the information about the mean value of the phonon numbers in the condensate, but also its distribution. One of the important features of the distribution is captured by its the Mandel- Q parameter defined as $Q = (\langle n_0^2 \rangle - \langle n_0 \rangle^2) / \langle n_0 \rangle - 1$, which characterizes the fluctuation of a distribution as well as its distance from the classical Poisson distribution [44]. For any classical probability distribution the range of the Mandel parameter is $Q \geq 0$, where $Q = 0$ corresponds to the Poisson distribution. Negative values of Q means no classical analog and sub-Poissonian statistics exemplified by certain squeezed states of light [45].

We reduce the density matrix into the lowest diagonal mode to retrieve the information of only the condensate modes, $\rho_{n_0, n_0} = \sum_{\{n_l\}} \langle n_0, \{n_l\} | \rho | n_0, \{n_l\} \rangle$, where $\{n_l\} = \{n_1, n_2, \dots, n_D\}$ is the configuration of the excited states, and n_0 is the variable denoting the phonon number in the condensate. For one specific n_0 , the diagonal element has the physical interpretation of the probability of finding n_0 phonons on the lowest mode. The steady-state solution for the distribution of the condensate phonons can be solved exactly. For details, please refer to Supplemental Material [38]. For simplicity, we denote the probability as $P(m)$ where $m \in \{0-3 \dots\}$, then the reduced equations of motion of the system have the simple

solution as follows:

$$P(m) = P(0) \left(1 + \frac{1}{\bar{n}_s}\right)^m \frac{(\mathcal{N} - m)_{(m)}}{(\mathcal{N} + \mathcal{D} - m)_{(m)}}, \quad (7)$$

where $(q)_{(m)}$ is the rising Pochhammer symbol, \mathcal{N} is defined as $\mathcal{N} = \langle N \rangle + 1 + \frac{\phi\bar{n}_s + \Lambda n_{ex}}{\chi(\bar{n}_s + 1)}$ and $\mathcal{D} = D + \frac{\phi(\bar{n}_s + 1) + \Lambda(n_{ex} + 1)}{\chi\bar{n}_s} - \frac{\phi\bar{n}_s + \Lambda n_{ex}}{\chi(\bar{n}_s + 1)} - 1$. The probability of zero condensate phonon $P(0)$ can be determined by the normalization condition $\sum_m P(m) = 1$, which gives

$$P(0)^{-1} = {}_2F_1\left(1, -\mathcal{N}; -\mathcal{D} - \mathcal{N} + 1; 1 + \frac{1}{\bar{n}_s}\right), \quad (8)$$

where ${}_2F_1(1, -\mathcal{N}; -\mathcal{D} - \mathcal{N} + 1; 1 + \frac{1}{\bar{n}_s})$ is the Gauss hypergeometric function of type (2,1). As a reminder, D is the total number of oscillators in the system, and $\langle N \rangle$ is the total number of phonons in all modes given in Eq. (3). Examples of such distributions are shown in the Supplemental Material [38].

The mean phonon numbers in the condensate can be calculated by the summation $\langle n_0 \rangle = \sum_m m P(m)$. The fraction of the phonon condensate $\langle \bar{n}_s \rangle / \langle N \rangle$ is given as follows:

$$\begin{aligned} \frac{\langle n_0 \rangle}{\langle N \rangle} &= \frac{\mathcal{N} \left(1 + \frac{1}{\bar{n}_s}\right) {}_2F_1\left(2, 1 - \mathcal{N}; -\mathcal{D} - \mathcal{N} + 2; 1 + \frac{1}{\bar{n}_s}\right)}{(\mathcal{D} + \mathcal{N} - 1) {}_2F_1\left(1, -\mathcal{N}; -\mathcal{D} - \mathcal{N} + 1; 1 + \frac{1}{\bar{n}_s}\right)} \bigg/ \langle N \rangle. \end{aligned} \quad (9)$$

In deriving Eqs. (7)–(9), we have treated the total phonon number as its mean value $\langle N \rangle$ given in Eq. (3). The second moment of the condensate phonon number takes the analytic form

$$\langle n_0^2 \rangle = \frac{\mathcal{N} \left(1 + \frac{1}{\bar{n}_s}\right) {}_3F_2\left(2, 1 - \mathcal{N}; 1, -\mathcal{D} - \mathcal{N} + 2; 1 + \frac{1}{\bar{n}_s}\right)}{(\mathcal{D} + \mathcal{N} - 1) {}_2F_1\left(1, -\mathcal{N}; -\mathcal{D} - \mathcal{N} + 1; 1 + \frac{1}{\bar{n}_s}\right)}. \quad (10)$$

The Mandel- Q parameter defined by

$$Q = \frac{\text{Var}[n_0]}{\mathbb{E}[n_0]} - 1 = (\langle n_0^2 \rangle - \langle n_0 \rangle^2) / \langle n_0 \rangle - 1 \quad (11)$$

can be directly computed from the above expressions (see Fig. 1).

Nonequilibrium phase transition. For the Gauss hypergeometric function given in Eq. (9), the function ${}_2F_1(a, -b; -c; d)$ for positive $\{a, b, c, d\}$ is bounded when the ratio $\frac{c}{b} < d$ and it converges to a finite positive value as $b \rightarrow \infty$. Note that in the large- N limit, the total phonon number and the total vibrational modes are related by $D \simeq \frac{1}{(\bar{n}_s + \delta n)} \langle N \rangle$ where $\delta n = \frac{\Lambda}{\phi + \Lambda} (n_{ex} - \bar{n}_s)$. Therefore, in this case the fraction

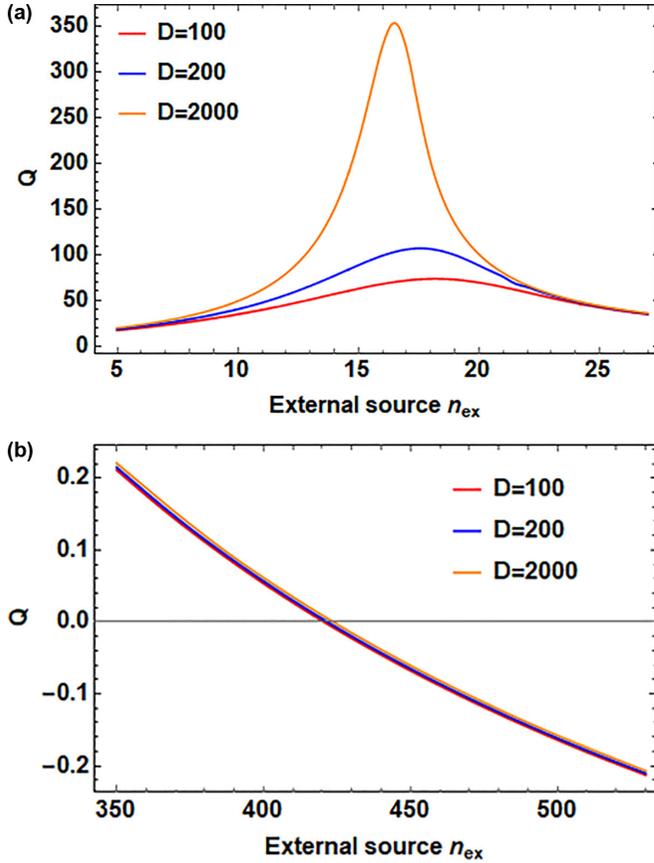


FIG. 1. Mandel- Q parameter for different values of the total mode number D . (a) The Mandel- Q parameter reaches maximal near the phase-transition points given by Eq. (16). (b) For the external source at high intensity, the Mandel parameter becomes negative. Parameters are $\bar{n}_s = 16$, $\phi = 5$ GHz, $\Lambda = 10$ GHz, and $\chi = 0.07$ GHz.

of condensate phonons is reduced to

$$\frac{\langle n_0 \rangle}{\langle N \rangle} \simeq \frac{\left(1 + \frac{1}{\bar{n}_s}\right)}{\left(1 + \frac{1}{\bar{n}_s + \delta n}\right)} \times \frac{{}_2F_1\left[2, -\langle N \rangle; -\left(1 + \frac{1}{\bar{n}_s + \delta n}\right)\langle N \rangle; 1 + \frac{1}{\bar{n}_s}\right]}{{}_2F_1\left[1, -\langle N \rangle; -\left(1 + \frac{1}{\bar{n}_s + \delta n}\right)\langle N \rangle; 1 + \frac{1}{\bar{n}_s}\right]} \Big/ \langle N \rangle. \quad (12)$$

It can be shown that for large integer values of $\langle N \rangle$ and $\delta n < 0$, the ratio of the hypergeometric functions is finite and the fraction vanishes

$$\frac{\langle n_0 \rangle}{\langle N \rangle} \xrightarrow{D \rightarrow \infty} 0 \quad \text{for } \delta n < 0 \text{ and } \langle N \rangle \in \mathbb{Z}^+,$$

$$\frac{d}{dn_{ex}} \left(\frac{\langle n_0 \rangle}{\langle N \rangle} \right) \xrightarrow{D \rightarrow \infty} 0 \quad \text{for } \delta n < 0 \text{ and } \langle N \rangle \in \mathbb{Z}^+. \quad (13)$$

For the case of $\delta n > 0$, the hypergeometric functions are unbounded as b goes to infinity and the ratio

${}_2F_1(2, -b; -c; d)/{}_2F_1(1, -b; -c; d)$ scales as b . This leads to

$$\frac{\langle n_0 \rangle}{\langle N \rangle} > 0 \quad \text{for } \delta n > 0 \text{ and } \langle N \rangle \in \mathbb{Z}^+$$

$$\left. \frac{d}{dn_{ex}} \left(\frac{\langle n_0 \rangle}{\langle N \rangle} \right) \right|_{\delta n=0^+} > 0 \quad \text{for } \langle N \rangle \in \mathbb{Z}^+. \quad (14)$$

One can verify easily that the limit $\lim_{\delta n \rightarrow 0} \langle n_0 \rangle / \langle N \rangle = 0$ in the large- D limit and the derivative is discontinuous at the transition point $\delta n = 0$. This confirms that as the external source intensifies, the NESS of the system goes through a continuous phase transition, similar to the second-order phase transition in the equilibrium superfluidity to the condensate phase. Near the transition point, i.e., $0 < (n_{ex} - \bar{n}_s) / (\bar{n}_s) \ll 1$, we apply the leading-order saddle-point approximation and obtain the fraction of the condensate,

$$\frac{\langle n_0 \rangle}{\langle N \rangle} \simeq \frac{1}{\bar{n}_s} \frac{\Lambda}{\phi + \Lambda} (n_{ex} - \bar{n}_s). \quad (15)$$

This confirms the result obtained by applying the decorrelation approximation Eq. (6) and the critical exponent $\beta = 1$.

For finite values of D , an equivalent condition for the condensation to occur, besides directly computing the fraction of condensation in Eq. (9), is to look at the statistics of the condensate phonons, namely, when $P(n_{cr} + 1) > P(n_{cr})$ for some $n_{cr} \geq 1$. This inequality gives the condensation condition,

$$n_{ex} > \frac{(D-1)\Lambda - 2\phi}{(D+1)\Lambda} \bar{n}_s + \left(\frac{\phi + \Lambda}{\chi} + n_{cr} - 1 \right) \frac{\phi + \Lambda}{(D+1)\Lambda}. \quad (16)$$

The transition point can be directly computed from Eq. (16) by setting $n_{cr} = 1$. Note that in the large- D limit, the critical number density reduces to the same as the surrounding solvent,

$$n_{ex} = \bar{n}_s, \quad (17)$$

which is the same as the condition given in Eqs. (6) and (15). In contrast with the cold atom equilibrium BEC, the Fröhlich condensate is a result of the nonequilibrium driving. In this case, the pump plays a role of setting the number of particles, and the medium plays a role of setting the temperature. Therefore, BEC either arises by reducing the medium temperature at the fixed pump (equilibrium case), or by increasing the pump at fixed medium temperature (nonequilibrium case). On the other hand, the emergence of the condensation also infers the off-diagonal long-range order in the system indicated by the Penrose-Onsager criterion [46,47]. In the long-distance limit, the single-particle density matrix becomes $\rho(x, x') = \langle \psi^\dagger(x) \psi(x') \rangle \rightarrow n_c$ where n_c stands for the density of the condensate. The emergence of the condensate, though obtainable from the dequantized or semiclassical equations, suggests a strong enhancement of nonclassicality of the system.

The phase behavior was studied in the case of a classical pumping field [22] where the pump coupling $V_p = \sum_s [F_s^*(t) a_s e^{-i\omega_s t} + \text{H.c.}]$ is featured by a broad spectrum $\langle F_s(t') F_s^*(t) \rangle = \frac{r}{2} \delta(t - t')$ with the control parameter r denoting the pumping rate. However, the issue with the classical

pumping field is that it is qualitatively similar to an external source at an infinitely high temperature in that the emission and absorption rates are the same in a microprocess. The only parameter describing such classical pumps is the pumping rate r . Since the key to determine the phase transition is the comparison of the pump particle density with that of the bath, this requires a quantum description of not only the bath but also the pump. By treating the pump classically, all modes obtain the same gaining rate due to the pump regardless of the number of phonons already on the modes. Therein many of the critical properties at low temperatures and near the transition are erased. For instance, the critical energy supply at which the condensation emerges, in this situation, approaches zero in the large- D limit: $r = \frac{\phi}{D+1} (1 + \frac{\phi}{\chi}) \xrightarrow{D \rightarrow \infty} 0$. It means that the condensate phonons at the lowest mode start to accumulate from the zero pumping and increase with the strength of the pumping field until saturation. It can be further shown that the fraction of the condensation in the large- D limit is roughly $\frac{r/\phi}{r/\phi + \bar{n}_s}$. As shown in Figs. 2 and 3, the condensation will emerge regardless the types of irradiating energy, but the transition to the condensation phase is a continuous crossover with no real distinction between the phases in this case (Fig. 3).

In Fig. 1, we show that the Mandel- Q parameter reaches the maximal at the transition point near $n_{ex} = \bar{n}_s = 16$ [the exact value is given in Eq. (16)] and decays rapidly away from the phase transition point. For an extremely large energy input, Q becomes negative, and it suggests a sub-Poissonian statistics similar to that in the resonance fluorescence of a single atom. In Fig. 2, the fraction of condensate phonons as the occupation of the external source is simulated. For a relatively small total phonon numbers (e.g., $\langle N \rangle = 200$), the transition from the ordinary nonequilibrium phase to the condensation phase is similar to a continuous crossover due to the finiteness of the system. In particular, in this case the condensation fraction is nonzero even for zero external energy input due to the finiteness of the system and the thermal equilibrium with the

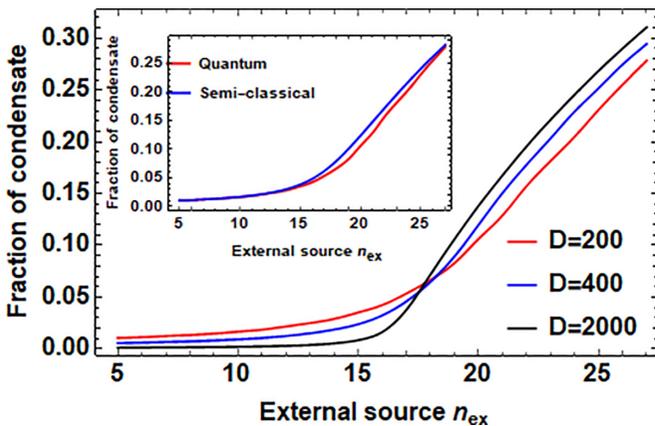


FIG. 2. Fractions of condensate for different values of D demonstrate the second-order phase transition at the critical external occupation number. Parameters are $\bar{n}_s = 16$, $\phi = 5$ GHz, $\Lambda = 10$ GHz, and $\chi = 0.07$ GHz. The inset: Comparison between the decorrelation solution Eq. (5) (semiclassical) and the solution without the decorrelation assumption (quantum) according to Eq. (9) for $D = 200$.

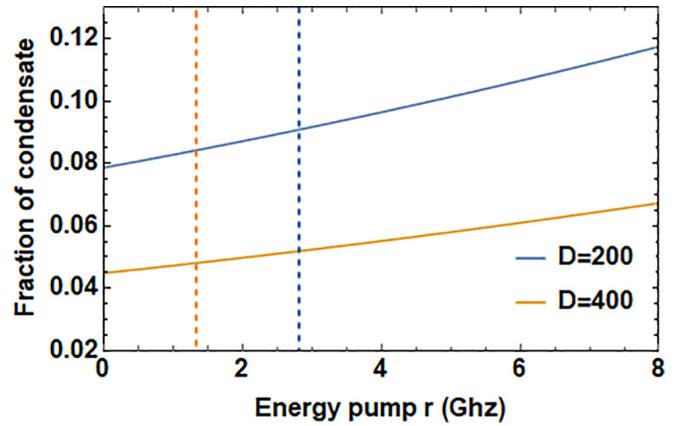


FIG. 3. Fraction of condensate vs energy input for classical pumping field. The vertical lines are the threshold pumping values. For larger- D values, the behaviors are similar, but the threshold values are much closer to the vertical axis $r = 0$. Parameters are $\bar{n}_s = 16$, $\phi = 5$ GHz, $\chi = 0.07$ GHz.

surrounding solvent. However, in the large- D case, the transition becomes sharp and the fraction is negligible at zero input, which is expected for the thermodynamic limit. This agrees with the findings reported in a recent experiment [21]. We compare the solution with the decorrelation approximation Eq. (5) and the solution without the assumption Eq. (9). The relative difference maximizes near the transition point (for $D = 200$, the critical point is at $n_{ex} \simeq 17.4$). The numerical simulations verify that the transition behaves in accordance with our analytical result Eq. (16). In Fig. 3, we show that in the case of a classical broad-spectrum pumping, such a transition does not show up.

Conclusions. It has been long debated if molecules go through certain phase transitions to the condensate states during the Fröhlich process. In this Letter, we derived a full quantum theory of the Fröhlich condensation and demonstrated the critical phenomenon. In particular, we presented an analytical proof of the existence of the nonequilibrium phase transition based on the Wu-Austin Hamiltonian and outlined the conditions for witnessing such transitions. We analyzed the phonon distributions and fluctuations near the transition and showed that the phase transition is only realizable in the large- D limit. In biological systems, this condition can be naturally realized, and the analysis demonstrates the viability of broad experimental prospect to observe such a nonequilibrium phase transition of the molecular vibrations into a coherent quantum state in much broader systems than the equilibrium BEC. Recent experiments have made tremendous progress in the nonequilibrium condensation in biological systems, and signs of such phase transition as shown in Fig. 2 were witnessed. Further experimental investigations and smoking-gun evidence are in need to exclude all potential artifacts and to confirm the finding. It is hopeful that this will open a new door for further explorations of out-of-equilibrium collective oscillations in broader nonequilibrium systems.

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