Semi-classical statistical description of Fröhlich condensation

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Abstract Fröhlich’s model equations describing phonon condensation in open systems of biological relevance are reinvestigated within a semi-classical statistical framework. The main assumptions needed to deduce Fröhlich’s rate equations are identified and it is shown how they lead us to write an appropriate form for the corresponding master equation. It is shown how solutions of the master equation can be numerically computed and can highlight typical features of the condensation effect. Our approach provides much more information compared to the existing ones as it allows to investigate the time evolution of the probability density function instead of following single averaged quantities. The current work is also motivated, on the one hand, by recent experimental evidences of long-lived excited modes in the protein structure of hen-egg white lysozyme, which were reported as a consequence of the condensation effect, and, on the other hand, by a growing interest in investigating long-range effects of electromagnetic origin and their influence on the dynamics of biochemical reactions.

Keywords Fröhlich condensation · Low-frequency modes of proteins · Far-from-equilibrium systems

1 Introduction

Some decades ago, the study of open systems far from thermodynamic equilibrium showed, under suitable conditions, the emergence of self-organization. Striking similarities were observed among very different physical systems having in common the fact of being composed of many nonlinearly interacting subsystems. When a control parameter, typically the

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energy input rate, exceeds a critical value, then the subsystems act cooperatively to self-organize in what is commonly referred to as a non-equilibrium phase transition. This is at variance with equilibrium phase transitions (e.g., Bose-Einstein condensation), for which the transition from disorder to order is driven by a lowering of temperature – the control parameter – below a critical value. Paradigmatic examples of non-equilibrium phase transitions are provided by the laser transition and by the Rayleigh-Bénard convective instability, a quantum and a classical system, respectively. In the early '80s of the last century, the emergence of collective properties in open systems was studied in a general and interdisciplinary framework referred to as “Synergetics” [1]. This fascinating topic was pioneered in the late '60s by H. Fröhlich in a biological context [2–4].

Fröhlich pointed out that most molecular systems in living organisms display typical properties of open systems inherent in inducing non-thermal collective effects, that is, they are composed of many nonlinearly interacting subunits and energy is supplied to most of them from endogenous sources (biochemical reactions, ATP hydrolysis, endogenous electromagnetic field...). Fröhlich introduced the following generic model to shed light on those kinds of collective behavior.

Let a system consist in z normal modes of frequency ω_k ($\omega_1 < \omega_2 < \dots < \omega_z$), each of them being characterized by a discrete energy spectrum (phonons). Due to the interactions with a surrounding heat bath, it is supposed that the dynamics associated with the energy of each normal mode is ruled by several kinds of stochastic events. First, linear events accounting for the absorption or the emission of one phonon from a single normal mode. Second, nonlinear events accounting for the simultaneous absorption of one phonon from one normal mode, and emission of one phonon from another mode. Besides interactions with the heat bath, energy is assumed to be provided to each normal mode by an external endogenous source. Calling $\langle N_k \rangle$ the average number of phonons in the mode of frequency ω_k , Fröhlich suggested that the dynamics of the system was described by the following set of rate equations:

$$\begin{aligned} \frac{d\langle N_k \rangle}{dt} = & s_k + \varphi_k(\beta) (\langle N_k \rangle + 1 - \langle N_k \rangle e^{\beta \hbar \omega_k}) + \\ & \sum_{j \neq k} \Lambda_{kj}(\beta) [\langle N_k + 1 \rangle \langle N_j \rangle - \langle N_k \rangle \langle N_j + 1 \rangle e^{\beta \hbar (\omega_k - \omega_j)}], \quad k = 1, \dots, z \end{aligned} \quad (1)$$

where $\beta = 1/kT$, with T the temperature of the heat bath. The first term on the RHS, s_k , is the rate of external energy supply to the mode k whereas the second and third terms account for the rate of change due to linear and nonlinear events, with temperature-dependent coupling constants φ_k and Λ_{kj} , respectively. Fröhlich analytically solved (1) in the stationary case showing that the total number of phonons linearly increases when increasing the rate of energy supply s_k beyond some threshold, while nonlinear processes contribute to channeling the energy excess into the mode of lowest frequency [2]. In other words, for sufficiently large values of s_k , the stationary state will satisfy $\langle N_1 \rangle \gg \langle N_k \rangle$ with $k \neq 1$. Physically, every degree of freedom of the system oscillates mainly at the lowest frequency ω_1 of the spectrum. This state of collective excitation is better known as *Fröhlich condensation*.

Over the last decades, Fröhlich condensation has been theoretically investigated by many authors [5]. A generic model of Hamiltonian was introduced by Wu and Austin to derive Fröhlich's rate equations (1) from a microscopic quantum basis [6, 7]. The same Hamiltonian was found to induce excitations propagating coherently in a similar way as Davydov's solitons [8, 9]. Fröhlich suggested that the normal modes involved in the condensation effect can be identified as rotational and vibrational modes of biomolecular

structures (DNA, proteins) whose typical absorption spectra involve frequencies in the terahertz domain – from 0.1 to 10 THz typically [3, 4]. From an experimental point of view, the detection of non-thermal features of biomolecules at such frequencies is particularly challenging [10]. This is because most biomolecular systems including cell water strongly absorb radiation at THz frequencies. Therefore, experimental devices involving high-power THz radiation are assumed to cause thermal effects in biological materials, making non-thermal effects hard to detect [11]. This, together with the fact that suitable THz sources have been widely unavailable for many years explains why no experimental evidences or refutations of Fröhlich condensation has been reported for decades since Fröhlich's first proposal. As emphasized by Reimers et al. [12], if a coherent effect similar to Fröhlich's effect was experimentally validated, this could lead to numerous applications in physics [13], biology [14–16] and medicine [17, 18]. Indeed, other phenomena that give rise to similar collective properties of a system such as lasing, superconductivity, and Bose-Einstein condensation are of great importance.

Recently, Lundholm et al. [19] used combined terahertz techniques with a highly sensitive X-ray crystallographic method to visualize low-frequency vibrational modes in the crystal structure of hen-egg white lysozyme. It was reported that 0.4 THz electromagnetic radiation induces non-thermal changes in electron density. In particular a local increase of electron density in a long α -helix motif was observed consistent with a subtle longitudinal compression of the helix characterized by a micro- to milli-second lifetime. Such a coherent vibration was reported by the authors as a consequence of Fröhlich's effect even though no direct connection with Fröhlich's model was provided. Many authors point out that microtubules and cell membranes – for which the hydrolysis of adenosine triphosphate (ATP) or guanosine triphosphate (GTP) represents a significant source of energy supply – would also be good candidates for Fröhlich's effect [5, 20]. Pokorný experimentally observed a strong excitation in the spectrum of vibration of microtubules localized in the 10 MHz range that could be a further evidence of Fröhlich condensation at lower frequencies [21, 22]. Recently, Weightman has provided a review of studies reporting non-thermal effects of THz radiation on cellular systems although it is not yet possible to determine if those are a direct consequence of Fröhlich's effect [23].

Among other applications of the condensation effect, Fröhlich suggested that the excitation of a particular mode of polar oscillations in macromolecular systems could lead to strong long-range dipole-dipole forces. Applied to biological systems, it is surmised that such forces would have a profound influence on the dynamics of recruitment of biological structures [4, 24, 25], including, e.g., the initiation of physiologically relevant cascades of chemical reactions. While long-range forces have been reported at the cellular level [26, 27], their possible role at the biomolecular level still remains an open question but noticeable effort has been undertaken recently to probe their possible contribution in a biological context [28, 29].

Most theoretical studies about Fröhlich condensation – including the derivation of (1) – are based on a quantum Hamiltonian description akin to the one proposed originally by Wu and Austin. Given the semi-classical nature of the rate equations postulated by Fröhlich, one can legitimately wonder how necessary a quantum description is to account for Fröhlich condensation or even what are the main ingredients needed to generate such a phenomenon. In the present paper, we suggest to tackle this issue from a semi-classical point of view. In Section 2, Fröhlich rate equations (1) are derived from semi-classical arguments [Sections 2.1 and 2.2] and we show qualitatively how Fröhlich condensation is induced [Section 2.3]. In Section 3, comparison with the Wu-Austin quantum description [6] and the 3 types of condensate introduced by Reimers et al. [12] is made. In

Section 4, Fröhlich condensation is statistically studied by estimating the solution of the master equation numerically. Important information is thus provided which can be of particular relevance to identify the phenomenon experimentally.

2 Derivation of the rate equations

The derivation of the Fröhlich rate equations is given in the two following subsections. The first subsection [Section 2.1] is devoted to the derivation of the second term on the RHS of (1), which accounts for linear events, whereas in the second subsection [Section 2.2], the third term on the RHS of (1) is also derived. As far as linear events are concerned, it is enough to consider the presence of a single normal mode in the system. Thus, the first subsection will provide a good introduction to the second one where the dynamics of all normal modes must be taken into account simultaneously in order to describe nonlinearities. Finally, the Section 2.3 has been added to show how Fröhlich condensation can be qualitatively “predicted” on the basis of the transition probabilities given in the Sections 2.1 and 2.2.

2.1 One-variable process

Although not clearly mentioned in the literature, Fröhlich’s equations are primarily based on the assumption that the time dependence of the number of phonons in each normal mode can be described as a homogeneous Markov process. Here only one normal mode of frequency ω_k is considered and we call $N_k(t)$ the stochastic process that accounts for the number of phonons in this mode. Under homogeneous Markov assumption, it is possible to work with time-translation invariant conditional probabilities $p(n_k, t|n'_k)$ so that

$$p(n_k, t|n'_k) \equiv \text{Prob}\{N_k(t + t') = n_k | N_k(t') = n'_k, \forall t' \geq 0\},$$

satisfies the following master equation [30]

$$\partial_t p(n_k, t|n'_k) = \sum_{m_k} W(n_k|m_k) p(m_k, t|n'_k) - W(m_k|n_k) p(n_k, t|n'_k). \quad (2)$$

The transition probabilities $W(n_k|m_k)$ are defined as

$$W(n_k|m_k) = \lim_{\Delta t \rightarrow 0} \frac{p(n_k, \Delta t|m_k)}{\Delta t}.$$

Since (2) is valid regardless of the initial condition n'_k , conditional probabilities of the type $p(\dots, t|n'_k)$ will be noted $p(\dots, t)$ in the following. As mentioned in the heading of the section, only interactions which lead to the absorption or the emission of a single phonon at a time are considered here. Thus, $W(n_k|m_k)$ is zero except when $m_k = n_k \pm 1$ or $m_k = n_k$ (birth-and-death process). The equation for the evolution of the average number of phonons in the mode k is easily deduced:

$$\begin{aligned} \frac{d\langle N_k \rangle}{dt} &= \sum_{n_k > 0} n_k \partial_t p(n_k, t) \\ &= \sum_{n_k > 0} n_k [W(n_k|n_k - 1) p(n_k - 1, t) + W(n_k|n_k + 1) p(n_k + 1, t) \\ &\quad - (W(n_k + 1|n_k) + W(n_k - 1|n_k)) p(n_k, t)]. \end{aligned} \quad (3)$$

Using appropriate substitutions in the sum indices with suitable relabeling, one gets

$$\frac{d\langle N_k \rangle}{dt} = \sum_{n_k > 0} [W(n_k + 1|n_k) - W(n_k - 1|n_k)] p(n_k, t), \quad (4)$$

where the boundary conditions

$$W(-1|0) = 0, \text{ and } p(n_k, t) = 0, \text{ if } n_k < 0, \quad (5)$$

have been used. Next, let us look for an appropriate expression of $W(n_k + 1|n_k)$ and $W(n_k - 1|n_k)$ as a function of n_k . First, it is supposed that the phonons are all “independent” so that

$$W(n_k - 1|n_k) = \alpha_k(\beta)n_k, \quad (6)$$

where $\alpha_k(\beta)$ is the temperature-dependent probability per time unit that one phonon is emitted from the mode k . Second, $W(n_k + 1|n_k)$ can be obtained by noticing that a birth-and-death process following boundary conditions (5) has a single stationary solution $p^s(n_k)$ through (2) (see the Appendix), and that this solution satisfies the detailed balance condition

$$W(n_k + 1|n_k)p^s(n_k) = W(n_k|n_k + 1)p^s(n_k + 1), \quad \forall n_k \geq 0. \quad (7)$$

Moreover, due to the coupling between the system and the surrounding heat bath, it is required that the stationary solution is given by a Bose-Einstein distribution

$$p^s(n_k) = e^{-\beta\hbar\omega_k n_k} / Z, \quad (8)$$

where $Z = \sum_{n_k \geq 0} e^{-\beta\hbar\omega_k n_k}$ is the one-normal mode partition function. (7) leads to:

$$W(n_k + 1|n_k) = W(n_k|n_k + 1)e^{-\beta\hbar\omega_k} \stackrel{(6)}{=} \alpha_k(\beta)(n_k + 1)e^{-\beta\hbar\omega_k}. \quad (9)$$

Substituting the above equation and (6) into (4), the second term on the RHS of (1) can be deduced:

$$\frac{d\langle N_k \rangle}{dt} = \varphi_k(\beta) \left(\langle N_k \rangle + 1 - \langle N_k \rangle e^{\beta\hbar\omega_k} \right), \quad (10)$$

where we have set $\varphi_k(\beta) \equiv \alpha_k(\beta)e^{-\beta\hbar\omega_k}$.

2.2 Many-variables process

Let us next consider the influence of all the other normal modes on the mode of frequency ω_k . Let $\mathbf{N}(t) = (N_1(t), N_2(t), \dots, N_z(t))$ be the vector of all the Markovian processes describing the number of phonons in each normal mode, so that the conditional probabilities are noted as $p(\mathbf{n}, t|\mathbf{n}')$, with $\mathbf{n}, \mathbf{n}' \in \mathbb{N}^z$, $\mathbf{n} = (n_1, n_2, \dots, n_z)$ and $\mathbf{n}' = (n'_1, n'_2, \dots, n'_z)$.

As a large number of interactions between the normal modes and the heat bath is expected, we call R^μ , $\mu = 1, \dots, s$, all the possible events accounting for the simultaneous absorption(s) and/or emission(s) of phonon(s) from specific normal modes. Each event is characterized by a vector $\mathbf{r}^\mu$ whose element r_i^μ ($1 \leq i \leq z$) is equal to the corresponding change in the number of phonons in the mode of frequency ω_i . Hence, the master equation reads as [30]

$$\partial_t p(\mathbf{n}, t|\mathbf{n}') = \sum_{\mu=1}^s W(\mathbf{n}|\mathbf{n} - \mathbf{r}^\mu)p(\mathbf{n} - \mathbf{r}^\mu, t|\mathbf{n}') - W(\mathbf{n} - \mathbf{r}^\mu|\mathbf{n})p(\mathbf{n}, t|\mathbf{n}'). \quad (11)$$

In this case, the evolution of the average number of phonons in the mode k is immediately deduced (similarly to the previous subsection, initial conditions are omitted in the notation):

$$\frac{d\langle N_k \rangle}{dt} = \sum_{\mu=1}^s \sum_{\mathbf{n}} n_k [W(\mathbf{n}|\mathbf{n} - \mathbf{r}^\mu)p(\mathbf{n} - \mathbf{r}^\mu, t) - W(\mathbf{n} - \mathbf{r}^\mu|\mathbf{n})p(\mathbf{n}, t)], \quad (12)$$

where the sum $\sum_{\mathbf{n}}$ corresponds to $\sum_{n_1 \geq 0} \sum_{n_2 \geq 0} \dots \sum_{n_z \geq 0}$. In addition, since events which do not imply a change in the number of phonons in the mode k have zero contribution to the equation, (12) is readily simplified.

1. To derive the second term on the RHS of (1), we should consider each event R^μ corresponding to the absorption or the emission of one phonon from a specific mode. There are only two events involving the mode k ($2z$ events involving all the normal modes) and they are given by $r_j^\mu = \pm \delta_{jk}$, for $j = 1, \dots, z$. This case corresponds to the case examined in the previous subsection whereby (10) was finally found.
2. To derive the third term on the RHS of (1), we should consider each event R^μ corresponding to the simultaneous absorption of one phonon from a normal mode, and emission of one phonon from another mode. For a specific mode k , there are $2(z-1)$ events ($2z(z-1)$ events involving all the normal modes), each characterized by $\mathbf{r}^\mu$ so that

$$\mathbf{r}^\mu = (0, \dots, 0, \overset{k}{\downarrow} \pm 1, 0, \dots, 0, \overset{j}{\downarrow} \mp 1, 0, \dots, 0), \quad \forall j \neq k, j \in \llbracket 1, z \rrbracket, \quad (13)$$

where $j \in \llbracket 1, z \rrbracket$ means $j = 1, 2, \dots, z$. In what follows, we will note $W_{\mathbf{n}}(n_k; n_j | n_k \pm 1; n_j \mp 1)$ the transition probabilities $W(\mathbf{n} | \mathbf{n} - \mathbf{r}^\mu)$ associated with those particular events. Likewise, $p(\mathbf{n} - \mathbf{r}^\mu, t)$ will be written as $p_{\mathbf{n}}(n_k \pm 1; n_j \mp 1, t)$. Note, in this case, that $p(\mathbf{n}, t)$ may be sometimes written as $p_{\mathbf{n}}(n_k; n_j, t)$. In this way, (12) reads

$$\begin{aligned} \frac{d\langle N_k \rangle}{dt} = & \sum_{j \neq k} \sum_{\mathbf{n}} n_k [W_{\mathbf{n}}(n_k; n_j | n_k - 1; n_j + 1) p_{\mathbf{n}}(n_k - 1; n_j + 1, t) \\ & + W_{\mathbf{n}}(n_k; n_j | n_k + 1; n_j - 1) p_{\mathbf{n}}(n_k + 1; n_j - 1, t) \\ & - W_{\mathbf{n}}(n_k + 1; n_j - 1 | n_k; n_j) p_{\mathbf{n}}(n_k; n_j, t) \\ & - W_{\mathbf{n}}(n_k - 1; n_j + 1 | n_k; n_j) p_{\mathbf{n}}(n_k; n_j, t)]. \end{aligned} \quad (14)$$

Some appropriate substitutions on the sum indices with suitable relabeling lead to

$$\begin{aligned} \frac{d\langle N_k \rangle}{dt} = & \sum_{j \neq k} \sum_{\mathbf{n}} [W_{\mathbf{n}}(n_k + 1; n_j - 1 | n_k; n_j) \\ & - W_{\mathbf{n}}(n_k - 1; n_j + 1 | n_k; n_j)] p_{\mathbf{n}}(n_k; n_j, t), \end{aligned} \quad (15)$$

where the boundary conditions

$$\begin{aligned} W_{\mathbf{n}}(-1; n_j + 1 | 0; n_j) = 0, \quad W_{\mathbf{n}}(n_k + 1; -1 | n_k; 0) = 0, \quad \text{and} \\ p_{\mathbf{n}}(n_k; n_j, t) = 0, \text{ if } n_k \text{ or } n_j < 0, \end{aligned} \quad (16)$$

have been used.

For each normal mode $j \neq k$, it is supposed that the phonons have the same probability $\gamma_{kj}(\beta, n_k)$ of being emitted while a phonon is absorbed in the mode k . We thus get

$$\begin{aligned} W_{\mathbf{n}}(n_k + 1; n_j - 1 | n_k; n_j) & \equiv W_{\mathbf{n}}(n_j - 1; n_k + 1 | n_j; n_k) = \gamma_{kj}(\beta, n_k) n_j, \\ \forall n_k, n_j & \geq 0 \text{ and } \forall j \neq k, j \in \llbracket 1, z \rrbracket. \end{aligned} \quad (17)$$

The transition probabilities computed so far imply that the graph of the master equation is connected. According to general results on master equations [30], this ensures

that a stationary solution of (11) always exists and is unique. As long as no external energy source is considered, this stationary solution is given by a Bose-Einstein distribution and must satisfy the detailed balance condition:

$$W_{\mathbf{n}}(n_k+1; n_j-1|n_k; n_j)p_{\mathbf{n}}^s(n_k; n_j) = W_{\mathbf{n}}(n_k; n_j|n_k+1; n_j-1)p_{\mathbf{n}}^s(n_k+1; n_j-1), \\ \forall n_k, n_j \geq 0 \text{ and } \forall j \neq k, j \in \llbracket 1, z \rrbracket, \quad (18)$$

with $p_{\mathbf{n}}^s(n_k; n_j) = \prod_i e^{-\beta \hbar \omega_i n_i} / Z$, where $Z = \prod_i \sum_{n_i \geq 0} e^{-\beta \hbar \omega_i n_i}$.

Using (17), (18) becomes

$$\frac{\gamma_{kj}(\beta, n_k)}{n_k+1} = \frac{\gamma_{jk}(\beta, n_j-1)}{n_j} e^{-\beta \hbar (\omega_k - \omega_j)},$$

which should depend on k and j , but not on n_k or on n_j . We finally deduce the properties

$$\gamma_{kj}(\beta, n_k) = \Lambda_{kj}(\beta)(n_k+1), \quad (19)$$

with

$$\Lambda_{jk}(\beta) = \Lambda_{kj}(\beta) e^{\beta \hbar (\omega_k - \omega_j)}, \quad \forall j \neq k, j \in \llbracket 1, z \rrbracket. \quad (20)$$

Using these equations and (17) in (15), one obtains

$$\frac{d\langle N_k \rangle}{dt} = \sum_{j \neq k} \Lambda_{kj}(\beta) \left[\langle (N_k+1)N_j \rangle - \langle N_k(N_j+1) \rangle e^{\beta \hbar (\omega_k - \omega_j)} \right], \quad (21)$$

which is exactly the third term on the RHS of Fröhlich's (1) as long as linear correlations between normal modes are negligible, i.e., $\langle N_k(N_j+1) \rangle \simeq \langle N_k \rangle \langle N_j+1 \rangle$, that is, $p(\mathbf{n}, t) \simeq \prod_i p(n_i, t)$.

3. The first term on the RHS of (1) (source term) may be worked out by considering the external source as a heat bath with infinite temperature, with which the system interacts linearly. Thus, the rate of change in the mode k due to the source is given by an equation similar to (10):

$$\frac{d\langle N_k \rangle}{dt} = \varphi_k^s(\beta_s) \left(\langle N_k \rangle + 1 - \langle N_k \rangle e^{\beta_s \hbar \omega_k} \right)$$

where $\beta_s \rightarrow 0$, so that

$$\frac{d\langle N_k \rangle}{dt} = s_k \equiv \varphi_k^s(\beta_s). \quad (22)$$

Here, $\beta_s = 1/kT_s$ with T_s the temperature of the source, and $\varphi_k^s(\beta_s) = \alpha_k^s(\beta_s) e^{-\beta_s \hbar \omega_k}$ where $\alpha_k^s(\beta_s)$ is the probability per time unit that a phonon is emitted from the mode k to the source.

Finally, by merging together all the events listed above (points 1, 2 and 3), one gets

$$\frac{d\langle N_k \rangle}{dt} = s_k + \varphi_k(\beta) \left(\langle N_k \rangle + 1 - \langle N_k \rangle e^{\beta \hbar \omega_k} \right) + \\ \sum_{j \neq k} \Lambda_{kj}(\beta) \left[\langle N_k+1 \rangle \langle N_j \rangle - \langle N_k \rangle \langle N_j+1 \rangle e^{\beta \hbar (\omega_k - \omega_j)} \right], \quad k = 1, \dots, z \quad (23)$$

which corresponds to (1) with $\varphi_k(\beta) = \alpha_k(\beta) e^{-\beta \hbar \omega_k}$ and $\Lambda_{jk}(\beta) = \Lambda_{kj}(\beta) e^{\beta \hbar (\omega_k - \omega_j)}$.

2.3 Qualitative approach to Fröhlich condensation

As mentioned in the Introduction, Fröhlich condensation state is a stationary state for the system described by (23) achieved when the rate of energy supply s_k exceeds some threshold value. In this case, the energy of the system is primarily located in the mode of lowest frequency, i.e., it can be found that $\langle N_1 \rangle \sim \langle N \rangle \equiv \sum_j \langle N_j \rangle$.

Although the existence of this coherent state has been emphasized both analytically [2, 4] and numerically [7] from (23), Fröhlich condensation may be highlighted more directly on the basis of the transition probabilities computed in the previous subsection. Fröhlich condensation is actually obtained as a consequence of the energy redistribution due to non-linear interactions between the system and the heat bath [4]. It was found in the previous subsection that the probability per time unit that one phonon is emitted from the mode j while one phonon is simultaneously absorbed in the mode k (see (17) and (19)) is

$$W_{\mathbf{n}}(n_k + 1; n_j - 1 | n_k; n_j) = \Lambda_{kj}(\beta)(n_k + 1)n_j. \quad (24)$$

Alternatively, the probability per time unit that one phonon is emitted from the mode k while one phonon is absorbed in the mode j is simply $W_{\mathbf{n}}(n_k - 1; n_j + 1 | n_k; n_j) = \Lambda_{jk}(\beta)n_k(n_j + 1)$. Using (20), one gets

$$W_{\mathbf{n}}(n_k - 1; n_j + 1 | n_k; n_j) = \Lambda_{kj}e^{\beta\hbar(\omega_k - \omega_j)}n_k(n_j + 1). \quad (25)$$

From (24) and (25), it turns out that the probability that one phonon is absorbed in the mode of lower frequency is always greater than the probability that one phonon is emitted from that mode. This is due to the pre-factor $e^{\beta\hbar(\omega_k - \omega_j)}$ which stems directly from the detailed balance condition (20). When $n_k, n_j \gg 1$, one has $(n_k + 1)n_j \sim n_k(n_j + 1)$. Hence, the ratio between the transition probabilities (24) and (25) can be approximated by $e^{\beta\hbar(\omega_k - \omega_j)}$. If $\omega_k < \omega_j$, $e^{\beta\hbar(\omega_k - \omega_j)} < 1$ so that the probability of a simultaneous absorption in the mode k and emission from the mode j will be larger. On the contrary, if $\omega_k > \omega_j$, $e^{\beta\hbar(\omega_k - \omega_j)} > 1$, the larger probability will be that of a simultaneous absorption in the mode mode j and emission from the mode k . Thus, the pre-factor $e^{\beta\hbar(\omega_k - \omega_j)}$ in (25) is directly responsible for Fröhlich condensation as it contributes to the channeling of the energy into the mode of lowest frequency regardless of the values of the parameters Λ_{kj} . Unphysical values of Λ_{kj} which do not satisfy the detailed balance condition (20) could lead to stationary states characterized by the excitation of modes of higher frequencies. The condition $n_k, n_j \gg 1$ specified above is satisfied whenever the rates of energy supply s_k are large enough. In the previous section, it was shown that the interactions between the system and the external source could be described in a similar way to linear interactions between the system and the heat bath assuming a large enough temperature. As mentioned in Section (2.1), the probability that one phonon is emitted from the mode k through linear events reads as

$$W_{\mathbf{n}}(n_k - 1 | n_k) = \alpha_k(\beta)n_k, \quad (26)$$

while the probability of absorption is given by

$$W_{\mathbf{n}}(n_k + 1 | n_k) = \alpha_k(\beta)(n_k + 1)e^{-\beta\hbar\omega_k}. \quad (27)$$

In the absence of source, the condition of large values of n_k for all k can never be fulfilled since emission will be favored over absorption whenever n_k becomes too large. On the contrary, when only the external source is considered, one has $\beta = \beta_s \rightarrow 0$ so that, according to (26) and (27) – substituting s_k for α_k –, absorption is always favored. Considering now both the presence of the heat bath and an external source, the ability of having a large number of phonons in each normal mode will depend on the ratio s_k/α_k . In that case,

assuming $s_k \gg \alpha_k$ for all k , one will get $n_k \gg 1$ after a long enough time so that nonlinear interactions will redistribute the energy into the mode of lowest frequency.

3 The Fröhlich master equation

Most theoretical studies on Fröhlich condensation are based on the numerical integration of the rate equations (23) whereas the fluctuations of the number of phonons in each normal mode remain largely unexplored. A study of the distribution of the occupation numbers is relevant to experimentally identify Fröhlich condensation on a qualitative basis. The computations done in the previous section allowed to derive not only the Fröhlich rate equations but also the corresponding master equation for the probability density function:

$$\partial_t p(\mathbf{n}, t) = \partial_t p_s(\mathbf{n}, t) + \partial_t p_\alpha(\mathbf{n}, t) + \partial_t p_\Lambda(\mathbf{n}, t). \quad (28)$$

$p_s(\mathbf{n}, t)$, $p_\alpha(\mathbf{n}, t)$ and $p_\Lambda(\mathbf{n}, t)$, with $\mathbf{n} = (n_1, n_2, \dots, n_z)$, are the probability density functions of the number of phonons in every normal mode associated with linear interactions between the system and the external source, linear interactions between the system and the heat bath, and nonlinear interactions between the system and the heat bath, respectively. Substituting (26) and (27) into (11), one gets the master equation for $p_\alpha(\mathbf{n}, t)$:

$$\partial_t p_\alpha(\mathbf{n}, t) = \sum_i \alpha_i(\beta) \{ [(n_i + 1)p_{\mathbf{n}}(n_i + 1, t) - n_i p_{\mathbf{n}}(n_i, t)] + e^{-\beta \hbar \omega_i} [n_i p_{\mathbf{n}}(n_i - 1, t) - (n_i + 1)p_{\mathbf{n}}(n_i, t)] \}. \quad (29)$$

The master equation for $p_s(\mathbf{n}, t)$ is found in a similar way by setting $\beta = \beta_s \rightarrow 0$ and substituting s_i for α_i :

$$\partial_t p_s(\mathbf{n}, t) = \sum_i s_i(\beta_s) \{ (n_i + 1)p_{\mathbf{n}}(n_i + 1, t) + n_i p_{\mathbf{n}}(n_i - 1, t) - (2n_i + 1)p_{\mathbf{n}}(n_i, t) \}. \quad (30)$$

$p_{\mathbf{n}}(m_i, t)$ is the probability of getting n_1 phonons in the mode of frequency ω_1 , n_2 phonons in the mode of frequency $\omega_2, \dots, n_z$ phonons in the mode of frequency ω_z but m_i phonons – instead of n_i phonons – in the mode of frequency ω_i . A similar notation $p_{\mathbf{n}}(m_i; m_j, t)$ is used when the exception involves two modes. In that case, $p_{\mathbf{n}}(n_i, t)$ and $p_{\mathbf{n}}(n_i; n_j, t)$ are, of course, the same as $p(\mathbf{n}, t)$. Finally, the master equation associated with nonlinear interactions is given by substituting (24) and (25) into (11) so that:

$$\begin{aligned} \partial_t p_\Lambda(\mathbf{n}, t) = & \sum_{i,j>i} \Lambda_{ij}(\beta) n_i (n_j + 1) p_{\mathbf{n}}(n_i - 1; n_j + 1, t) - \\ & \Lambda_{ij}(\beta) (n_i + 1) n_j p_{\mathbf{n}}(n_i; n_j, t) + \\ & \Lambda_{ji}(\beta) (n_i + 1) n_j p_{\mathbf{n}}(n_i + 1; n_j - 1, t) - \\ & \Lambda_{ji}(\beta) n_i (n_j + 1) p_{\mathbf{n}}(n_i; n_j, t), \end{aligned} \quad (31)$$

with $\Lambda_{ji}(\beta) = \Lambda_{ij}(\beta) e^{\beta \hbar (\omega_i - \omega_j)}$. (28) together with (29), (30) and (31) are the master equations describing Fröhlich's systems. When used to compute the average number of phonons in every normal mode, i.e., $\langle N_k \rangle = \sum_{\mathbf{n}} n_k p(\mathbf{n}, t)$, the above equations directly lead to the rate equations (23) in case linear correlations involving any pair of normal mode are negligible, i.e., $\langle N_k (N_j + 1) \rangle \simeq \langle N_k \rangle \langle N_j + 1 \rangle$, for all k and j . Alternatively, Wu and Austin [6, 7] have provided a quantum Hamiltonian from which the rate equations (23) may be derived. The Hamiltonian has the following form: $H = H_0 + H_{int}$, where H_0 is

the unperturbed Hamiltonian of the system of normal modes, the heat bath and the external source, and is given by:

$$H_0 = \sum_{i=1}^{z_s} \hbar \omega_i a_i^\dagger a_i + \sum_{k=1}^{z_b} \hbar \Omega_k b_k^\dagger b_k + \sum_{p=1}^{z_s} \hbar \Omega'_p c_p^\dagger c_p,$$

where $a_i^\dagger$, a_i are the creation and annihilation operators for the normal mode of the system with frequency ω_i , $b_k^\dagger$, b_k correspond to the operators for the normal mode of the heat bath with frequency Ω_k , and $c_p^\dagger$, c_p are the operators for the normal mode of the source with frequency Ω'_p . At the same time, H_{int} is the interaction Hamiltonian given by

$$H_{int} = \sum_{i,k} \lambda_{i,k} a_i^\dagger b_k + \sum_{i,j,k} \chi_{i,j,k} a_i a_j^\dagger b_k + \sum_{i,p} \xi_{ip} a_i^\dagger c_p + H.C. \quad (32)$$

It can be shown that a master equation similar to (28) to (31) can be obtained from the above Hamiltonian. The derivation can be managed starting from the von Neumann equation for the reduced density operator $S(t)$, which is defined as the standard density operator traced over the degrees of freedom of the heat bath and the source [31]. As is well-known, an important step to recover classical master equations is to suppose that all quantum coherences have been erased. In other words, it is assumed that the off-diagonal elements of the reduced density operator decay rapidly to zero. The diagonal elements will then be simply the classical probability density function as the one involved in (28):

$$\langle \mathbf{n} | S(t) | \mathbf{m} \rangle = p(\mathbf{n}, t) \delta_{\mathbf{n}, \mathbf{m}}, \quad \forall \mathbf{n}, \mathbf{m}, \quad (33)$$

where $|\mathbf{n}\rangle$, with $\mathbf{n} = (n_1, n_2, \dots, n_z)$, is the quantum state of the unperturbed system characterized by n_1 phonons in the mode ω_1 , n_2 phonons in the mode ω_2 , and so on. A similar definition is implied for $|\mathbf{m}\rangle$.

A few years ago, Reimers et al. performed a numerical study of the Wu-Austin Hamiltonian showing what coupling constant values, frequencies and temperatures will most likely induce Fröhlich condensation [12]. They also suggested to classify Fröhlich condensates into 3 types: weak condensates where most of the energy of the system is channeled into the mode of lowest frequency ω_1 , strong condensates characterized by extremely large amounts of energy ($> 90\%$) populating the lowest frequency mode, coherent condensates in which the energy is placed into a single quantum state. It was concluded that coherent condensates, which were first suggested to play a key role in cognitive function [32], are actually very fragile and can not be maintained at physiological conditions. Such a result clearly warrants the above assumption of decoherence and the use of a classical master equation approach to describe Fröhlich condensate. Therefore, only weak and strong types of condensate are expected with the approach introduced in the current paper.

4 Numerical computations

In this section, a numerical study of the master equation, (28) to (31), and its solutions is performed. As a result, Fröhlich condensation is investigated in statistical terms from the probability density function contrary to standard approaches where only the average numbers of phonons are examined. Master equations with many variables, are, in general, very difficult to solve analytically. However, several algorithms can still provide good numerical estimates of their solutions. For our study, we have used a popular algorithm introduced by Gillespie, which allows the generation of stochastic trajectories of a master equation

based on Monte-Carlo sampling [33]. Starting from an initial configuration of numbers of phonons in every normal mode $\mathbf{n}_0 = (n_{0,1}, n_{0,2}, \dots, n_z)$, the main steps of the procedure are as follows:

1. Compute all the transition probabilities W_i 's from the current number of phonons in every normal mode. In our case, the transition probabilities are given by (26) and (27) for the absorption or emission of one phonon involving the system and the heat bath or the external source, and (24) and (25) for the simultaneous absorption and emission of one phonon involving the system and the heat bath. The sum of all the transition probabilities $W_0 = \sum_i W_i$ should also be computed.
2. Generate two random numbers r_1 and r_2 from a uniform distribution between 0 and 1. These two numbers are used to determine the duration of the time step and which transition will occur during that time. The duration of the time step is given by $\tau = \ln(r_1^{-1}) / W_0$ whereas the transition is given by the smallest integer j satisfying $\sum_{i=1}^j W_i > r_2 W_0$.
3. Update the number of phonons according to the transition associated with the transition probability W_j , where j is the integer computed in step 2. Update the current simulation time t to $t + \tau$.
4. Return to step 1 or end the simulation.

From trajectories generated using the above procedure, histograms were eventually built to approximate the probability density functions $p(\mathbf{n}, t)$. In order to guide and validate our computations, numerical integration of the rate equations (23) was performed separately from a short Python script where the function `odeint` available within the `scipy` module was used. For the generation of stochastic trajectories, the Gillespie algorithm was implemented using a fortran code.

As a simple application of our procedure, a set of four normal modes with frequencies uniformly selected between 1 and 4 THz was considered. The coefficients $\alpha_k(\beta)$ involved in the transition probability of emission (26) or absorption (27) of one phonon through the heat bath, are directly related to the rate at which energy is dissipated from a given mode, and, as a result, are relatively easy to estimate. In the low-frequency limit ($\hbar\omega_k \ll kT$), simple analysis of the rate equations (23) shows that a characteristic decay time τ_k within the mode k is given by

$$\tau_k = \frac{1}{\beta \hbar \omega_k \alpha_k(\beta)} \quad (34)$$

with $\beta = 1/k_B T$. In all our simulations, the coefficients $\alpha_k(\beta)$ have been set in such way that $\tau_k = 2\text{ps}$ for every normal mode, with $T = 300\text{K}$. This assumption is consistent with recent experimental results reporting underdamped delocalized vibrational modes of lysozyme complexes in water at THz frequencies with damping coefficient around 0.5 – 1 THz. Giving realistic estimates of the coefficients Λ_{kj} 's accounting for the simultaneous absorption or emission of phonons, is, however, relatively challenging as nonlinear processes are hard to quantify without the full knowledge of the original Hamiltonian operator. For our simulations, different values of $\Lambda = \Lambda_{kj}$, for all $k < j$, were tested (Λ_{kj} with $k > j$ are deduced from $\Lambda_{jk} = \Lambda_{kj} e^{\beta \hbar (\omega_k - \omega_j)}$) even though it was always supposed that $\Lambda \ll \alpha_k$ since nonlinear transitions are considered less probable than linear ones. Finally, the system was always assumed to be initially in thermal equilibrium so that the number of phonons in each mode at $t = 0$ is distributed according to Planck statistics:

$$p(n_k, t = 0) = \frac{1}{Z_k} e^{-\beta \hbar \omega_k n_k}, \quad \text{with } Z_k = \frac{1}{1 - e^{-\beta \hbar \omega_k}}. \quad (35)$$

Representative plots of the evolution of the average numbers of phonons in each normal mode obtained by directly integrating the rate equations, are depicted on Fig. 1 for two values of the external energy rate s , namely, $s_k = 1 \text{ ps}^{-1}$ and $s_k = 50 \text{ ps}^{-1}$. Other parameter values were kept the same (in particular, Λ was set to 0.5 ps^{-1}). Plots in Fig. 1 give a clear overview of how Fröhlich condensation takes place. At low supply rate, the system evolves to a state close to thermal equilibrium. On the contrary, a high value of s will drive the system towards a state where most of the energy has been channeled into the lowest-frequency mode ω_1 . Interestingly, the set of modes always reaches a stationary state at long times t for any value of the parameters used. In Fig. 2, we have plotted the average

Fig. 1 Time evolution of the average energies $\hbar\omega_k \langle N_k(t) \rangle$ of the four normal modes considered in our study as obtained by numerically integrating the rate equations (23). Top: the rate of energy supply is $s_k = 1 \text{ ps}^{-1}$ for all k . Bottom: $s_k = 50 \text{ ps}^{-1}$. In both cases, the normal frequencies have been set to $\omega_k = k \text{ THz}$ with $k = 1, 2, 3, 4$. The values of the coupling constants α_k are given by formula (34) so that $\tau_k = 2 \text{ ps}$ for all k . The values of Λ_{kj} when $k > j$ were all set equal to $\Lambda = 0.5 \text{ ps}^{-1}$ (Λ_{kj} with $k > j$ are deduced from $\Lambda_{jk} = \Lambda_{kj} e^{\beta \hbar(\omega_k - \omega_j)}$). Initially, the system is supposed to be in thermal equilibrium, so that $\langle N_k(t=0) \rangle$ is given by the Planck formula

Fig. 2 In blue: averaged energy density in the lowest-frequency mode $\rho_1 = \hbar\omega\langle N_1\rangle/\sum \hbar\omega_k\langle N_k\rangle$, in the stationary limit, as a function of the supply rate $s_k = s$. In red: corresponding energies $\hbar\omega_1\langle N_1\rangle$, in kT units, as a function of the supply rate $s_k = s$. Other parameter values are the same as the ones used to generate Fig. 1

energy density in the lowest-frequency mode $\rho_1 = \hbar\omega\langle N_1\rangle/\sum \hbar\omega_k\langle N_k\rangle$ as a function of the supply rate s (blue curve). The corresponding energy values $\hbar\omega_1\langle N_1\rangle$, in kT units, are also provided (red curve). All average values were computed in the stationary limit ($t = 40$ ps). As expected, it is found that ρ_1 gets closer to 1 as s increases. Interestingly, fairly reasonable values of the energy in the lowest-frequency mode ($\sim 10kT$) already provide significant Fröhlich condensate $\rho_1 \simeq 0.6$. Finally, it is shown, in Fig. 3, how the average energy density ρ_1 varies as a function of $\Lambda = \Lambda_{kj}$ for different values of s . We recall that Λ_{kj} with $k > j$ are deduced from $\Lambda_{jk} = \Lambda_{kj}e^{\beta\hbar(\omega_k - \omega_j)}$. Clearly, it is found that no condensation occurs

Fig. 3 Average energy density in the lowest-frequency mode $\rho_1 = \hbar\omega\langle N_1\rangle/\sum \hbar\omega_k\langle N_k\rangle$, in the stationary limit, as a function of the coefficient Λ involved in nonlinear interactions between modes. The results are obtained from integration of the rate equations (23) and are given for different values of the supply rate s . Other parameter values are the same as those used for previous plots

when $\Lambda < 0.3 \text{ ps}^{-1}$ as the energy density in the lowest-frequency mode becomes ≤ 0.5 . At large enough values of Λ , ρ_1 reaches a plateau whose corresponding value increases when increasing the supply rate s . For our simulations, we always picked $\Lambda = 0.5 \text{ ps}^{-1}$ which ensures that Fröhlich condensation is always possible. More detailed investigation of the Hamiltonian operators of protein systems is, however, needed to estimate realistic values of Λ [34].

As mentioned above, the Gillespie algorithm was used to generate stochastic trajectories of the Fröhlich master equations (28) to (31). For each set of parameters tested, 5000 trajectories were generated to build the histograms. In order to validate our study, the average numbers of phonons were compared to the values calculated when directly integrating the rate equations. In Fig. 4, average energy densities ρ_1 , computed in the stationary limit ($t = 40 \text{ ps}$) using both methods, were superimposed for different values of s . From the figure, it is seen that values of ρ_1 are in excellent agreement. Good correspondence is also obtained when comparing directly the average numbers of phonons in other modes. In the previous section, it was emphasized that the rate equations can be deduced from the master equations (28) to (31) only if linear correlations between the normal modes are negligible: $\langle N_k(N_j + 1) \rangle \simeq \langle N_k \rangle \langle N_j + 1 \rangle$ for all k and j . This is clearly the case in our study. Absence of linear correlation between the modes is also verified, in a straightforward way, by calculating the Pearson product-moment correlation coefficients c_{N_k, N_j} given by:

$$c_{N_k, N_j} = \frac{(\langle N_k - \langle N_k \rangle \rangle (\langle N_j - \langle N_j \rangle \rangle))}{\sigma_{N_k} \sigma_{N_j}},$$

where σ_{N_k} and σ_{N_j} are the standard deviations associated with the number of phonons in modes k and j , respectively. Simple estimates of the c_{N_k, N_j} 's from the data generated with the Gillespie method show that $c_{N_k, N_j} \simeq 0$ or is slightly negative when $j \neq k$ for the different values of s tested. Although normal modes do not appear to be linearly correlated,

Fig. 4 Averaged energy density in the lowest-frequency mode $\rho_1 = \hbar\omega\langle N_1 \rangle / \sum \hbar\omega_k \langle N_k \rangle$, in the stationary limit, as a function of the supply rate s . The blue curve corresponds to the results obtained by directly integrating the rate equations (23). The dots are the corresponding values of ρ_1 computed from stochastic trajectories of the master equations (28) to (31) generated with the Gillespie algorithm. For each value, 5000 trajectories were generated

nonlinear correlations may still exist so that the total joint probability density $p(\mathbf{n}, t)$ would not simply be the product of single-variable probability densities $p(n_k, t)$. Simple comparison of histograms accounting for $p(n_k, n_j, t)$ and $p(n_k, t)p(n_j, t)$ with $j \neq k$ indicate, however, that both probabilities are similar, which suggests that the numbers of phonons in every mode are indeed independent variables (results not shown here).

Fröhlich condensation was investigated in probabilistic terms by computing the distribution of the energy density in the lowest-frequency mode

$$\rho_1 = \hbar\omega_1 n_1 / \sum_{k \geq 1} \hbar\omega_k n_k,$$

as a function of the supply rate s (see Fig. 5). Figure 5 gives a clear overview of Fröhlich condensation even when the supply rate is fairly low ($s \simeq 20 \text{ ps}^{-1}$). At $s = 0$, a peak of probability is observed around $\rho_1 = 0$ implying a very low contribution of the lowest-frequency mode on the total energy. As s increases, the peak is shifted to higher values of ρ_1 (~ 0.6 when $s = 30 \text{ ps}^{-1}$). In addition, the peak becomes wider, which indicates that fluctuations increase significantly when the condensation phenomenon occurs. This result is consistent with Reimers et al.'s work suggesting that the system becomes more noisy when Fröhlich condensation occurs [12]. Finally, we have plotted, in Fig. 6, the distribution of the number of phonons n_k in the first two modes of lowest frequency for different values of s . When s is very low, the distributions are close to the Planck distributions (35). Similarly to the distribution of ρ_1 , increasing s will make the average number of phonons in the first mode larger while the variance is also increased. The distribution of n_2 will remain close to the Planck distribution regardless of the value of s . Interestingly, plots in Fig. 6 show an analogy with the change in the statistical distribution of photon occupation numbers below and above the laser transition. The photon statistics below the laser transition is a thermal equilibrium one, peaked at zero, whereas, above the transition, the photon statistics gives a non-zero most probable value of the number of photons in the lasing mode with a well-known Poisson distribution [35]. Something similar occurs for the condensation transition explored here,

Fig. 5 Distribution of the energy density in the lowest-frequency mode $\rho_1 = \hbar\omega_1 n_1 / \sum \hbar\omega_k n_k$, in the stationary limit, as a function of the supply rate s . The probabilities are normalized in such a way that the sum of the probability densities for a given s is equal to 1

Fig. 6 Distribution of the number of phonons n_k as a function of the supply rate s . The probabilities are normalized in such a way that the sum of the probability densities for a given s is equal to 1. Top: fundamental mode ($k = 1$). Bottom: second lowest-frequency mode ($k = 2$)

which reveals that the Fröhlich condensation transition displays a phenomenology typical of non-equilibrium phase transitions in open systems.

5 Concluding remarks

In the present paper, Fröhlich condensation has been investigated within a semi-classical framework. The classical master equation describing this coherent behavior has been emphasized. The quantum approaches hitherto suggested are based on the microscopic Hamiltonian originally investigated by Wu and Austin or on slightly modified versions of it. Here, we have suggested a different approach to highlight what are the assumptions required to yield Fröhlich's effect. Fröhlich's phenomenon can be relevant in very different physical contexts, and, in particular, to biologically relevant systems undergoing self-organization at

different scales (from single macromolecules up to collections of cells). Thus, the approach suggested in the present paper, on the one hand, has the merit of a critical reviewing of the physics underlying Fröhlich condensation and, on the other hand, has the advantage of providing the time evolution of the probability density function, which allows the computation of higher moments of the number of phonons as well as their average quantities. From our study, analysis of the distribution of energy density in the lowest-frequency mode reveals a clear signature of a Fröhlich condensate which can be identified even at low rates of energy supply. Moreover, a significant change in the distribution of the number of phonons associated with the condensation transition has been observed. In addition, from the distributions of the number of phonons in the lowest-frequency mode, qualitative similarities with the laser transition have been reported, clearly ranking Fröhlich's effect among non-equilibrium phase transitions in open systems.

Appendix: Detailed balance and *Birth and Death* process

We consider the homogeneous Markov process $N_k(t)$ of Section 2.1. According to the *birth and death* nature of $N_k(t)$, the stationary solution $p^s(n_k)$ of (2) is given $\forall n_k \geq 0$ by

$$0 = J(n_k) - J(n_k - 1), \quad (36)$$

where $J(n_k) = W(n_k|n_k + 1)p^s(n_k + 1) - W(n_k + 1|n_k)p^s(n_k)$. We now sum (36) so

$$0 = \sum_{n_i=0}^{n_k} [J(n_i) - J(n_i - 1)] = J(n_k) - J(-1), \quad (37)$$

According to conditions (5), $J(-1) = 0$, so that the detailed balance condition is obtained:

$$0 = J(n_k) = W(n_k|n_k + 1)p^s(n_k + 1) - W(n_k + 1|n_k)p^s(n_k), \quad \forall n_k \geq 0. \quad (38)$$

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