Condensation kinetics for bosonic excitons interacting with a thermal phonon bath

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We develop a theory of the kinetics of the Bose-Einstein condensation of bosonic excitons interacting with a thermal bath of acoustic phonons. We emphasize several delicate aspects of the condensation kinetics within the framework of rate equations. We give detailed proofs about the existence and uniqueness of the solution with a condensate and illustrate details within exactly or almost exactly solvable models. In particular, we predict an exciton condensation time in Cu_2O which is shorter than the lifetime of paraexcitons.

I. INTRODUCTION

The Bose-Einstein condensation (BEC) is a fascinating subject enjoying a revival due to the experimental observations in atomic traps[1,2] and experimental evidences for excitons in semiconductors.[3–5] We focus our attention in this paper on the treatment of the condensation of excitons taken as bosons interacting with thermal acoustic phonons. In order to be able to observe the BEC of excitons, e.g., in Cu_2O, the condensation time has to be shorter than the recombination lifetime of paraexcitons in this material. Earlier theoretical simulations in the framework of rate equations[6,7] did not result in a condensation. Here we describe theoretical simulations and calculations of the BEC giving rise to condensation times which are for the example of Cu_2O shorter than the lifetime of the paraexcitons.

In order to develop a kinetic theory, one has to analyze carefully the general mechanism of BEC in real time within the framework of rate equations for the average particle occupation numbers in order to avoid possible mistakes or deadlocks in the description of this delicate process. We prove some theorems about the occurrence of condensation in time by discussing the situation for a finite volume, as well as the proper thermodynamic limit. These enable us to avoid shortcomings of previous numerical simulations. In Sec. II we shortly review the equilibrium phase transition theory of the BEC, particularly the symmetry breaking concept of Bogoliubov. We show in Sec. III that a proper treatment has to separate the macroscopical degrees of freedom before any numerical discretization and has to introduce either finite volume effects in order to preserve spontaneous transition rates into the condensate, or a small, but finite initial condensate population. The necessity of separating the condensate was realized earlier in Refs. 8,9. We illustrate our statements in Secs. IV and V within exactly solvable models of increasing complexity.

We prove also the phenomenon of ''critical slowing down'' of the relaxation by approaching the critical point from the noncondensation side. It is shown that under condensation conditions the condensate density approaches its asymptotic equilibrium value very slowly (not exponentially), but from above. Thus the condensate population overshoots at early times and later relaxes afterwards very slowly. This phenomenon allows to observe a condensate at times much shorter than those given by the Liapunov exponent. This overshoot is closely related to a ''threshold rule,'' which holds under very general conditions.

For the interaction of excitons with acoustic phonons treated in Sec. VI there is a supplementary pathology related to the fact, that the golden rule gives rise to a transition rate which is a distribution, not a function. Thus a broadening of the energy conservation through life-time effects has to be taken into account. The broadening has to be introduced without destroying the detailed balance property. We briefly treat the temporal evolution of the phase of the condensate.

Extended numerical calculations are performed for an exciton BEC by interaction with acoustic phonons for the example of Cu_2O. The reader interested only in the phenomenological aspects may skip Secs. IV and V as well as the mathematical details given in the Appendixes.

II. BEC AS AN EQUILIBRIUM PHASE TRANSITION

Although already textbook matter, for sake of completeness and for fixing the terminology and notations, we sketch here the equilibrium theory of the condensation of a free Bose gas in the spirit of Bogoliubov's quasiaverages. We consider the system in a periodic box of volume V within the second quantization. The energy of a boson is

$$e_{\vec{k}}=\frac{\hbar^2\vec{k}^2}{2m}, \tag{2.1}$$

the wave vector $\vec{k}$ takes discrete values. The grand-canonical statistical sum is

$$Z=\mathrm{Tr}\{e^{-\beta(H-\mu N)}\}, \tag{2.2}$$

with

$$H-\mu N=\sum_{\vec{k}}(e_{\vec{k}}-\mu)a_{\vec{k}}^{+}a_{\vec{k}}+\lambda^{*}\sqrt{V}a_0+\lambda\sqrt{V}a_0^{+}. \tag{2.3}$$

Here we added to the free-boson Hamiltonian supplementary terms which break the particle conservation law. After performing the thermodynamic limit, one takes the limit of vanishing symmetry breaking term.

By a shift of the zero mode creation and annihilation operators, which conserves the commutation relations

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$$A_0 = a_0 - \frac{\lambda\sqrt{V}}{\mu} \tag{2.4}$$

we can enforce again the quadratic form

$$H - \mu N = \sum_{\vec{k}\neq 0} (e_{\vec{k}} - \mu) a_{\vec{k}}^{+} a_{\vec{k}} - \mu A_0^{+} A_0 + \frac{|\lambda|^2 V}{\mu}. \tag{2.5}$$

The free energy is then

$$F = \frac{1}{\beta V} \sum_{\vec{k}} \ln\{1 - e^{-\beta(e_{\vec{k}} - \mu)}\} + \frac{|\lambda|^2}{\mu}, \tag{2.6}$$

and the average particle density is given by

$$\frac{\langle N \rangle}{V} = \frac{1}{V} \sum_{\vec{k}} \frac{1}{e^{\beta(e_{\vec{k}} - \mu)} - 1} + \frac{|\lambda|^2}{\mu^2}. \tag{2.7}$$

Now the thermodynamic limit has to be taken carefully. As long as one has a symmetry breaking term ($\lambda \neq 0$), the chemical potential has to be strictly negative ($\mu < 0$) in order to ensure the finiteness of the extra term. Therefore, each term in the sum is well-behaved and the limit of the three-dimensional Riemann sum can be taken safely according to the standard recipe

$$\frac{1}{V} \sum_{\vec{k}'} \rightarrow \int \frac{d^3k}{(2\pi)^3}. \tag{2.8}$$

For the total density ($n_{\mathrm{tot}} \equiv \lim_{V\to\infty} \langle N \rangle / V$) one gets

$$n_{\mathrm{tot}} = \frac{|\lambda|^2}{\mu^2} + \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(e_{\vec{k}} - \mu)} - 1}. \tag{2.9}$$

Above the critical density at a given temperature, the chemical potential will vanish if the symmetry breaking term vanishes ($\lambda \to 0$).

$$\mu \to \frac{|\lambda|}{\sqrt{n_0}} \quad (|\lambda| \to 0), \tag{2.10}$$

where n_0 is the condensate density. Importantly, the order parameter also survives in this limit

$$\lim_{V\to\infty} \frac{\langle a_0 \rangle}{\sqrt{V}} = \sqrt{n_0} e^{\imath\phi}, \tag{2.11}$$

where ϕ is the surviving phase of the symmetry breaking ($\lambda = |\lambda| e^{\imath\phi}$).

On the other hand, if one takes first the limit $\lambda \to 0$ and afterwards performs the thermodynamic limit, special care has to be devoted to the treatment of the sum over $\vec{k}$. The Riemann limit cannot be performed without separating the term at $\vec{k} = 0$, which above the critical density goes to a finite value since the chemical potential behaves as $\mu \sim -1/n_0\beta V$. The rest tends then to the Riemann sum with $\mu \equiv 0$. Recall, that the appearance of the condensate is the consequence of the fact, that

$$\int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(e_{\vec{k}} - \mu)} - 1} \leqslant \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta e_{\vec{k}}} - 1} = \frac{1}{\sqrt{2}\pi^2} \Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right) \left(\frac{m}{\beta\hbar^2}\right)^{3/2} \quad (\mu \leqslant 0) \tag{2.12}$$

and thus the Bose distribution cannot accommodate the whole particle density above a critical density. The only difference to the previous treatment is, that no nonvanishing order parameter appears. The mathematical clue of the BEC is just the correct treatment of the Riemann limit.

III. RATE EQUATION FOR BOSONS COUPLED TO A THERMAL BATH

We will show in the following that within a simple rate equation approach most of the abovementioned results are obtained also in the real time evolution. We consider here only the average occupation numbers $\langle a_{\vec{k}}^{+} a_{\vec{k}} \rangle$ for arbitrary $\vec{k}$. Later within a microscopical phonon model, we discuss also the order parameter $\langle a_0(t) \rangle$.

The Markovian rate equations describing the transitions due to the interaction with a thermostat at the inverse temperature β read

$$\frac{\partial}{\partial t} \langle a_{\vec{k}}^{+} a_{\vec{k}} \rangle = -\frac{1}{V} \sum_{\vec{k}'} \{ W_{\vec{k}\vec{k}'} \langle a_{\vec{k}}^{+} a_{\vec{k}} \rangle (1 + \langle a_{\vec{k}'}^{+} a_{\vec{k}'} \rangle) - (\vec{k} \rightleftharpoons \vec{k}') \}. \tag{3.1}$$

The transition rates $W_{\vec{k}\vec{k}'}$ are supposed to be well-defined functions satisfying the detailed balance relation

$$W_{\vec{k}\vec{k}'} = W_{\vec{k}'\vec{k}} e^{\beta(e_{\vec{k}} - e_{\vec{k}'})}. \tag{3.2}$$

These equations conserve automatically the total average particle number

$$\sum_{\vec{k}} \langle a_{\vec{k}}^{+} a_{\vec{k}} \rangle$$

and the positivity of the average occupation numbers. They have as stationary solution (fixed point), the Bose distribution (with the chemical potential $\mu < 0$ for $V < \infty$)

$$f_{\vec{k}} = f^0(e_{\vec{k}}, \mu) \equiv \frac{1}{e^{\beta(e_{\vec{k}} - \mu)} - 1}, \tag{3.3}$$

which is stable and under certain connectivity conditions for $W_{\vec{k}\vec{k}'}$ it is also unique. The proof of these statements is left for the Appendix A.

From the above statements it already follows, that BEC occurs in real time as $\lim_{V\to\infty} \lim_{t\to\infty}$, taken in this order, but we are interested in what follows in the more physical inverse order of the limits. Let us define the densities of the noncondensed particles

$$f_{\vec{k}}(t) \equiv \langle a_{\vec{k}}(t)^{+} a_{\vec{k}}(t) \rangle \quad (\vec{k} \neq 0), \tag{3.4}$$

and the condensate density

$$n_0(t)\equiv\frac{1}{V}\langle a_0(t)^+a_0(t)\rangle=\frac{1}{V}f_0(t). \tag{3.5}$$

One has to be careful in separating from the sum in the rate equation the terms containing the condensate n_0:

$$\frac{\partial}{\partial t}f_{\vec{k}}=-\frac{1}{V}\sum_{\vec{k}\,'\neq 0}\{W_{\vec{k}\vec{k}\,'}f_{\vec{k}}(1+f_{\vec{k}\,'})-(\vec{k}\rightleftharpoons\vec{k}\,')\}$$
$$-\left[W_{\vec{k}0}f_{\vec{k}}\left(n_0+\frac{1}{V}\right)-W_{0\vec{k}}(1+f_{\vec{k}})n_0\right], \tag{3.6}$$

$$\frac{\partial}{\partial t}n_0=\frac{1}{V}\sum_{\vec{k}\,'\neq 0}\left[W_{\vec{k}\,'0}f_{\vec{k}\,'}\left(n_0+\frac{1}{V}\right)-W_{0\vec{k}\,'}(1+f_{\vec{k}\,'})n_0\right]. \tag{3.7}$$

Only after this subtraction, all the $\vec{k}$- and $\vec{k}\,'$-dependent functions are supposed to be continuous, so that in the $V\rightarrow\infty$ limit the sums are legitimately interpreted as Riemann integrals and we get

$$\frac{\partial}{\partial t}f_{\vec{k}}(t)=-\int\frac{d^3k'}{(2\pi)^3}\{W_{\vec{k}\vec{k}\,'}f_{\vec{k}}(t)[1+f_{\vec{k}\,'}(t)]-(\vec{k}\rightleftharpoons\vec{k}\,')\}$$
$$-\{W_{\vec{k}0}f_{\vec{k}}(t)-W_{0\vec{k}}[1+f_{\vec{k}}(t)]\}n_0(t), \tag{3.8}$$

$$\frac{\partial}{\partial t}n_0(t)=\int\frac{d^3k'}{(2\pi)^3}\{W_{\vec{k}\,'0}f_{\vec{k}\,'}(t)-W_{0\vec{k}\,'}[1+f_{\vec{k}\,'}(t)]\}n_0(t). \tag{3.9}$$

We consider that the transition rates are bounded and continuous overall, including $\vec{k}=0$ (which holds in our models). We take also bounded and continuous initial conditions $f_{\vec{k}}(0)$. Equations (3.8), (3.9) obviously conserve the total average particle density

$$n_{\rm tot}=n_0(t)+\int\frac{d^3k}{(2\pi)^3}f_{\vec{k}}(t) \tag{3.10}$$

the positivity of $f_{\vec{k}}(t)$ and $n_0(t)$ and have two attractive fixed points (see Appendix A): the ''normal'' one with $f_{\vec{k}}=f^0(e_{\vec{k}},\mu)(\mu<0)$, $n_0(\infty)=0$; and the ''condensed'' one with $f_{\vec{k}}=f^0(e_{\vec{k}},0)$, $n_0(\infty)\neq 0$, where $n_0(\infty)$ is determined by the particle conservation law.

This is strongly reminiscent of the analysis made in the equilibrium theory of the BEC: If the density is subcritical, a negative chemical potential can adapt the Bose distribution to the required value. If the density is supercritical, a condensate is needed to make up for the difference.

However, in the present kinetic approach we encounter a paradox: Because Eq. (3.9) for $n_0(t)$ is homogenous, one cannot reach the equilibrium solution described above for $n_0(0)=0$ and $n_{\rm tot}>n_{\rm cr}$, because $n_0(t)$ remains zero for any t. On the other hand (see Appendix A), the H-theorem analysis seems to leave no other option.

The solution to this conflicting situation relies on abandoning the hypothesis that the functions remain continuous for $t\rightarrow\infty$. We will argue that, for supercritical conditions even in the absence of an initial, arbitrarily small condensate, a precursor of a δ distribution grows around $\vec{k}=0$ and becomes a true δ in the limit $t\rightarrow\infty$. We will illustrate this point with the example of the instant thermalization model in Sec. V, where explicit proofs can be given. This way a condensate is formed, if the density and temperature conditions are appropriate. If this condensate is treated separately from the beginning, the rest of the particle distribution function remains well behaved.

It is obvious that this growth of the condensate out of a continuous distribution cannot be observed numerically by the discretization of the integrals in the rate equation. The stationary solutions of Eqs. (3.8),(3.9) obtained without an initial condensate, i.e., with $n_0(0)=0$, can accommodate all particles in a discretized spectrum by bringing μ sufficiently close to the lowest energy level. Therefore, by discretizing the $\vec{k}$ integral the phenomenon is lost, because it is essentially connected to the continuous nature of the spectrum. Thus the separation of the condensate is an essential ingredient of any numerical simulation. This is also intuitively clear, because any grid becomes eventually too coarse for a precursor of a δ distribution.

Equations (3.8), (3.9) for vanishing temperature coincide with the rate equations of Ref. 8 except for the extra source terms included there. The proper separation of the condensate also has been taken into account in the framework of the rate equations with boson-boson collisions in Ref. 9.

In the derivation of Eqs. (3.8), (3.9) we used the fact that

$$\lim_{V\rightarrow\infty}\frac{1}{V}(1+\langle a_0^+a_0\rangle)=\lim_{V\rightarrow\infty}\frac{1}{V}\langle a_0^+a_0\rangle\equiv n_0.$$

We shall see later that one may conceive a mixed treatment, in which the summations are already transformed in integrals but one still keeps the small $1/V$ correction to the above relation describing spontaneous transitions into the condensed state. Then, the most important finite volume effect is already taken into account and Bose condensation occurs even in the absence of a condensation seed. The situation is analogous to that already known in the kinetic theory of semiconductor lasers,[10] where the rate of spontaneous emission into the laser mode which starts the laser action would be lost in the infinite volume limit.

In Appendix B we show that the asymptotic large-time behavior is exponential for subcritical densities and becomes nonexponential at criticality (''critical slowing down''). This slower nonexponential behavior persists also above the critical density. However, this does not imply that condensation occurs at this pace. On the contrary, we will show in Sec. VI, that an overshooting occurs in an early stage and only the return to the stationary value of the condensate is very slow. This overshooting is related to the above mentioned ''threshold rule.'' Again this is similar to a phenomenon known from the kinetics of semiconductor as relaxation oscillations[11] which are triggered by switching on the laser rapidly.

IV. A SOLVABLE BOSON MODEL

All the essential features of the BEC are contained also in an exactly solvable boson model consisting of a nondegenerate ground-state (particle energy ϵ_0) and an excited state (particle energy ϵ_1). The lowest state is taken nondegenerate, while the higher state is taken to be macroscopically degenerate (i.e., the degeneracy is Vn_1, proportional to the volume). Here the real time condensation within the rate equation approach can be studied analytically.

The rate equations for a finite volume are

$$\frac{\partial}{\partial t}f_1=-\frac{w}{V}[f_1(1+f_0)e^{-\beta\epsilon_0}-f_0(1+f_1)e^{-\beta\epsilon_1}], \quad (4.1)$$

$$\frac{\partial}{\partial t}f_0=-n_1 w[f_0(1+f_1)e^{-\beta\epsilon_1}-f_1(1+f_0)e^{-\beta\epsilon_0}]. \quad (4.2)$$

They conserve the average particle density

$$\frac{\partial}{\partial t}\left(n_1 f_1+\frac{1}{V}f_0\right)=0. \quad (4.3)$$

In the infinite volume limit, with a finite initial condensate $f_0(0)=Vn_0(0)$ one finds the usual BEC with the critical temperature defined by

$$\frac{n_1}{e^{\beta_c(\epsilon_1-\epsilon_0)}-1}=n_{\text{tot}}. \quad (4.4)$$

The rate equations are exactly solvable for any set of parameters. For sake of simplicity, we take $\epsilon_0=0$, $w=1$ and denote $e^{-\beta(\epsilon_1-\epsilon_0)}\equiv\xi<1$.

We eliminate f_1 in favor of f_0 through the conservation equation and get a closed equation for f_0:

$$\frac{\partial}{\partial t}f_0=-\frac{1-\xi}{V}f_0^2+f_0\left(n_{\text{tot}}(1-\xi)-n_1\xi-\frac{1}{V}\right)+n_{\text{tot}}. \quad (4.5)$$

The discriminant of the polynomial on the right side is

$$\Delta\equiv 4ac-b^2=-4\frac{1-\xi}{V}-\left(n_{\text{tot}}(1-\xi)-n_1\xi-\frac{1}{V}\right)^2<0, \quad (4.6)$$

with

$$b=n_{\text{tot}}(1-\xi)-n_1\xi-\frac{1}{V}. \quad (4.7)$$

With the integral

$$\int dx\frac{1}{ax^2+bx+c}=\frac{-2}{\sqrt{-\Delta}}\tanh^{-1}\left(\frac{2ax+b}{\sqrt{-\Delta}}\right) \quad (4.8)$$

we find

$$\frac{1}{V}f_0(\tau)=\frac{1}{2(1-\xi)}\left\{b-\sqrt{-\Delta}\tanh\left[-\frac{\sqrt{-\Delta}}{2}t+\tanh^{-1}\left(\frac{b-\frac{2(1-\xi)}{V}f_0(0)}{\sqrt{-\Delta}}\right)\right]\right\}. \quad (4.9)$$

Simplifying the notations by

$$\tau=\frac{\sqrt{-\Delta}}{2}t, \quad \mathcal{V}\equiv\frac{\sqrt{-\Delta}}{2(1-\xi)}V, \quad \alpha\equiv\frac{b}{\sqrt{-\Delta}}=\frac{b}{\sqrt{b^2+\frac{2}{\mathcal{V}}}}, \quad (4.10)$$

one gets

$$\frac{1}{\mathcal{V}}f_0(\tau)=\alpha-\tanh\left[-\tau+\tanh^{-1}\left(\alpha-\frac{1}{\mathcal{V}}f_0(0)\right)\right] \quad (4.11)$$

with $|\alpha|<1$.

Because $\lim_{\mathcal{V}\to\infty}|\alpha|=1$, one gets

$$\lim_{\mathcal{V}\to\infty}\lim_{\tau\to\infty}\frac{1}{\mathcal{V}}f_0(\tau)=\begin{cases}0 & \text{for} \quad \alpha<0,\\ 2 & \text{for} \quad \alpha>0\end{cases} \quad (4.12)$$

for an arbitrary initial condition $f_0(0)$. Thus the BEC occurs below the critical temperature. The opposite order of the limits yields the same result, however the condensation occurs only if $\lim_{\mathcal{V}\to\infty}(1/\mathcal{V})f_0(0)\neq 0$. In this case it results directly from the conservation of the particle density, that no evolution occurs at all $[f_1(\tau)=f_1(0)]$.

The critical slowing down has a very simple form in this model. At the critical density $\Delta\to 0$ and therefore the time scaling factor diverges.

V. INSTANT THERMALIZATION MODEL

For the classical Boltzmann equation a special model (called ''instant thermalization'') with the transition rates given in terms of a scattering time τ

$$W_{\vec{k}\vec{k}'}\equiv\frac{1}{\tau Z}e^{-\beta e_{\vec{k}'}} \quad \text{with} \quad Z\equiv\int\frac{d^3k}{(2\pi)^3}e^{-\beta e_{\vec{k}}} \quad (5.1)$$

is known to be exactly solvable. Though the exact solvability for the boson rate equation is lost due to the nonlinearity, we consider this more realistic and more complex model because here we can still study the solution of the rate equations without initial condensate. In the thermodynamic limit we have the rate equations with time units τZ

$$\frac{\partial}{\partial t}f_{\vec{k}}(t)=-\int\frac{d^3k'}{(2\pi)^3}\{f_{\vec{k}}(t)[1+f_{\vec{k}'}(t)]e^{-\beta e_{\vec{k}'}}-(\vec{k}\rightleftharpoons\vec{k}')\}-\{f_{\vec{k}}(t)-e^{-\beta e_{\vec{k}}}[1+f_{\vec{k}}(t)]\}n_0(t), \quad (5.2)$$

$$\frac{\partial}{\partial t}n_0(t)=\int\frac{d^3k'}{(2\pi)^3}\{f_{\vec{k}'}(t)-e^{-\beta e_{\vec{k}'}}[1+f_{\vec{k}'}(t)]\}n_0(t). \quad (5.3)$$

For this model we can discuss the properties of the solution of the rate equation for a supercritical density even without an initial condensate ($n_0\equiv 0$), which cannot be tackled by discretization.

The rate equation in this case reduces to

$$\frac{\partial}{\partial t} f_{\vec{k}} = -f_{\vec{k}} \int \frac{d^3k'}{(2\pi)^3}(1+f_{\vec{k}'})e^{-\beta e_{\vec{k}'}} + (1+f_{\vec{k}})e^{-\beta e_{\vec{k}}} \int \frac{d^3k'}{(2\pi)^3} f_{\vec{k}'} . \tag{5.4}$$

We introduce moments of the distributions $f_{\vec{k}}$ and $1+f_{\vec{k}}$ by

$$K_n(t) = \int \frac{d^3k}{(2\pi)^3} f_{\vec{k}} e^{-n\beta e_{\vec{k}}}, \quad n \geqslant 0, \tag{5.5}$$

$$M_n(t) = \int \frac{d^3k}{(2\pi)^3}(1+f_{\vec{k}}) e^{-n\beta e_{\vec{k}}}, \quad n \geqslant 1, \tag{5.6}$$

$$L_n(t) = M_n - K_n = \int \frac{d^3k}{(2\pi)^3} e^{-n\beta e_{\vec{k}}}, \quad n \geqslant 1. \tag{5.7}$$

For $M_n(t)$, the $n=0$ moment was not considered, because its existence depends on the existence of an upper energetic cutoff, an assumption which is not necessary here. These moments are positive and decreasing with n.

With these notations the rate equation becomes

$$\frac{\partial}{\partial t} f_{\vec{k}} = -f_{\vec{k}} M_1 + (1+f_{\vec{k}}) e^{-\beta e_{\vec{k}}} K_0 . \tag{5.8}$$

K_0 is in fact the particle density and is independent of time. M_1 is a function of time, whose knowledge would allow the complete solution of the problem. Unfortunately, one has no closed equation for M_1 but a hierarchy of equations involving higher and higher moments.

$$\frac{\partial}{\partial t} M_n = \frac{\partial}{\partial t} K_n = -K_n M_1 + K_0 M_{n+1} . \tag{5.9}$$

One may attempt a numerical solution of this set of equations, but presently we will be concerned only with the stationary solution. The $t \to \infty$ limits of the moments obey the recurrence relation

$$K_{n+1} = \alpha K_n - L_{n+1}, \tag{5.10}$$

where $\alpha = M_1/K_0$. The solution is

$$K_n = \alpha^n \left[K_0 - \sum_{p=1}^{n} \frac{L_p}{\alpha^p} \right] = \alpha^n \left[K_0 - \int \frac{d^3k}{(2\pi)^3} \frac{1}{\alpha e^{\beta e_{\vec{k}}} - 1} \right] + \int \frac{d^3k}{(2\pi)^3} \frac{e^{-n\beta e_{\vec{k}}}}{\alpha e^{\beta e_{\vec{k}}} - 1}. \tag{5.11}$$

By examining the rate equation for $\vec{k}=0$, one has

$$\alpha = \frac{M_1}{K_0} = \frac{1+f_0(\infty)}{f_0(\infty)} \geqslant 1. \tag{5.12}$$

Bearing in mind that K_n is positive and decreasing with n, one is left with only two possibilities.

(a) If $\alpha > 1$ [i.e., $f_0(\infty)$ is finite], the only case in which the moments Eq. (5.11) do not grow indefinitely is

$$K_0 = \int \frac{d^3k}{(2\pi)^3} \frac{1}{\alpha e^{\beta e_{\vec{k}}} - 1}, \tag{5.13}$$

$$K_n = \int \frac{d^3k}{(2\pi)^3} \frac{e^{-n\beta e_{\vec{k}}}}{\alpha e^{\beta e_{\vec{k}}} - 1}. \tag{5.14}$$

This situation obviously corresponds to the subcritical condition with $\alpha = e^{-\beta\mu}$.

(b) If $\alpha = 1$ [i.e., $f_0(\infty) = \infty$], Eq. (5.11) becomes

$$K_n = \left[K_0 - \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta e_{\vec{k}}} - 1} \right] + \int \frac{d^3k}{(2\pi)^3} \frac{e^{-n\beta e_{\vec{k}}}}{e^{\beta e_{\vec{k}}-1}}. \tag{5.15}$$

This describes a Bose distribution with $\mu=0$ to which a δ distribution is added at $\vec{k}=0$ whose strength is equal to the difference between the given density K_0 and the critical one [second term on the right-hand side (RHS) of Eq. (5.15)].

A similar result has been obtained earlier within a certain simplifying approximation to the rate equation with a constant coupling to a fermionic thermostat.[12] We have to point out that this result is an essential property of the continuum and cannot be seen in any discretization of the spectrum.

In Appendix B it will be shown for this model, that the longtime behavior is exponential below the critical density and becomes slower than exponential when reaching criticality (''critical slowing down''). Such a behavior has been illustrated recently numerically[13] within the framework of a boson-boson collision rate equation.

VI. INTERACTION WITH THERMAL ACOUSTIC PHONONS

The transition rates for the rate equation are usually calculated from an underlying microscopic many-body model with the quantum mechanical ''golden rule.'' The interaction Hamiltonian between bosonic excitons and acoustic phonons (which is derived from the interaction of conduction and valence band electrons with acoustic phonons through the deformation potential) is in the long wave-length limit

$$H = \sum_{\vec{k}} e_{\vec{k}} a^+_{\vec{k}} a_{\vec{k}} + \sum_{\vec{q}} \hbar\omega_{\vec{q}} b^+_{\vec{q}} b_{\vec{q}} + \frac{1}{\sqrt{V}} \sum_{\vec{k},\vec{q}} g_{\vec{q}} a^+_{\vec{k}+\vec{q}} a_{\vec{k}} (b_{\vec{q}} + b^+_{-\vec{q}}) \tag{6.1}$$

with

$$e_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}, \quad \omega_{\vec{q}} = c|\vec{q}|, \quad g_{\vec{q}} = G\sqrt{\hbar\omega_{\vec{q}}}. \tag{6.2}$$

The coupling constant G is related to the material parameters by $G^2 = D^2/\rho c^2$, where D is the band gap deformation potential constant, ρ is the crystal density, and c is the sound velocity. The crystal volume is V with periodic boundary conditions, therefore a conservation of the discrete momenta holds. Strictly speaking transition rates can be defined only in the infinite volume limit, where the spectrum is continuous. In this limit the ''golden rule'' gives rise to the transition rates containing emission and absorption of thermal phonons

$$W_{\vec{k}\vec{k}'} = \frac{2\pi G^2}{\hbar} |e_{\vec{k}} - e_{\vec{k}'}| [\mathcal{N}_{\vec{k}'-\vec{k}} \delta(e_{\vec{k}} - e_{\vec{k}'} + \hbar\omega_{\vec{k}'-\vec{k}}) + (1+\mathcal{N}_{\vec{k}-\vec{k}'}) \delta(e_{\vec{k}} - e_{\vec{k}'} - \hbar\omega_{\vec{k}-\vec{k}'})], \tag{6.3}$$

where the thermal phonon distribution is

$$\mathcal{N}_{\vec{q}} = \frac{1}{e^{\beta\hbar\omega_{\vec{q}}} - 1}. \tag{6.4}$$

Using $\omega_{\vec{k}-\vec{k}'} = \omega_{\vec{k}'-\vec{k}}$, the transition rate becomes

$$W_{\vec{k}\vec{k}'} = \frac{2\pi G^2}{\hbar} \frac{|e_{\vec{k}} - e_{\vec{k}'}|}{|e^{\beta(e_{\vec{k}'} - e_{\vec{k}})} - 1|} \delta(|e_{\vec{k}} - e_{\vec{k}'}| - \hbar\omega_{\vec{k}-\vec{k}'}). \tag{6.5}$$

These transition rates of course are positive and satisfy the detailed balance relation, but nevertheless have pathological properties. Namely, they are not functions, but distributions. They are meaningless if the momenta take discrete values, i.e., in a finite volume. But even in the thermodynamic limit these rates lead to the terms in Eq. (3.8) containing $W_{\vec{k}0}$ which are meaningless.

In order to avoid mathematical inconsistencies we shall consider a regularized version of the above model by explicitly introducing a continuous spectrum for the phonons from the beginning. This procedure may be interpreted either as a mathematical regularization of the model, or as a phenomenological introduction of life-time effects. Formally we assume, that the phonon quantum numbers are $\vec{q}$ and another quantum number s which goes to a continuum even at a finite volume V. The phonon energy is $\hbar\omega_{\vec{q},s} = c|\vec{q}| + \epsilon_s$ and the corresponding density of states is $\mathcal{G}(\epsilon_s)$.

With these modifications we get the smeared out transition rates

$$W_{\vec{k}\vec{k}'} = \frac{2\pi G^2}{\hbar} \frac{|e_{\vec{k}} - e_{\vec{k}'}|}{|e^{\beta(e_{\vec{k}'} - e_{\vec{k}})} - 1|} \int d\epsilon_s \mathcal{G}(\epsilon_s) \times \delta(|e_{\vec{k}} - e_{\vec{k}'}| - \hbar\omega_{\vec{k}-\vec{k}'} - \epsilon_s) \tag{6.6}$$

$$= \frac{2\pi G^2}{\hbar} \frac{|e_{\vec{k}} - e_{\vec{k}'}|}{|e^{\beta(e_{\vec{k}'} - e_{\vec{k}})} - 1|} \mathcal{G}(|e_{\vec{k}} - e_{\vec{k}'}| - \hbar\omega_{\vec{k}-\vec{k}'}). \tag{6.7}$$

It is essential that this broadening of the δ-function does not destroy the detailed balance property of the transition rates, while a broadening directly in Eq. (6.3) would destroy it. In the numerical simulations we choose

$$\mathcal{G}(\epsilon) = \frac{1}{\pi} \frac{\gamma}{\epsilon^2 + \gamma^2}, \tag{6.8}$$

and recover the original model as $\gamma \to 0$. Thus we consider

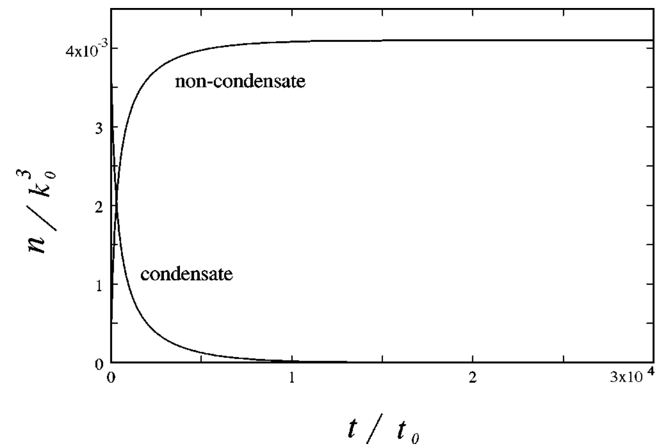

FIG. 1. Evolution of the condensate and noncondensate densities for a subcritical total density ($n_{\rm tot} = 4.1\times 10^{-3} k_0^3$, $n_c = 5.65 \times 10^{-3} k_0^3$) with a collision broadening $\gamma = 0.1\epsilon_0$.

$$W_{\vec{k}\vec{k}'} = \frac{2\pi G^2}{\hbar} \frac{|e_{\vec{k}} - e_{\vec{k}'}|}{|e^{\beta(e_{\vec{k}'} - e_{\vec{k}})} - 1|} \frac{1}{\pi} \times \frac{\gamma}{(|e_{\vec{k}} - e_{\vec{k}'}| - \hbar\omega_{\vec{k}-\vec{k}'})^2 + \gamma^2}, \tag{6.9}$$

which for any finite γ is a well defined function, satisfying all the previously discussed criteria.

Obviously the $\vec{k}=0$ mode can be reached only from the neighborhood of the $\vec{k}_0$ mode with $k_0 = 2mc/\hbar$. Then it is useful to take k_0 as the inverse length scale, $\epsilon_0 = \hbar^2 k_0^2/2m$ as the energy unit and $t_0 = \hbar/k_0^3 G^2$ as the time unit.

We have solved Eqs. (3.8) and (3.9) numerically with the above described phonon scattering rates. For the case of Cu_2O the time unit is $t_0 = 57.8$ ps, the length unit is $k_0^{-1} = 4.76$ nm the characteristic energy is $\epsilon_0 = 0.62$ meV. We illustrate the evolution of the condensate population below and above the critical density at $k_B T = 0.21\epsilon_0$ (equivalent to 1.5 K) giving rise to $n_c = 5.65\times 10^{-3} k_0^3$ equivalent to 5.23×10^{16} cm^{-3} for Cu_2O. Using a collision broadening energy $\gamma = 0.1\epsilon_0$ we show in the first two figures the resulting kinetics for the condensate and noncondensate concentration for a subcritical and a supercritical density. In Fig. 1 the total density is subcritical. Starting with excitons only in the state $k = 0$ with $n_0 = 4.1\times 10^{-3} k_0^3 < n_c = 5.65\times 10^{-3} k_0^3$ one sees that the initial condensate density decreases rapidly and vanishes completely. Correspondingly the noncondensate density builds up.

In Fig. 2 a supercritical density $n_{\rm tot} = 9.4\times 10^{-3} k_0^3$ with $n_0(t=0) = 10^{-4} k_0^3$ is assumed. Rapidly the condensate population builds up and correspondingly the concentration of noncondensed excitons decreases on a timescale of $3 \times 10^3 t_0$ which corresponds to about 180 ns for Cu_2O.

The initial distribution of the normal phase is chosen to be isotropic and Gaussian, centered at the energy of $0.7\epsilon_0$ with a width of $0.3\epsilon_0$. Figure 2 shows that the condensate density shoots over its stationary value $n_{\rm tot} - n_c = 3.75\times 10^{-3} k_0^3$, and

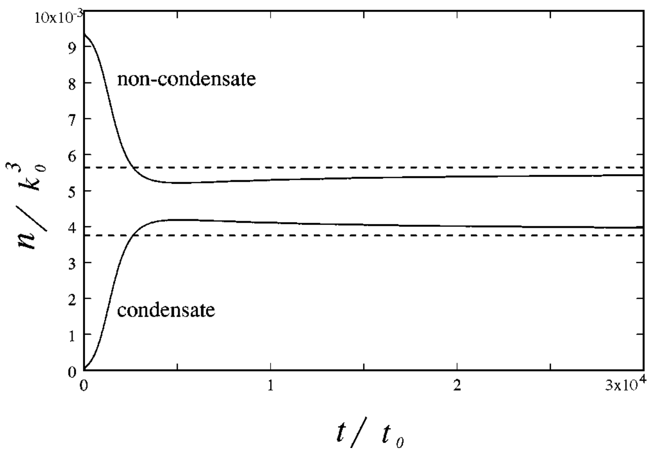

FIG. 2. Evolution of the condensate and non-condensate densities at $n_{\text{tot}}=9.4\times10^{-3}k_0^3$ above the critical density $n_c=5.65\times10^{-3}k_0^3$ and $\gamma=0.1\epsilon_0$.

correspondingly the noncondensate density undershoots its stationary value $n_c=5.65\times10^{-3}k_0^3$ given by the horizontal dashed lines in Fig. 2. Such overshooting is also known from the switching-on kinetics of the electrons in the conduction and valence bands, respectively, and the photons in the laser mode of a semiconductor laser.[11] The kinetics of this system has striking analogies with the BEC kinetics treated here. Although the stationary values are approached extremely slowly, probably with a power-law decay on a completely different time scale, the condensation sets in early. This is in agreement with the general analysis and the discussion of the Liapunov exponent given in Appendix B. This overshooting may be important for the experimental observation of an exciton BEC.

In Fig. 3 the resulting distribution of the noncondensed excitons $e_k f_k(t_f)$ at the final time t_f of the calculation is shown and compared with the equilibrium distribution $e_k f_k^0$ with $f_k^0=1/(e^{\beta e_k}-1)$ for the same parameters as in Fig. 2. The equilibrium distribution times energy approaches for $k\rightarrow 0$ the value $k_B T$ which has been assumed to be $0.21\epsilon_0$. The calculated distribution times energy for the rather large time t_f, however, goes to zero as $k\rightarrow 0$. This is a simple consequence of the ''threshold rule''

$$\lim_{\vec{k}\rightarrow 0} k^2 \frac{\partial f_{\vec{k}}}{\partial t}=0 \tag{6.10}$$

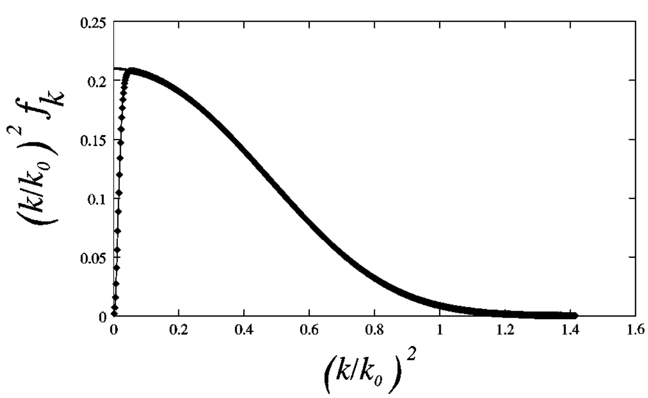

FIG. 3. The final distribution $e_k f_k$ compared to $e_k[1/e^{\beta e}(k-1)]$.

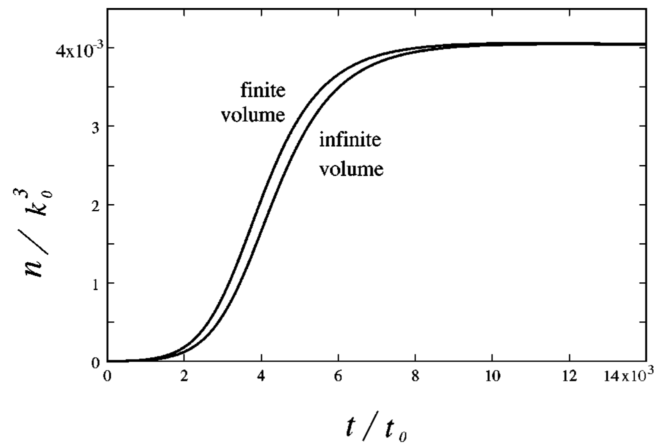

FIG. 4. BEC kinetics by acoustic phonon scattering with finite volume effect ($V=10^7 k_0^{-3}$) with $n_0(0)=0$ compared with the BEC kinetics in the thermodynamic limit, but with an initial condition $n_0(0)=10^{-7}k_0^3$.

stemming from boundedness of the collision term, due to the regularity of the transition rates around $\vec{k}=0$ and the boundedness of the initial condition. If $\lim_{k\rightarrow 0} e_k f_k(0)=0$ it will stay so according Eq. (6.10) at any finite time. As a consequence one has always a small lack of noncondensate concentration as compared to the ideal Bose value as it is seen in Fig. 3. Due to total particle conservation, the condensate overshoots. This feature is not related to specific features of the acoustical phonon model.

Such long-lasting differences between the calculated distribution function and the corresponding equilibrium distribution around $\vec{k}=0$ have already been found by Ivanov *et al.*,[7] but the significance for the condensation is different in Ref. 7 and in our treatment. In Ref. 7 it has been interpreted as an obstacle to condensation, while in our context it is related to an overshooting condensation.

As we have seen, BEC in the framework of rate equations occurs in the thermodynamic limit as an instability. An arbitrarily small initial condensate gets amplified. On the other hand, as we already emphasized, it occurs also as a spontaneous condensation, if finite volume effects pertaining to spontaneous scattering events into the condensate state are kept. In Fig. 4 we compare the solution of the rate equations Eq. (3.7) for a rather large volume and no initial condensate with that of the thermodynamic limit Eq. (3.8),(3.9) with a very small initial condensate $n_0(0)=1/V$ with the same V. The two solutions are seen to be close to each other. All the above described scenarios of condensation can be reproduced also within the instant thermalization model of Sec. IV.

For a small -but finite- broadening γ, one gets condensation in the phonon model, however, the kinetics will be asymptotically slow. For a large value of γ, the condensation kinetics is again rather inefficient, because the broadened δ-function extends below the spectrum. The dependence of the condensation time τ_c (defined as the time needed to achieve $\frac{1}{2}$ of the final condensate population) on the broadening γ is shown in Fig. 5, indicating the simple dependence

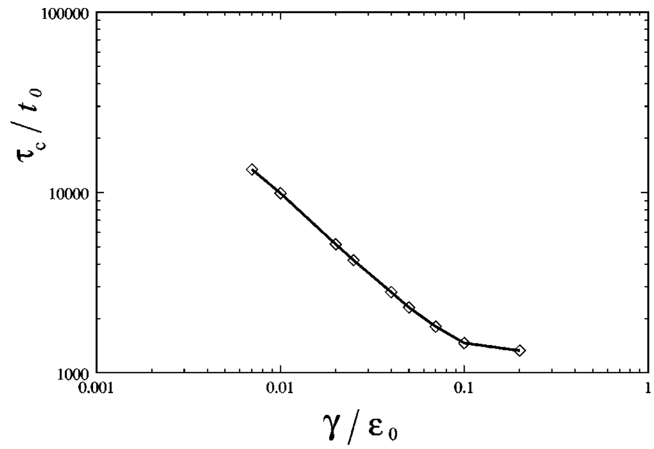

FIG. 5. Condensation time as a function of γ.

$$\tau_c = 139.68 t_0 \left(\frac{\gamma}{\epsilon_0} \right)^{-0.8938}. \tag{6.11}$$

Here we took a finite volume $V = 10^5 k_0^{-3}$, which for Cu_2O corresponds to 0.01 μm^3. This is an important ingredient, since the speed of condensation kinetics still depends either on the value of the initial condensate or on the volume.

The simple γ-dependence of the condensation time according to Eq. (6.11) allows an extrapolation to very small values of γ without excessive requirements on computer time and memory.

We want to emphasize that the above results are independent of the initial distribution of the incoherent population. The differences occur only at a very short time scale.

To predict the condensation time of excitons, e.g., in Cu_2O, the knowledge of the broadening γ is necessary. Of course, there might be several sources of broadening, but we can estimate a minimal one, which is given by the inverse scattering lifetime of the excitons due to acoustic phonons themselves

$$\frac{1}{\tau(\vec{k})} = \lim_{\gamma \to 0} \int \frac{d^3 k'}{(2\pi)^3} W_{\vec{k}\vec{k}'}. \tag{6.12}$$

This k-dependent function is shown in Fig. 6. Because the broadening is only important for the transitions between the states in the neighborhood of $k/k_0 = 1$ to $k = 0$, we may estimate the minimal broadening as

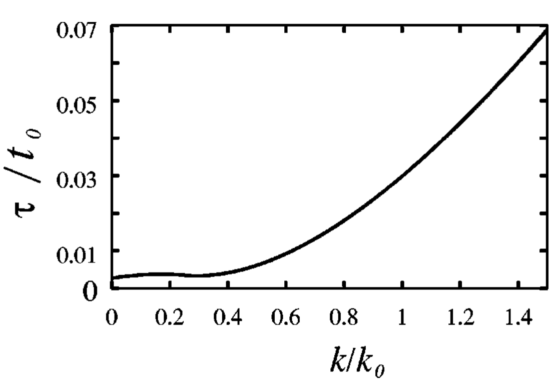

FIG. 6. The inverse scattering lifetime as function of k/k_0.

$$\gamma = \frac{\hbar}{2} \left(\frac{1}{\tau(k_0)} + \frac{1}{\tau(0)} \right) \tag{6.13}$$

which yields $\gamma = 0.187$ μeV (or $0.0003\epsilon_0$) with the above mentioned parameter. The extrapolated maximal condensation time is then $\tau_c = 1.9535 \times 10^5 t_0$ or 11.2 μs, which is comparable with the recombination time 10 μs of the paraexcitons in this material. Because our estimates are underestimating the broadening, we expect a BEC indeed might occur with acoustic phonon scattering under the conditions of the experiments of Ref. 3. To the acceleration of the condensation would contribute any other source of energy broadening, as well as additional exciton-exciton collisions, which we did not discuss here.

VII. THE ORDER PARAMETER IN THE PHONON MODEL

Here we describe within the model of an interacting exciton-phonon system the evolution of the order parameter $\langle a_0 \rangle$ and relate it to the kinetics of $\langle a_0^+ a_0 \rangle$ which has been discussed before. We do this within the standard approach of the equation of motion method with decoupling in the second stage.

The Heisenberg equation of motion leads to

$$\imath\hbar \frac{\partial}{\partial t} \langle a_0 \rangle = -\frac{1}{\sqrt{V}} \sum_{\vec{k}} g_{-\vec{k}} \langle a_{\vec{k}} (b_{-\vec{k}} + b_{\vec{k}}^+) \rangle, \tag{7.1}$$

and

$$\left[\imath\hbar \frac{\partial}{\partial t} - (e_{\vec{k}} - \hbar\omega_{\vec{k}}) \right] \langle a_{\vec{k}} b_{\vec{k}}^+ \rangle = \frac{1}{\sqrt{V}} \sum_{\vec{k}',\vec{q}} g_{\vec{q}} \langle [a_{\vec{k}'}^+ a_{\vec{k}'-\vec{q}} (b_{\vec{q}} + b_{-\vec{q}}^+), a_{\vec{k}} b_{\vec{k}}^+] \rangle. \tag{7.2}$$

After a factorization in the basic variables and formal integration with vanishing initial condition at $t=0$ we have

$$\langle a_{\vec{k}} b_{\vec{k}}^+ \rangle_t = \frac{g_{-\vec{k}}}{\imath\hbar\sqrt{V}} \int_0^t dt' \, e^{-(\imath/\hbar)(e_{\vec{k}} - \hbar\omega_{\vec{k}})(t-t')} \langle a_0 \rangle_{t'} \times \{ \langle a_{\vec{k}}^+ a_{\vec{k}} \rangle_{t'} (\langle b_{\vec{k}}^+ b_{\vec{k}} \rangle_0 + 1) - (\langle a_{\vec{k}}^+ a_{\vec{k}} \rangle_{t'} + 1) \times \langle b_{\vec{k}}^+ b_{\vec{k}} \rangle_0 \}. \tag{7.3}$$

We replaced already the average phonon occupation number with its equilibrium value at the inverse bath temperature β

$$\langle b_{\vec{q}}^+ b_{\vec{q}} \rangle_t \approx \langle b_{\vec{q}}^+ b_{\vec{q}} \rangle_0 = \frac{1}{e^{\beta\hbar\omega_{\vec{q}}} - 1}. \tag{7.4}$$

A similar equation holds for $\langle a_{\vec{k}} b_{-\vec{k}} \rangle_t$. Inserting these results in Eq. (7.1), one gets

$$\frac{\partial}{\partial t}\langle a_0\rangle_t=\frac{1}{\hbar^2 V}\sum_{\vec{k}\neq 0}|g_{\vec{k}}|^2\int_0^t dt'\langle a_0\rangle_{t'} \times\{e^{-(\imath/\hbar)(e_{\vec{k}}-\hbar\omega_{\vec{k}})(t-t')}[\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_{t'}(\langle b_{\vec{k}}^+ b_{\vec{k}}\rangle_0+1) -(\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_{t'}+1)\langle b_{\vec{k}}^+ b_{\vec{k}}\rangle_0]+e^{-(\imath/\hbar)(e_{\vec{k}}+\hbar\omega_{-\vec{k}})(t-t')} \times[\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_{t'}\langle b_{\vec{q}}^+ b_{\vec{q}}\rangle_0-(\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_{t'}+1) \times(\langle b_{\vec{q}}^+ b_{\vec{q}}\rangle_0+1)]\}. \tag{7.5}$$

Next one considers the variables as slowly varying in time and pulls them outside the time integral. Moreover, by pushing the time integration to infinity one gets the so-called Markov approximation

$$\frac{\partial}{\partial t}\langle a_0\rangle_t=\langle a_0\rangle_t\frac{1}{\hbar V}\sum_{\vec{k}\neq 0,\pm}|g_{\vec{k}}|^2 \times\left\{\left(\pi\delta(e\vec{k}\mp\hbar\omega_{\vec{k}})-\imath P\frac{1}{e_{\vec{k}}\mp\hbar\omega_{\vec{k}}}\right) \times[\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t\mathcal{N}_{\vec{k}}^{\pm}-(\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t+1)\mathcal{N}_{\vec{k}}^{\mp}]\right\}, \tag{7.6}$$

where

$$\mathcal{N}_{\vec{k}}^{\pm}\equiv\langle b_{\vec{q}}^+ b_{\vec{q}}\rangle_0+\frac{1}{2}\pm\frac{1}{2}.$$

Of course the δ symbol stays here for the precursor of the Dirac function at large times. The true δ function is meaningful only after the thermodynamic limit, i.e., in the continuous spectrum (or better within the regularized version of the model). The second δ function, having positive argument does not contribute. The equations for the occupation numbers may be derived along the same lines, but we do not need to go in these details, since they are well known.

One sees that the equations for $|\langle a_0\rangle|^2$ and $\langle a_0^+ a_0\rangle$ are identical in the thermodynamic limit. Naturally the order-parameter Eq. (7.6) is a homogeneous equation, so its solution will stay zero if the initial value has been zero. Thus the order parameter equation (7.6) allows only a condensation with a small but finite initial value. Again similar arguments are known in the theory of lasers. A convenient way out of this dilemma is to introduce stochastic Langevin fluctuation sources which make the order parameter equation an inhomogeneous differential equation. The moments of the fluctuation terms are linked via the dissipation-fluctuation theorem to the dissipative processes. Here we do not want to follow this approach further, but assume that a finite amplitude exists, which can be calculated with the rate equations with a small initial population of the condensate.

The equation of motion for the phase ϕ of $\langle a_0\rangle=|\langle a_0\rangle|e^{\imath\phi}$ is

$$\frac{\partial}{\partial t}\phi(t)=-\frac{1}{\hbar V}\sum_{\vec{k}\neq 0}|g_{\vec{k}}|^2\left\{P\frac{1}{e_{\vec{k}}-\hbar\omega_{\vec{k}}}\left[\frac{\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t}{e^{-\beta\hbar\omega_{\vec{k}}}-1}-\frac{\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t+1}{e^{\beta\hbar\omega_{\vec{k}}}-1}\right]+P\frac{1}{e_{\vec{k}}+\hbar\omega_{-\vec{k}}}\left[\frac{\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t}{e^{\beta\hbar\omega_{-\vec{k}}}-1}-\frac{\langle a_{\vec{k}}^+ a_{\vec{k}}\rangle_t+1}{e^{-\beta\hbar\omega_{-\vec{k}}}-1}\right]\right\}. \tag{7.7}$$

The expressions under the $\vec{k}$ summations actually have to be cutoff at the Debye wavelength.

Now we have the complete system of equations. One has to solve only the rate equations and get the phase through a simple time integration.

One sees that the derivative of the phase at $t\to\infty$ is nothing else but the lowest order equilibrium (real) self-energy correction due to the interaction with the phonons. In comparison with equilibrium theory of the free Bose gas, one should ignore this energy correction and therefore the phase stays constant in this framework.

In order to treat the stochastic phase diffusion one would have to use the abovementioned Langevin equation techniques. Actually for a rather wide class of nonpathological interactions with a thermal bath there is a rigorous derivation of the Master equations for both the diagonal and off-diagonal density matrix elements[14] in the van Hove limit, which at least formally is equivalent to our results.

VIII. CONCLUSIONS

We presented a detailed discussion of the rate equations describing excitons treated as massive bosons interacting with a thermal bath of acoustic phonons with special emphasis on the BEC properties. Both the finite volume and the thermodynamic limit are treated. We proved the relaxation to equilibrium below and above the critical density. BEC always occurs above the critical density under a proper mathematical treatment. Some fine points regarding the thermodynamic limit of the equation have been treated exactly within the instant thermalization model. For a better understanding also an exactly solvable two-level model with condensation has been studied.

The equilibrium situation is reached exponentially only for subcritical densities. The decay time goes to infinity as one approaches the critical density making the large time behavior very slow for $n_{\mathrm{tot}}\geqslant n_c$. Nevertheless, we found condensation to occur effectively due to an overshooting of the condensate density at early times.

From our analysis of the mathematics of the problem, the necessary ingredients for a proper numerical simulation of the condensation (through discretization of the continuum) also follow. Namely, (i) separation of the macroscopical degrees of freedom in the rate equation and (ii) a small, but nonvanishing initial condensate population or taking spontaneous transition terms into the condensate state of order $1/V$ into account. Another supplementary problem appears in the case of the interaction with a thermal bath of acoustic phonons, because the transition rates are distributions. The energy-conserving δ-function has to be broadened without violating the detailed balance relation. After these requirements are fulfilled, the numerical simulations are easily performed and they indeed are in perfect agreement with the exact properties of the integral equations of the thermodynamic limit, as we have proven.

All these investigations enabled us to perform successful numerical simulations of BEC of excitons in Cu_2O, a timely subject because of several interesting experimental observations[3–5] related to a possible exciton BEC, but still under controversial discussion. We calculate that the condensation time of paraexcitons in Cu_2O is indeed shorter than the recombination time and therefore, condensation can occur with exciton-phonon scattering.

ACKNOWLEDGMENTS

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APPENDIX A

For the following discussion, it is useful to define the symmetrized transition rates

$$W_{\vec{k}\vec{k}'}e^{\beta e_{\vec{k}'}} = W_{\vec{k}'\vec{k}}e^{\beta e_{\vec{k}}} = \mathcal{W}_{\vec{k}\vec{k}'} = \mathcal{W}_{\vec{k}'\vec{k}} \geqslant 0. \tag{A1}$$

Properties of the rate equation in a finite volume. The properties of the rate equation stem from the special ''gain-loss'' structure of the equation, from the positivity of the transition rates and from another property of the rates known as connectivity. In order to explain the latter, we can regard the set of the states $\{\vec{k}\}$ as split into connectivity classes defined as follows: $\vec{k}$ and $\vec{k}'$ belong to the same class if one can reach the state $\vec{k}'$ from the state $\vec{k}$ by a finite number of allowed transitions. This means there is a sequence $\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_n$, so that $\mathcal{W}_{\vec{k}\vec{k}_1}, \mathcal{W}_{\vec{k}_1\vec{k}_2}, \ldots, \mathcal{W}_{\vec{k}_n\vec{k}'}$ are all non-vanishing. It is clear that states belonging to different classes evolve separately, without influencing each other (separate fluids). In what follows, we will assume the following connectivity property of the transition rates: *the states* $\{\vec{k}\}$ *form one connectivity class*. In other words, any state can be reached starting from any state. We are now in a position to formulate the abovementioned properties.

(a) *Positivity*. If the initial condition is positive $f_{\vec{k}}(0) \geqslant 0$, then $f_{\vec{k}}$ stays positive for any later time. For the proof consider the situation in which some $f_{\vec{k}}$ components are vanishing, while the others are strictly positive. For the derivative of the vanishing components the rate equation gives

$$\frac{\partial}{\partial t} f_{\vec{k}} = \frac{1}{V} \sum_{\vec{k}'} \mathcal{W}_{\vec{k}\vec{k}'} f_{\vec{k}'} e^{-\beta e_{\vec{k}}} \geqslant 0. \tag{A2}$$

If the derivative is strictly positive, the corresponding component is strictly increasing and becomes strictly positive. Therefore we are left with discussing the case when the derivative is zero too, and the result depends on the sign of higher derivatives. On the other hand, the above equation shows that $(\partial/\partial t) f_{\vec{k}} = 0$, if and only if $f_{\vec{k}'} = 0$ for any $\vec{k}'$ for which $\mathcal{W}_{\vec{k}\vec{k}'} \neq 0$. In other words, for a vanishing $f_{\vec{k}}$ component, the vanishing of its first derivative is equivalent to the vanishing of the components which are one jump apart. In this situation the second derivative is

$$\frac{\partial^2}{\partial t^2} f_{\vec{k}} = \frac{1}{V^2} \sum_{\vec{k}'\vec{k}''} \mathcal{W}_{\vec{k}\vec{k}'} \mathcal{W}_{\vec{k}'\vec{k}''} f_{\vec{k}''} e^{-\beta(e_{\vec{k}} + e_{\vec{k}'})} \geqslant 0. \tag{A3}$$

If the second derivative is vanishing, the components two jumps away are vanishing too. The argument goes on recursively, until a strictly positive component is reached (this is bound to happen due to the connectivity property). If this occurs after n steps, the first $n-1$ derivatives are zero and the nth is strictly positive. This concludes the proof of our statement. Note that we have shown in fact a stronger result, namely, that for $t>0$, one has $f_{\vec{k}}(t)>0$ for any $\vec{k}$.

(b) Convergence to equilibrium. In order to show that the rate equation describes the irreversible relaxation to the equilibrium Bose Einstein distribution, one makes use of the famous H theorem. The H function is defined as

$$H = \frac{1}{V} \sum_{\vec{k}} [(1+f_{\vec{k}})\ln(1+f_{\vec{k}}) - f_{\vec{k}} \ln f_{\vec{k}} - \beta e_{\vec{k}} f_{\vec{k}}], \tag{A4}$$

and makes sense even if some $f_{\vec{k}}=0$, because one may define by continuity $x \ln x = 0$ for $x=0$.

The time derivative of the H-function is given by

$$\frac{\partial}{\partial t} H = \frac{1}{V} \sum_{\vec{k}} [\ln(1+f_{\vec{k}}) - \ln f_{\vec{k}} - \beta e_{\vec{k}}] \frac{\partial}{\partial t} f_{\vec{k}} \frac{1}{2V^2}$$
$$\times \sum_{\vec{k}\vec{k}'} \mathcal{W}_{\vec{k}\vec{k}'} \{\ln[f_{\vec{k}}(1+f_{\vec{k}'})e^{-\beta e_{\vec{k}'}}]$$
$$- \ln[f_{\vec{k}'}(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}} n]\}[f_{\vec{k}}(1+f_{\vec{k}'})e^{-\beta e_{\vec{k}'}}$$
$$- f_{\vec{k}}(1+f_{\vec{k}'})e^{-\beta e_{\vec{k}}}]. \tag{A5}$$

In the derivation the symmetry of $\mathcal{W}_{\vec{k}\vec{k}'}$ has been used. Since the logarithmic function is increasing, the difference between the two logarithms has the same sign as the difference between their arguments. Therefore one has the following statement, known as the H theorem

$$\frac{\partial}{\partial t} H \geqslant 0, \tag{A6}$$

and which says that H is an increasing function of time. Next we show that H is bounded from above and therefore it has a finite limit at $t \to \infty$. First note that there exist $a,b>0$, so that

$$h(x) = (x+1)\ln(x+1) - x \ln x < ax + b \quad \text{for any} \quad x \geqslant 0. \tag{A7}$$

Indeed, for large x one has the result

$$\lim_{x\to\infty} \frac{h(x)}{x} = 0, \tag{A8}$$

implying that $h(x)$ grows slower than any linear function, so we can choose any $a>0$ so that $h(x)-ax$ is bounded from above by some positive constant b.

Using this inequality one may write

$$H \leqslant \frac{1}{V} \sum_{\vec{k}} [a f_{\vec{k}} + b - \beta e_{\vec{k}} f_{\vec{k}}] \leqslant a n_{\rm tot} + \frac{b}{V} N, \tag{A9}$$

where N is the total number of the states $\{\vec{k}\}$. We assume this number to be finite, i.e., we impose an upper cutoff in energy, in order to simplify the proof. We see now that the H function is smaller than a time-independent quantity.

The conclusion is that in the limit $t \to \infty$ a stationary state is reached, for which the inequality in the H theorem becomes a strict equality. This entails the vanishing of all the terms in the sum giving $\partial/\partial t H$ and thus

$$f_{\vec{k}}(1+f_{\vec{k}'})e^{-\beta e_{\vec{k}'}} = f_{\vec{k}'}(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}, \quad \text{if} \quad \mathcal{W}_{\vec{k}\vec{k}'} \neq 0. \tag{A10}$$

In other words the quantity

$$\frac{(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}}{f_{\vec{k}}} = \alpha \tag{A11}$$

is constant, by the connectivity property, for all the states of the system. This is equivalent to

$$f_{\vec{k}} = \frac{1}{e^{\beta(e_{\vec{k}} - \mu)} - 1} = f^0(e_{\vec{k}}, \mu), \tag{A12}$$

where f^0 is the Bose function and μ is defined by $\alpha = e^{-\beta\mu}$.

Properties of the rate equation in an infinite volume. The same properties hold in this case too.

(a) Positivity is shown by a similar argument. A new feature is the fact, obvious by the examination of the rate equation (3.9), that if $n_0(0)=0$ then $n_0(t)=0$ for any $t>0$.

(b) Convergence to equilibrium. This is proven along the same lines. The infinite volume version of the H function is

$$H = \int \frac{d^3k}{(2\pi)^3} [(1+f_{\vec{k}})\ln(1+f_{\vec{k}}) - f_{\vec{k}} \ln f_{\vec{k}} - \beta e_{\vec{k}} f_{\vec{k}}], \tag{A13}$$

with no contribution from the condensate. This stems from the fact that

$$\frac{1}{V} h(f_0) = \frac{f_0}{V} \frac{h(f_0)}{f_0} \tag{A14}$$

goes to zero in the limit $f_0 \to \infty$, $V \to \infty$, $f_0/V = n_0$.

In order to establish the H theorem, we use the rate equation to calculate $\partial/\partial t H$ and obtain

$$\begin{aligned} \frac{\partial}{\partial t} H = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \frac{d^3k'}{(2\pi)^3} \mathcal{W}_{\vec{k}\vec{k}'} (\ln\{f_{\vec{k}}[1+f(\vec{k}\,')]e^{-\beta e_{\vec{k}'}}\} \\ - \ln[f(\vec{k}\,')(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}]) \{f_{\vec{k}}[1+f(\vec{k}\,')]e^{-\beta e_{\vec{k}'}} \\ - f(\vec{k}\,')(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}\} + n_0 \int \frac{d^3k}{(2\pi)^3} \mathcal{W}_{\vec{k}0} \\ \times \{\ln f_{\vec{k}} - \ln[(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}]\}[f_{\vec{k}} - (1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}], \end{aligned} \tag{A15}$$

which is positive, by the same argument. The upper bound for H is established in the same way, under the assumption of a cutoff spectrum. At $t \to \infty$ one reaches a stationary state, for which $\partial/\partial t H = 0$. It is known that positive continuous functions can have vanishing integrals only if they are identically zero. This leads, as in the discrete case, to

$$\frac{(1+f_{\vec{k}})e^{-\beta e_{\vec{k}}}}{f_{\vec{k}}} = \alpha \tag{A16}$$

with the additional feature that if in the final state $n_0 \neq 0$ then $\alpha = 1$ $(\mu = 0)$.

In order to classify the possible scenarios, we remark that for any $\mu \leqslant 0$ one has the inequality

$$\int \frac{d^3k}{(2\pi)^3} f^0(e_{\vec{k}}, \mu) \leqslant \int \frac{d^3k}{(2\pi)^3} f^0(e_{\vec{k}}, 0) = n_{\rm cr}. \tag{A17}$$

Therefore, initial conditions with a density $n_{\rm tot}$ smaller than the critical density $n_{\rm cr}$ can be accommodated only if the final condensate is zero. The corresponding equilibrium situation is

$$n_0(\infty) = 0, \tag{A18}$$

$$f_{\vec{k}}(\infty) = f^0(e_{\vec{k}}, \mu), \tag{A19}$$

with μ given by the average particle density

$$n_{\rm tot} = \int \frac{d^3k}{(2\pi)^3} f^0(e_{\vec{k}}, \mu). \tag{A20}$$

If $n_{\rm tot} > n_{\rm cr}$ the final state should be

$$f_{\vec{k}}(\infty) = f^0(e_{\vec{k}}, 0), \tag{A21}$$

$$n_0(\infty) = n_{\rm tot} - \int \frac{d^3k}{(2\pi)^3} f^0(e_{\vec{k}}, 0). \tag{A22}$$

APPENDIX B

We describe the long-time asymptotic behavior of the solution of Eq. (3.8) by linearizing it around the fixed point and analyzing the spectral properties of the linear operator obtained in this way. To be specific, we take

$$f_{\vec{k}}(t) = f^0(\epsilon_{\vec{k}}, \mu) + \delta f_{\vec{k}}(t), \tag{B1}$$

$$n_0(t) = n_0(\infty) + \delta n_0(t) \tag{B2}$$

and keep only linear terms in the departures from equilibrium. One gets

$$\frac{\partial}{\partial t} \delta f_{\vec{k}}(t) = -(\mathcal{A}\delta f)_{\vec{k}}(t). \tag{B3}$$

Now let λ be an eigenvalue of the operator $\mathcal{A}$ defined above

$$(\mathcal{A}\delta f)_{\vec{k}} = \lambda\, \delta f_{\vec{k}}, \tag{B4}$$

or explicitly, by using the symmetrized transition rates Eq. (A1)

$$\int \frac{d^3k}{(2\pi)^3}\mathcal{W}_{\vec{k}\vec{k}'}\{u_{\vec{k},\mu}\delta f_{\vec{k}} f^0(\epsilon_{\vec{k}'},\mu)-f^0(\epsilon_{\vec{k}},\mu)u_{\vec{k}',\mu}\delta f_{\vec{k}'}\}$$
$$+u_{\vec{k},\mu}\delta f_{\vec{k}}\mathcal{W}_{\vec{k}0}n_0(\infty)=\lambda\,\delta f_{\vec{k}}, \tag{B5}$$

where

$$u_{\vec{k},\mu}=e^{-\beta\mu}-e^{-\beta\epsilon_{\vec{k}}}. \tag{B6}$$

We prove now the following statements.

(a) For any $n_0(\infty)\neq 0$, the spectrum of $\mathcal{A}$ is positive and starts from the origin. Note that in this case $\mu=0$ and $u_{\vec{k}0}=[1+f^0(\epsilon_{\vec{k}},0)]^{-1}$. We use a variational procedure after transforming the problem to a self-adjoint form. To this end we define $\eta_{\vec{k}}$ by

$$u_{\vec{k}0}\delta f_{\vec{k}}=f^0(\epsilon_{\vec{k}},0)\,\eta_{\vec{k}} \tag{B7}$$

and get

$$\int \frac{d^3k}{(2\pi)^3}f^0(\epsilon_{\vec{k}},0)\mathcal{W}_{\vec{k}\vec{k}'}f^0(\epsilon_{\vec{k}'},0)(\eta_{\vec{k}}-\eta_{\vec{k}'})$$
$$+\eta_{\vec{k}}f^0(\epsilon_{\vec{k}},0)\mathcal{W}_{\vec{k}0}n_0(\infty)$$
$$=\lambda f^0(\epsilon_{\vec{k}},0)[1+f^0(\epsilon_{\vec{k}},0)]\,\eta_{\vec{k}}. \tag{B8}$$

Variationally, the lowest spectral point is obtained as the infimum over test functions of the ratio between the quadratic forms defined by the operators in the right-hand side (RHS) and LHS respectively, which can be written as

$$\inf_\eta\left\{\frac{\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3}f^0(\epsilon_{\vec{k}},0)\mathcal{W}_{\vec{k}\vec{k}'}f^0(\epsilon_{\vec{k}'},0)(\eta_{\vec{k}}-\eta_{\vec{k}'})^2+\int\frac{d^3k}{(2\pi)^3}\eta_{\vec{k}}^2 f^0(\epsilon_{\vec{k}},0)\mathcal{W}_{\vec{k}0}n_0(\infty)}{\int\frac{d^3k}{(2\pi)^3}f^0(\epsilon_{\vec{k}},0)[1+f^0(\epsilon_{\vec{k}},0)]\,\eta_{\vec{k}}^2}\right\}. \tag{B9}$$

It is obvious from Eq. (B9) above, that the spectrum is positive. On the other hand, the factor $f(\epsilon_{\vec{k}},0)[1+f^0(\epsilon_{\vec{k}},0)]$ in the denominator has a nonintegrable singularity at $\vec{k}=0$, so that by taking suitable sequences of test functions $\eta_{\vec{k}}$, the denominator can be made arbitrarily large. Since the Bose functions appearing in the numerator have integrable singularities, in this process the numerator stays bounded, if the transition rates do not introduce supplementary singularities around zero energy. The considered models have no such singularities.

(b) For $n_0(\infty)=0$, the spectrum consists of an isolated zero eigenvalue and a positive part separated from zero. We are able to prove this statement only for the instant thermalization model of Sec. IV. In this case, the eigenvalue problem of Eq. (B5) reads

$$(\mathcal{A}\delta f)_{\vec{k}}\equiv u_{\vec{k}\mu}\delta f_{\vec{k}}n_{\rm tot}-f^0(\epsilon_{\vec{k}},\mu)\int\frac{d^3k'}{(2\pi)^3}u_{\vec{k}',\mu}\delta f_{\vec{k}'}=\lambda\,\delta f_{\vec{k}}. \tag{B10}$$

The operator $\mathcal{A}$ consists of a multiplicative part $u_{\vec{k}\mu}n_{\rm tot}$, whose spectrum is continuous, positive and starts from $u_{0\mu}n_{\rm tot}=(e^{-\beta\mu}-1)n_{\rm tot}$ and a one-dimensional projection perturbation. It is known, that such perturbations cannot change the continuous spectrum, except for splitting off a single nondegenerate eigenvalue. In our case, this is easily identified as $\lambda=0$, corresponding to the eigenvector $\delta f_{\vec{k}}=f^0(\epsilon_{\vec{k}},\mu)/u_{\vec{k}\mu}$. This describes an infinitesimal change in μ, which is, however, forbidden by the total particle number conservation. The rest of the spectrum describes an exponential decay to equilibrium with a time scale given by $1/[(e^{-\beta\mu}-1)n_{\rm tot}]$. The resulting Liapunov exponent goes to zero as μ appproaches zero (i.e., one obtains a critical slowing down).

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