Thermodynamic properties of a Kerr nonlinear blackbody

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Within the framework of quantum field theory, we present the superfluid state of photons in a blackbody whose interior is filled by a Kerr nonlinear crystal. The thermodynamic properties of a Kerr nonlinear blackbody are investigated. At the transition temperature, the Gibbs free energy of the two phases is continuous but the entropy density of the two phases is discontinuous. Hence, there is a jump in the entropy density and this leads to a latent heat density. The photon system undergoes a first-order phase transition from the normal to the superfluid state. The transition temperature is characteristic of a concrete crystal. The entropy density and specific heat capacity are monotonically increasing functions of the temperature but are monotonically decreasing functions of the Kerr nonlinear coefficient.

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I. INTRODUCTION

Nowadays it is recognized that superfluidity is a common quantum property of many-particle systems in which the number of particles is conserved. In 1911, Kamerlingh Onnes at the University of Leiden discovered that the electrical resistance of metal mercury fell sharply at about 4 K and below this temperature the mercury exhibited no resistance whatsoever [1]. Onnes realized that below 4 K electrons in the mercury pass into a new state called the superconducting state. In 1938, P. L. Kapitza at the Institute for Physical Problems discovered that at a temperature of 2.17 K liquid helium undergoes a second-order phase transition and below this temperature liquid helium flows without friction through narrow capillaries [2]. Kapitza realized that at temperatures lower than the λ point liquid helium passes into a new phase called the superfluid phase. In 1995, Cornell and Wieman observed Bose-Einstein condensation in a vapor of rubidium-87 atoms at temperatures of about 170 nK [3]. In such a condensate the atoms can flow without friction, and so the gas is a superfluid. At temperatures of about 10 nK, by increasing the intensity of the laser beams in an optical lattice, Greiner *et al.* can reversibly switch a gas of rubidium-87 atoms from a superfluid to an insulating phase [4].

Since the electromagnetic field is a quantum system of photons, the electromagnetic field in certain nonlinear media can exhibit the superfluidity. As shown in Fig. 1, the model of a Kerr nonlinear blackbody was described in Ref. [5]. In Ref. [5] we have shown that the photon system in a Kerr nonlinear blackbody can be in a superfluid state. Kerr nonlinear crystals must be centrosymmetric and can possess a nonvanishing third-order susceptibility. More importantly the third-order response leads to the intensity-dependent refractive index, which is the basis of most nonlinear optical switching devices. The crystal studied is determined as a specific crystal with a diamond structure, such as C. In an earlier work [6,7], we have shown that a photon blackbody field in Kerr nonlinear crystal is a squeezed thermal radiation state. In a previous work [8,9], we have studied the radiation properties of a Kerr nonlinear blackbody. In the present paper, we shall investigate the thermodynamic properties of a Kerr nonlinear blackbody. Inasmuch as such thermodynamics was not explored previously, new features that are worthy of exploration are pointed out here.

Within the framework of quantum field theory, we show that the bare photons in blackbody radiation can sense an attractive effective interaction by exchange of virtual nonpolar phonons. Such an interaction leads to a photon superfluid state, in which the bare photons with opposite wave vectors and helicities are bound into pairs and single, unpaired bare photons are transformed into a new kind of quasiparticle, the nonpolariton. The photon superfluid state possesses some peculiar thermodynamic properties. First, the Gibbs free energy of normal and superfluid states is identically equal to zero. Therefore, at the transition temperature, the Gibbs free energy of the two phases is continuous. Second, at the transition temperature, the entropy density of the two phases is discontinuous. Hence, there is a jump in the entropy density and this leads to a latent heat density. Third, the photon system undergoes a first-order phase transition from the normal to the superfluid state. The transition temperature is characteristic of a concrete crystal. Fourth, the entropy density and specific heat capacity are monotonically increasing functions of the temperature but are monotonically decreasing functions of the Kerr nonlinear coefficient. The predicted properties might be verified in present-day physics laboratories.

The remainder of this paper is organized as follows. Section II describes some properties of a normal blackbody. In Sec. III, we diagonalize the Hamiltonian of the photon system in a Kerr nonlinear blackbody. Section IV computes fundamental thermodynamic functions of a Kerr nonlinear blackbody. In Sec. V, we describe the thermodynamics of phase transitions of a Kerr nonlinear blackbody. The comprehensive discussion is given in Sec. VI.

II. NORMAL BLACKBODY

A. Quantization procedure

The electromagnetic field is composed of mutually exciting electric and magnetic fields **E** and **B**. The electromagnetic field is a transverse field, propagates in vacuum with the speed c of light, and satisfies the Maxwell equations. Since there are no

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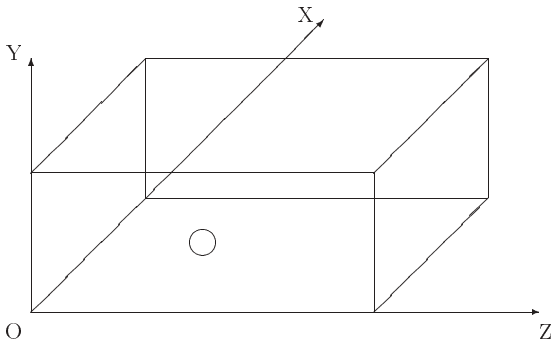

FIG. 1. A Kerr nonlinear blackbody: a rectangular Kerr nonlinear crystal enclosed by perfectly conducting walls and kept at a constant temperature; there is a very small hole in a wall.

free charges in the blackbody, we can set the scalar potential of the electromagnetic field to zero. Hence, the electromagnetic field can be characterized by a single vector potential $\mathbf{A}$, which satisfies the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$. Consequently, the electric and magnetic fields are given by

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}. \tag{1}$$

The Hamiltonian of the electromagnetic field reads as

$$H_{\rm em} = \int d\mathbf{r} \left(\frac{\epsilon_0}{2}\mathbf{E}^2 + \frac{1}{2\mu_0}\mathbf{B}^2 \right), \tag{2}$$

where ϵ_0 and μ_0 are the permittivity and the permeability of vacuum, respectively, with $\epsilon_0\mu_0 = c^{-2}$.

Now we need to quantize the electromagnetic field. Since plane-wave modes constitute a complete orthonormal set, they can be used for the expansion of the electromagnetic field in any arbitrary geometry. The blackbody occupies a volume V. In terms of the creation and annihilation operators $a^\dagger_{\mathbf{k}\sigma}$ and $a_{\mathbf{k}\sigma}$ of circularly polarized photons with wave vector $\mathbf{k}$ and helicity $\sigma = \pm 1$, the vector potential of the electromagnetic field is expanded as

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k}\sigma} \left(\frac{\hbar}{2V\epsilon_0\omega_{\mathbf{k}}} \right)^{1/2} \times \left[a_{\mathbf{k}\sigma}(t)\mathbf{e}_{\mathbf{k}\sigma} e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger_{\mathbf{k}\sigma}(t)\mathbf{e}^*_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}} \right], \tag{3}$$

where $\hbar$ is Planck's constant reduced, $\omega_{\mathbf{k}} = c|\mathbf{k}|$ is the angular frequency of a photon, and $\mathbf{e}_{\mathbf{k},\pm 1}$ are two orthonormal circular polarization vectors perpendicular to $\mathbf{k}$. On substituting Eqs. (1) and (3) into Eq. (2), the Hamiltonian of the electromagnetic field is quantized as

$$H_{\rm em} = \sum_{\mathbf{k}\sigma} \hbar\omega_{\mathbf{k}} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}, \tag{4}$$

where the zero-point energy terms are dropped. Equation (4) represents the Hamiltonian of the system of noninteracting photons in a normal blackbody.

$N_{\mathbf{k}\sigma} = a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}$ are known as the number operators of photons. The number operators have the eigenvalues $n_{\mathbf{k}\sigma} = 0,1,2,\ldots$. Since the number operators commute with $H_{\rm em}$, the number of photons in each mode $\mathbf{k}\sigma$ is constant in time. The number operators form a complete commuting set and simultaneous eigenstates of this set are given by

$$|\{n_{\mathbf{k}\sigma}\}\rangle = \prod_{\mathbf{k}\sigma} \left[\frac{1}{\sqrt{n_{\mathbf{k}\sigma}!}} (a^\dagger_{\mathbf{k}\sigma})^{n_{\mathbf{k}\sigma}} \right] |0\rangle, \tag{5}$$

where $|0\rangle$ is the vacuum state of the electromagnetic field. State vector (5) is symmetric under the interchange of any two creation operators, consistent with the Bose-Einstein statistics. Since the number of photons is variable, the chemical potential of the photon system is null. Consequently, $H_{\rm em}$ is a grand canonical Hamiltonian.

B. Thermal radiation state

State vector (5) signifies a multimode number state of photons, which is a pure state and, therefore, far from thermal equilibrium. However, the electromagnetic field within a blackbody is in thermal equilibrium [10]. Such equilibrium is established via the continual absorption and emission of photons by matter. An electromagnetic field in thermal equilibrium is called blackbody radiation or thermal radiation and characterized by a definite temperature T. The photons in blackbody radiation are in a thermal radiation state, which is called a normal state. In order to characterize the thermal radiation state, we need to conceive a grand canonical ensemble of photons. Some identical systems of the ensemble may be in an eigenstate of the Hamiltonian $H_{\rm em}$ given by Eq. (4), while the distribution of the ensemble over the eigenstates is described by the density operator of the thermal radiation state,

$$\rho = \frac{\exp(-H_{\rm em}/k_BT)}{\mathrm{Tr}\,\exp(-H_{\rm em}/k_BT)}, \tag{6}$$

where k_B is Boltzmann's constant. The basis states used in the trace are the eigenstates of the Hamiltonian $H_{\rm em}$, which are given by Eq. (5). A main thermodynamic quantity in normal blackbody radiation is the total photon number N_n, which is the ensemble average of the corresponding microscopic quantity,

$$N_n = \sum_{\mathbf{k}\sigma} \langle N_{\mathbf{k}\sigma} \rangle, \tag{7}$$

where we have utilized the average notation $\langle N_{\mathbf{k}\sigma}\rangle = \mathrm{Tr}(\rho N_{\mathbf{k}\sigma})$.

It is easily found that the ensemble average of the number operator of photons in a mode $\mathbf{k}\sigma$ satisfies the well-known Bose-Einstein distribution,

$$\langle N_{\mathbf{k}\sigma} \rangle = \frac{1}{e^{\hbar\omega_{\mathbf{k}}/k_BT} - 1}. \tag{8}$$

Putting Eq. (8) into Eq. (7) and in the usual way altering the summation to an integration, we obtain $N_n = Vn_n$, where

$$n_n = \frac{1}{\pi^2 c^3} \int_0^\infty \frac{\omega^2}{e^{\hbar\omega/k_BT} - 1} d\omega. \tag{9}$$

Here n_n is the photon number density of normal blackbody radiation. With the new variable of integration $x = \hbar\omega/k_BT$, the resulting integral in Eq. (9) is equal to $2\zeta(3)$, where $\zeta(3) = 1.20206$ is theRiemann ζ function of 3. Equation (9) yields

$$n_n = \frac{2\zeta(3)}{\pi^2} \left(\frac{k_BT}{\hbar c} \right)^3. \tag{10}$$

In Ref. [5], the total energy E_n of normal blackbody radiation is acquired as $E_n = Vu_n$, where u_n is the energy density of normal blackbody radiation and is given by

$$u_n = 4\sigma T^4/c, \tag{11}$$

where $\sigma = \pi^2 k_B^4/60\hbar^3 c^2$ is called the Stefan-Boltzmann constant. Thereby the pressure of normal blackbody radiation is given by

$$P_n(T) = \tfrac{1}{3}u_n(T). \tag{12}$$

For the constant-volume heat capacity of normal blackbody radiation $C_V^{(n)}$, we have

$$C_V^{(n)} = (\partial E_n/\partial T)_V = Vc_v^{(n)}, \tag{13}$$

where $c_v^{(n)}$ is the constant-volume specific heat capacity and is given by

$$c_v^{(n)} = 16\sigma T^3/c. \tag{14}$$

According to the relation $C_V^{(n)} = T(\partial S_n/\partial T)_V$, integration of the constant-volume heat capacity gives the entropy of normal blackbody radiation: $S_n = Vs_n$, where s_n is the entropy density of normal blackbody radiation and is given by

$$s_n = 16\sigma T^3/3c. \tag{15}$$

It is interesting to note that the Gibbs free energy of normal blackbody radiation is

$$G_n = E_n - TS_n + P_nV = 0, \tag{16}$$

which is consistent with zero chemical potential of photons.

III. KERR NONLINEAR BLACKBODY

The model of a Kerr nonlinear blackbody was described in Ref. [5]. The crystal under study is a covalent one. The optical vibration modes of a covalent crystal are all the nonpolar modes that carry no electric dipole moments, so they are infrared inactive. For convenience the crystal is taken to be of the cubic symmetry, so it is optically isotropic. A Kerr nonlinear crystal must be centrosymmetric. By "nonlinearity" we mean that the crystal is first-order Raman active. Nonpolar modes in a centrosymmetric crystal have even parity and are Raman active [11]. In the cubic system, the common covalent crystals that are both centrosymmetric and Raman active have a diamond structure. At this point the crystal studied is determined as a specific crystal with a diamond structure, such as C. In a diamond-structure crystal a primitive cell contains two identical atoms that exhibit a triply degenerate nonpolar mode at zero wave vector, which is Raman active. For the Raman-active mode, the two atoms in the primitive cell move in antiphase. Because the following treatment has no relation to acoustic modes, the vibrational modes of the crystal are limited to the Raman-active mode, whose zero-wave-vector frequency is denoted by ω_R.

In Ref. [7] we have known that the interaction between photons and phonons can lead to an attractive effective interaction among the photons themselves. The attractive effective interaction leads to bound photon pairs. In the standing-wave configuration a photon pair is stable only if the two photons have opposite wave vectors and helicities. The pair Hamiltonian of the photon system is

$$H'_{\rm em} = \frac{1}{2}\sum_{\mathbf{k}\sigma}\hbar\omega_{\mathbf{k}}(a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} + a^\dagger_{-\mathbf{k},-\sigma}a_{-\mathbf{k},-\sigma}) + \sum_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} V_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}a^\dagger_{\mathbf{k}'\sigma'}a^\dagger_{-\mathbf{k}',-\sigma'}a_{-\mathbf{k},-\sigma}a_{\mathbf{k}\sigma}, \tag{17}$$

where the photons have the pair potential

$$V_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} = \begin{cases} -V_0\hbar\omega_{\mathbf{k}}\hbar\omega_{\mathbf{k}'} & \text{if } 0 < \omega_{\mathbf{k}} < \infty \text{ and } 0 < \omega_{\mathbf{k}'} < \omega_R \\ 0 & \text{otherwise} \end{cases}, \tag{18}$$

where V_0 is a positive constant. We shall assume that the crystal has a dispersion-free linear refractive index n_0, so the photon frequency is given by $\omega_{\mathbf{k}} = c|\mathbf{k}|/n_0$.

Single, unpaired bare photons in the photon system are transformed into a new kind of quasi-particle, the nonpolariton. A nonpolariton is the condensate of virtual nonpolar phonons in momentum space, with a bare photon acting as the nucleus of condensation. The diagonalization of the pair Hamiltonian (17) can be performed by the Bogoliubov transformation: $c_{\mathbf{k}\sigma} = Ua_{\mathbf{k}\sigma}U^\dagger$ and $c^\dagger_{\mathbf{k}\sigma} = Ua^\dagger_{\mathbf{k}\sigma}U^\dagger$. $c^\dagger_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}$ are the creation and annihilation operators of nonpolaritons in the photon system. The transition from the operators of bare photons to those of nonpolaritons can be effected by a symplectic transformation:

$$U = \exp\left[\frac{1}{2}\sum_{\mathbf{k}\sigma}\varphi_{\mathbf{k}\sigma}(a^\dagger_{\mathbf{k}\sigma}a^\dagger_{-\mathbf{k},-\sigma} - a_{-\mathbf{k},-\sigma}a_{\mathbf{k}\sigma})\right], \tag{19}$$

where the parameter $\varphi_{\mathbf{k}\sigma}$ is assumed to be real and spherically symmetric: $\varphi_{-\mathbf{k},-\sigma} = \varphi_{\mathbf{k}\sigma}$. It is well known that the symplectic transformation does not change the energy spectrum of the photon system. The normalized state vector of photon pairs in the photon system may be constructed as $|G\rangle = U|0\rangle$, such that $c_{\mathbf{k}\sigma}|G\rangle = 0$.

As we know, the pair Hamiltonian (17) can be solved only when the pair potential $V_{\mathbf{k}\sigma,\mathbf{k}'\sigma'}$ is negative. Under the mean-field approximation [7,12], the pair Hamiltonian of the photon system is diagonalized into

$$H'_{\rm em} = E_p + \sum_{\mathbf{k}\sigma}\hbar\tilde{\omega}_{\mathbf{k}}(T)c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}. \tag{20}$$

The frequency of nonpolaritons is acquired as $\tilde{\omega}_{\mathbf{k}}(T) = v(T)|\mathbf{k}|$, where $v(T)$ is the velocity of nonpolaritons determined by the equation

$$v(T) = 2(c/n_0)V_0{\sum_{\mathbf{k}}}'\hbar\omega_{\mathbf{k}}\coth\frac{\hbar v(T)|\mathbf{k}|}{2k_BT}, \tag{21}$$

where the prefactor 2 arises from the summation over helicities and the prime on the summation symbol means that $\omega_{\mathbf{k}} < \omega_R$. E_p is the energy of the system of photon pairs. The velocity $v(T)$ determined by Eq. (21) is a monotonically increasing function of temperature T, which is equal to c/n_0 at transition temperature T_c. In Ref. [5] we have shown that below T_c the photon system is in a superfluid state, in which the photons with opposite wave vectors and helicities are bound into pairs and unpaired photons are transformed into nonpolaritons. At

T_c, both photon pairs and nonpolaritons become single bare photons. Above T_c, the Kerr nonlinear blackbody behaves like a normal blackbody.

The solution of Eq. (21) requires numerical methods. To this end, it is useful to introduce a dimensionless constant γ. The constant γ is meaningful only if $\gamma < 1$ and signifies the coupling strength between a bare photon and virtual nonpolar phonons. Because $v(T_c) = c/n_0$, we let $y = v(T)/v(T_c)$ and $x = k_B T/\hbar\omega_R$, such that Eq. (21) is transformed into a neat form,

$$y - \gamma = 8\gamma \int_0^1 \frac{t^3 dt}{\exp(yt/x) - 1}. \tag{22}$$

Therefore, $v(T)/v(T_c)$ is a universal function of $k_B T/\hbar\omega_R$ and γ, independently of any particular property of the blackbody. For future study we must know the temperature derivative $\partial v(T)/\partial T$ of the velocity. At first we infer from Eq. (21) that $\partial v(T)/\partial T = 0$ at zero temperature. We then let $y' = \partial y/\partial x$, such that the equation of y' is deduced from Eq. (22) as

$$y' = 8\gamma \int_0^1 \frac{(y - xy')\exp(yt/x)t^4 dt}{x^2[\exp(yt/x) - 1]^2}. \tag{23}$$

The temperature derivative of the velocity is also a universal function of $k_B T/\hbar\omega_R$ and γ.

IV. THERMODYNAMIC FUNCTIONS

We saw in the last section that the state of a Kerr nonlinear blackbody depends only on the values of temperature and volume. This implies that the transition from the superfluid to the normal state is reversible in the thermodynamic sense. We may therefore apply thermodynamic arguments to a Kerr nonlinear blackbody, using the temperature and volume as thermodynamic variables. In what follows we compute fundamental thermodynamic functions of these two variables.

A. Total nonpolariton number

For future study it will be convenient to define the number operators $N_{\mathbf{k}\sigma} = c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$ for nonpolaritons. The number operators have the eigenvalues $n_{\mathbf{k}\sigma} = 0,1,2,\ldots$. The eigenstates of number operators $N_{\mathbf{k}\sigma}$ are given by

$$|\{n_{\mathbf{k}\sigma}\}\rangle = \prod_{\mathbf{k}\sigma} \left[\frac{1}{\sqrt{n_{\mathbf{k}\sigma}!}}(c^\dagger_{\mathbf{k}\sigma})^{n_{\mathbf{k}\sigma}}\right]|G\rangle. \tag{24}$$

The Hilbert space of the photon system is spanned by the complete orthonormal basis vectors $|\{n_{\mathbf{k}\sigma}\}\rangle$. In Ref. [5] we have shown that the photon system in a Kerr nonlinear blackbody is in a superfluid state. In order to characterize the superfluid state, we need to conceive a grand canonical ensemble of nonpolaritons. Some identical systems of the ensemble may be in an eigenstate of the Hamiltonian H'_{em} given by Eq. (20), while the distribution of the ensemble over the eigenstates is described by the density operator of the superfluid state

$$\rho = \frac{\exp(-H'_{\text{em}}/k_B T)}{\text{Tr}\exp(-H'_{\text{em}}/k_B T)}, \tag{25}$$

where the basis states used in the trace are the eigenstates of the Hamiltonian H'_{em}, which are given by Eq. (24). The total nonpolariton number N_r in a Kerr nonlinear blackbody is the ensemble average of the corresponding microscopic quantity,

$$N_r = \sum_{\mathbf{k}\sigma} \langle N_{\mathbf{k}\sigma}\rangle. \tag{26}$$

It is easily found that the ensemble average of the number operator of nonpolaritons in a mode $\mathbf{k}\sigma$ satisfies the well-known Bose-Einstein distribution,

$$\langle N_{\mathbf{k}\sigma}\rangle = \frac{1}{e^{\hbar\tilde{\omega}_{\mathbf{k}}(T)/k_B T} - 1}. \tag{27}$$

Putting Eq. (27) into Eq. (26) and in the usual way altering the summation to an integration, we obtain $N_r = V n_r$, where n_r is the nonpolariton number density in a Kerr nonlinear blackbody and is given by

$$n_r = \frac{1}{\pi^2 v^3(T)} \int_0^\infty \frac{\tilde{\omega}^2(T)}{e^{\hbar\tilde{\omega}(T)/k_B T} - 1} d\tilde{\omega}(T), \tag{28}$$

where $\tilde{\omega}(T) = v(T)|\mathbf{k}|$. With the new variable of integration $x = \hbar\tilde{\omega}(T)/k_B T$, the resulting integral in Eq. (28) is equal to $2\zeta(3)$. Equation (28) yields

$$n_r = \frac{2\zeta(3)}{\pi^2}\left[\frac{k_B T}{\hbar v(T)}\right]^3. \tag{29}$$

At zero temperature n_r is equal to zero and at temperatures $T > 0 n_r$ is a monotonically increasing function of temperature T.

B. Constant-volume heat capacity

First, we briefly state the results of Ref. [9]. In the standing-wave configuration, the system of photon pairs cannot be detected and the gas of free nonpolaritons constitutes the thermal radiation of a Kerr nonlinear blackbody. The energy E_r of the thermal radiation is given by $E_r(T) = V u_r(T)$, where

$$u_r(T) = 4\sigma(T)T^4/v(T), \tag{30}$$

where $\sigma(T) = \pi^2 k_B^4/60\hbar^3 v^2(T)$ is the temperature-dependent Stefan-Boltzmann constant. $u_r(T)$ is the energy density of the thermal radiation and a monotonically increasing function of temperature T.

Having obtained the energy of a Kerr nonlinear blackbody, we now can compute its constant-volume heat capacity $C_V^{(r)}$. According to Eq. (13), we have

$$C_V^{(r)} = (\partial E_r/\partial T)_V = V(\partial u_r/\partial T). \tag{31}$$

From Eq. (30) one can gain the derivative

$$\partial u_r/\partial T = \frac{\pi^2 k_B^4 T^3}{15\hbar^3 v^3(T)}\left[4 - 3\frac{T}{v(T)}\frac{\partial v(T)}{\partial T}\right]. \tag{32}$$

The last derivative is positive at temperatures $T > 0$. A physical quantity amenable to calculation is the constant-volume specific heat capacity, which is defined by

$$c_v^{(r)} = C_V^{(r)}/V = \frac{16\sigma(T)T^3}{v(T)}\left[1 - \frac{3T}{4v(T)}\frac{\partial v(T)}{\partial T}\right]. \tag{33}$$

C. Entropy

We, first, compute the thermodynamic potential, which is only a function of temperature and volume, because the chemical potential of the nonpolariton system is zero. In the grand canonical ensemble at temperature T, the grand partition function Z is defined as

$$Z = \mathrm{Tr}\ \exp(-H'_{\mathrm{em}}/k_BT). \tag{34}$$

Here H'_{em} represents the Hamiltonian of the nonpolariton system and is given by

$$H'_{\mathrm{em}} = \sum_{\mathbf{k}\sigma} \hbar\tilde{\omega}_{\mathbf{k}}(T) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}. \tag{35}$$

The thermodynamic potential is related to the Hamiltonian of the nonpolariton system through the grand partition function,

$$\Omega(T,V) = -k_BT \ln Z. \tag{36}$$

Putting Eq. (35) into Eq. (34), the grand partition function is obtained as

$$Z = \prod_{\mathbf{k}\sigma} \mathrm{Tr}\ \exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}/k_BT]. \tag{37}$$

If the trace in Eq. (37) is written out in detail with the complete set of eigenstates $|n_{\mathbf{k}\sigma}\rangle$ of number operator $c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$, we have

$$\begin{aligned}
&\mathrm{Tr}\ \exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}/k_BT] \\
&= \sum_{n_{\mathbf{k}\sigma}=0}^{\infty} \langle n_{\mathbf{k}\sigma}|\exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T) c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}/k_BT]|n_{\mathbf{k}\sigma}\rangle \\
&= \sum_{n_{\mathbf{k}\sigma}=0}^{\infty} \exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T) n_{\mathbf{k}\sigma}/k_BT] \\
&= \{1-\exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T)/k_BT]\}^{-1}.
\end{aligned} \tag{38}$$

Thereby the grand partition function may be determined as

$$Z = \prod_{\mathbf{k}\sigma} \{1-\exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T)/k_BT]\}^{-1}. \tag{39}$$

The logarithm of Eq. (39) yields the thermodynamic potential

$$\Omega(T,V) = 2k_BT \sum_{\mathbf{k}} \ln\{1-\exp[-\hbar\tilde{\omega}_{\mathbf{k}}(T)/k_BT]\}. \tag{40}$$

In the usual way from summation to integration, we obtain

$$\Omega(T,V) = k_BT \frac{V}{\pi^2 v^3(T)} \int_0^{\infty} \tilde{\omega}^2 \ln[1-\exp(-\hbar\tilde{\omega}/k_BT)] d\tilde{\omega}. \tag{41}$$

With the new variable of integration $x = \hbar\tilde{\omega}/k_BT$, integration by parts gives

$$\Omega(T,V) = -V \frac{(k_BT)^4}{3\pi^2\hbar^3 v^3(T)} \int_0^{\infty} \frac{x^3 dx}{e^x-1}. \tag{42}$$

The integral is equal to $\pi^4/15$. Thus,

$$\begin{aligned}
\Omega(T,V) &= -V \frac{\pi^2(k_BT)^4}{45\hbar^3 v^3(T)} \\
&= V\left[-\frac{1}{3}u_r(T)\right],
\end{aligned}$$

where $u_r(T)$ is given by Eq. (30).

The entropy of a Kerr nonlinear blackbody is immediately given by

$$S_r = -\left(\frac{\partial\Omega}{\partial T}\right)_V = V\left(\frac{1}{3}\partial u_r/\partial T\right). \tag{43}$$

A physical quantity amenable to calculation is the entropy density, which is defined by

$$s_r = S_r/V = \tfrac{1}{3}\partial u_r/\partial T. \tag{44}$$

Since $\partial u_r/\partial T$ is given by Eq. (32), finally we obtain

$$s_r = \frac{16\sigma(T)T^3}{3v(T)}\left[1-\frac{3T}{4v(T)}\frac{\partial v(T)}{\partial T}\right]. \tag{45}$$

D. Gibbs free energy

We, first, notice that the radiation pressure of a Kerr nonlinear blackbody is given by

$$P_r(T) = \tfrac{1}{3}u_r(T). \tag{46}$$

One then notices that the total energy of a Kerr nonlinear blackbody is given by $E = E_p + E_r$, where E_p is the energy of the photon-pair system and E_r denotes the energy of the nonpolariton system. Although E_p cannot be detected in experiments, E_p can affect the Gibbs free energy of a Kerr nonlinear blackbody. Thereby we introduce an effective energy of a Kerr nonlinear blackbody by $E^*_r = Vu^*_r$, where u^*_r represents the effective energy density of a Kerr nonlinear blackbody and is given by

$$u^*_r = u_r(T)\left[1-\frac{T}{v(T)}\frac{\partial v(T)}{\partial T}\right]. \tag{47}$$

The Gibbs free energy of a Kerr nonlinear blackbody is defined as

$$G_r = E^*_r - TS_r + P_rV. \tag{48}$$

Putting Eqs. (45)–(47) into the last equation, we obtain

$$G_r = 0, \tag{49}$$

which is consistent with zero chemical potential of nonpolaritons.

V. THERMODYNAMICS OF PHASE TRANSITIONS

A. Numerical calculation

According to Eq. (23), if one defines an integral,

$$I(y/x) = \int_0^{y/x} \frac{e^u u^4 du}{(e^u-1)^2}, \tag{50}$$

then the temperature derivative of the velocity has an analytic expression,

$$y' = \frac{8\gamma x^3 y I(y/x)}{y^5 + 8\gamma x^4 I(y/x)}. \tag{51}$$

At this point, we should note that $x = k_BT/\hbar\omega_R$, $y = v(T)/v(T_c)$, and $y' = dy/dx$. Based on Eq. (51), the variation with x and γ of y' is shown in Fig. 2. For fixed γ, first, the velocity derivative increases from zero to a maximum

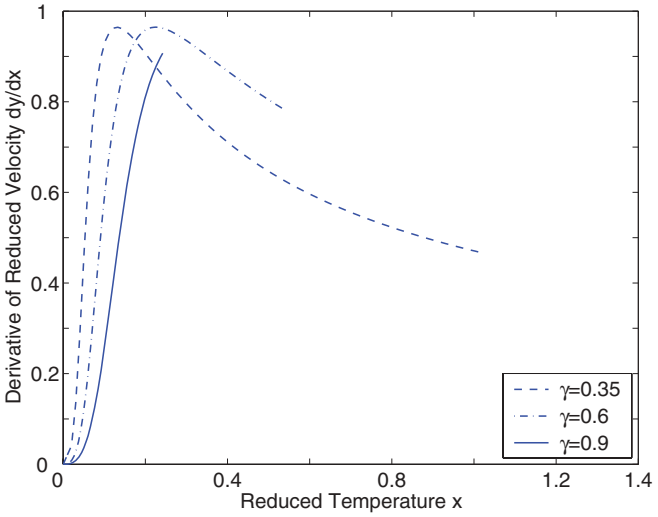

FIG. 2. (Color online) dy/dx: derivative of reduced velocity $y = v(T)/v(T_c)$ with respect to reduced temperature $x = k_B T/\hbar\omega_R$. For three values of γ, variation of derivative dy/dx with reduced temperature $x = k_B T/\hbar\omega_R$, where temperature T varies from zero to transition temperature T_c.

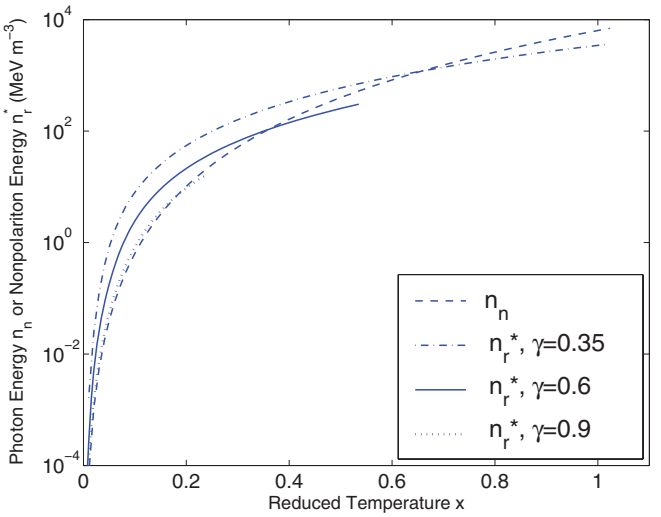

FIG. 4. (Color online) For three values of γ, variation of effective energy density u_r^* with reduced temperature $x = k_B T/\hbar\omega_R$, where temperature T varies from zero to transition temperature T_c. u_n denotes the energy density of a normal blackbody.

as the temperature increases from zero, and then the velocity derivative decreases as the temperature increases to the transition temperature T_c. Particularly, as $\gamma \to 1$, the temperature derivative of the velocity is a monotonically increasing function of T. For fixed T, the velocity derivative is a monotonically decreasing function of γ.

In this paragraph, the nonpolariton number density $n_r(T)$ in a Kerr nonlinear blackbody is compared with the photon number density $n_n(T)$ in a normal blackbody. $n_n(T)$ and $n_r(T)$ are given by Eqs. (10) and (29), respectively. The variation of $n_r(T)$ and $n_n(T)$ with reduced temperature $x = k_B T/\hbar\omega_R$ is shown in Fig. 3, where, for $n_r(T)$, temperature T varies from zero to transition temperature $T_c(\gamma)$ and for $n_n(T)$ temperature T varies from zero to transition temperature $T_c(\gamma = 0.35)$. There are four features: (1) $n_r(T)$ and $n_n(T)$ are monotonically increasing functions of T; (2) for fixed T, $n_r(T)$ is a monotonically decreasing function of γ; (3) at transition temperature $T_c(\gamma)$, $n_r(T) = n_n(T)$; and (4) the nonpolariton number density $n_r(T)$ of a Kerr nonlinear blackbody is always larger than the photon number density $n_n(T)$ of a normal blackbody. The reason for the fourth feature is that the nonpolariton number density is the sum of the photon number density and a part of the nonpolar phonon number density.

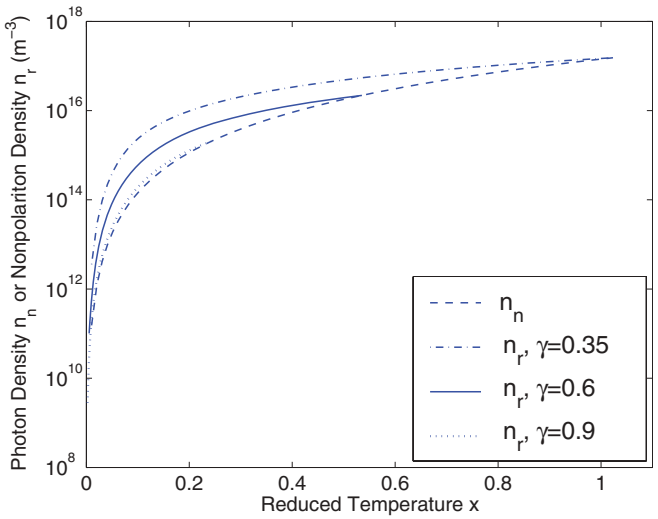

FIG. 3. (Color online) For three values of γ, variation of nonpolariton number density n_r with reduced temperature $x = k_B T/\hbar\omega_R$, where temperature T varies from zero to transition temperature T_c. n_n denotes the photon number density of a normal blackbody.

Now let us turn to the effective energy density $u_r^*(T)$ of a Kerr nonlinear blackbody. $u_r^*(T)$ is given by Eq. (47). The variation of $u_r^*(T)$ with reduced temperature $x = k_B T/\hbar\omega_R$ is shown in Fig. 4, where temperature T varies from zero to transition temperature $T_c(\gamma)$. Figure 4 also shows the energy density $u_n(T)$ of a normal blackbody, where temperature T varies from zero to transition temperature $T_c(\gamma = 0.35)$. There are three features: (1) for fixed γ, $u_r^*(T)$ is a monotonically increasing functions of T; (2) for fixed T, $u_r^*(T)$ is a monotonically decreasing function of γ; and (3) near zero temperature the effective energy density $u_r^*(T)$ of a Kerr nonlinear blackbody is larger than the energy density $u_n(T)$ of a normal blackbody but near transition temperature $T_c(\gamma)$, $u_r^*(T)$ becomes smaller than $u_n(T)$.

In this paragraph, the entropy density $s_r(T)$ of a Kerr nonlinear blackbody is compared with the entropy density $s_n(T)$ of a normal blackbody. $s_n(T)$ and $s_r(T)$ are given by Eqs. (15) and (45), respectively. The variation of $s_r(T)$ and $s_n(T)$ with reduced temperature $x = k_B T/\hbar\omega_R$ is shown in Fig. 5, where for $s_r(T)$ temperature T varies from zero to transition temperature $T_c(\gamma)$ and for $s_n(T)$ temperature T varies from zero to transition temperature $T_c(\gamma = 0.35)$. There are three features: (1) $s_r(T)$ and $s_n(T)$ are monotonically increasing functions of T; (2) for fixed T, $s_r(T)$ is a monotonically decreasing function of γ; and (3) near zero temperature the entropy density $s_r(T)$ of a Kerr nonlinear blackbody is

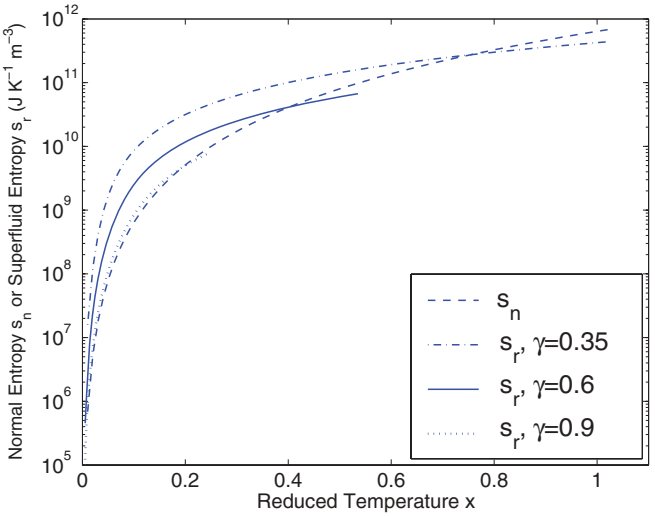

FIG. 5. (Color online) For three values of γ, variation of entropy density s_r with reduced temperature $x = k_B T/\hbar\omega_R$, where temperature T varies from zero to transition temperature T_c. s_n denotes the entropy density of a normal blackbody.

larger than the entropy density $s_n(T)$ of a normal blackbody but near transition temperature $T_c(\gamma)$, $s_r(T)$ becomes smaller than $s_n(T)$.

Finally, the constant-volume specific heat capacity $c_v^{(r)}$ of a Kerr nonlinear blackbody is compared with the constant-volume specific heat capacity $c_v^{(n)}$ of a normal blackbody. $c_v^{(n)}$ and $c_v^{(r)}$ are given by Eqs. (14) and (33), respectively. The variation of $c_v^{(r)}$ and $c_v^{(n)}$ with reduced temperature $x = k_B T/\hbar\omega_R$ is shown in Fig. 6, where for $c_v^{(r)}$ temperature T varies from zero to transition temperature $T_c(\gamma)$ and for $c_v^{(n)}$ temperature T varies from zero to transition temperature $T_c(\gamma = 0.35)$. There are three features: (1) $c_v^{(r)}$ and $c_v^{(n)}$ are monotonically increasing functions of T; (2) for fixed T, $c_v^{(r)}$ is a monotonically decreasing function of γ; and (3) near zero temperature the constant-volume specific heat capacity $c_v^{(r)}$ of a Kerr nonlinear blackbody is larger than the constant-volume specific heat capacity $c_v^{(n)}$ of a normal blackbody but near transition temperature $T_c(\gamma)$, $c_v^{(r)}$ becomes smaller than $c_v^{(n)}$.

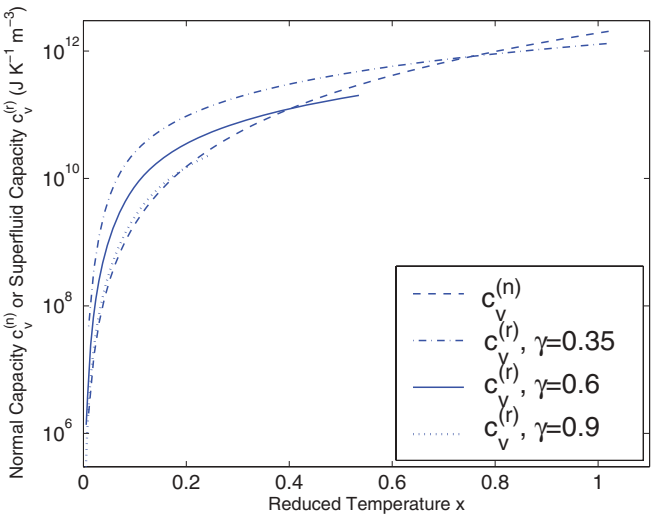

FIG. 6. (Color online) For three values of γ, variation of constant-volume specific heat capacity $c_v^{(r)}$ with reduced temperature $x = k_B T/\hbar\omega_R$, where temperature T varies from zero to transition temperature T_c. $c_v^{(n)}$ denotes the constant-volume specific heat capacity of a normal blackbody.

B. First-order phase transition

The thermodynamics of phase transitions is to describe phase transitions in terms of macroscopic variables. At phase transitions the Gibbs free energy of the two phases must be continuous. However, phase transitions can be divided into two classes according to the behavior of derivatives of the Gibbs free energy. Phase transitions which are accompanied by discontinuous first derivatives of the Gibbs free energy are called first-order phase transitions. Phase transitions which are accompanied by discontinuous second derivatives of the Gibbs free energy are called second-order phase transitions.

Generally, the Gibbs free energy G is a function of the temperature T, the pressure P, and the particle number N, namely, $G = G(T, P, N)$. The entropy S is related to the first derivative of G,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}. \tag{52}$$

Therefore, at first-order phase transitions the entropy of two phases a and b is discontinuous, $S_a \neq S_b$. The latent heat L for a transition between two phases a and b is given by $L = T(S_a - S_b)$. A first-order phase transition has two important characteristics: at the transition there is a latent heat, and there is a jump in the entropy. The transitions from gas to liquid phase, from liquid to solid phase, and from gas to solid phase are all first-order transitions. The heat capacity at constant P and N $C_{P,N}$ is related to the second derivative of G,

$$C_{P,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}. \tag{53}$$

Therefore, at second-order phase transitions the heat capacity of two phases a and b is discontinuous, $C_a \neq C_b$. A second-order phase transition has two important characteristics: (i) at the transition there is no latent heat and (ii) there is a jump in the heat capacity. In the absence of any magnetic field, the superconducting-normal transition of a metal is a second-order phase transition.

Now let us begin to describe the transition properties of a Kerr-nonlinear blackbody. As we know, the Gibbs free energy of normal and superfluid states is identically equal to zero. Therefore, at the transition temperature, the Gibbs free energy of the two phases is continuous, $G_n = G_r = 0$. As seen in Fig. 5, near the transition temperature, the entropy density of the superfluid state becomes smaller than that of the normal state, so the superfluid state is stable. At the transition temperature, the entropy density of the two phases is discontinuous, $s_n \neq s_r$. Hence, at transition temperature T_c, there is a jump in the entropy density and this leads to a latent heat density $l = T(s_n - s_r)$. This latent heat arises because at transition temperature T_c the entropy of the normal state is greater than that of the superfluid state, so heat must be supplied if the transition is to take place at T_c.

Consequently, the transition between normal and superfluid states is a first-order phase transition.

Between the entropy density and the constant-volume specific heat capacity, there are the following relations: $s_n = \frac{1}{3}c_v^{(n)}$ and $s_r = \frac{1}{3}c_v^{(r)}$. As a result, the latent heat density can be rewritten as

$$l = T(s_n - s_r) = \tfrac{1}{3}T\left(c_v^{(n)} - c_v^{(r)}\right). \tag{54}$$

First, we give a numerical impression of latent heat density l at transition temperature T_c. As we know, the transition temperature T_c is a monotonically decreasing function of the dimensionless Kerr nonlinear coefficient γ. At $\gamma = 0.35, 0.6, 0.9$, $T_c = 1962.7, 1026.8, 464.9$ K, respectively. Consequently, at $T_c = 1962.7, 1026.8, 464.9$ K, $l = 4.8008 \times 10^{14}, 2.9872 \times 10^{13}, 8.6567 \times 10^{11}$ J m^{-3}, respectively. It is seen that the latent heat density l at T_c is a monotonically decreasing function of γ. As shown in Fig. 6, at the transition temperature there is a jump in the constant-volume specific heat capacity. The jump δ in heat capacity is defined by

$$\delta = \frac{c_v^{(n)} - c_v^{(r)}}{c_v^{(n)}}. \tag{55}$$

Next we give a numerical impression of δ at T_c. At $T_c =$ 1962.7, 1026.8, 464.9 K, $\delta = 0.3575, 0.3024, 0.1969$, respectively. It is seen that the jump δ in heat capacity at T_c is a monotonically decreasing function of γ.

VI. DISCUSSION

Our basic point in this paper is that the photon system in a Kerr-nonlinear blackbody undergoes a first-order phase transition from the normal to the superfluid state. We expose the thermodynamic properties of a Kerr nonlinear blackbody. We find that the Gibbs free energy of normal and superfluid states is identically equal to zero. Therefore, at the transition temperature, the Gibbs free energy of the two phases is continuous. Near the transition temperature, the entropy density of the superfluid state becomes smaller than that of the normal state, so the superfluid state is stable. At the transition temperature, the entropy density of the two phases is discontinuous, $s_n \neq s_r$. Hence, at transition temperature T_c, there is a jump in the entropy density and this leads to a latent heat density $l = T(s_n - s_r)$. This latent heat arises because at transition temperature T_c the entropy of the normal state is greater than that of the superfluid state, so heat must be supplied if the transition is to take place at T_c. It is easy to understand why at T_c there is a jump in the constant-volume specific heat capacity. Our theory shows that at T_c there is a jump in the entropy density. According to Eq. (54), this jump in the entropy density accounts for the rapid jump in the constant-volume specific heat capacity at T_c.

It would be valuable to have some indication of location of the phase transition. In Sec. III, we have introduced a dimensionless constant γ. The constant γ represents the interaction strength between bare photons. In Ref. [7], the constant γ is given by

$$\gamma = \frac{\hbar}{2c^3\Omega n_0}\left[\frac{\mathcal{P}(\mathbf{0})\omega_R}{4\pi\epsilon_0}\right]^2, \tag{56}$$

where Ω is the cell volume. Here $\mathcal{P}(\mathbf{q})$ is defined by Eq. (21) in Ref. [7]. Further, in Ref. [7], the pair interaction parameter V_0 is given by

$$V_0 = \frac{1}{2}N\left[\frac{\mathcal{P}(\mathbf{0})}{2V\epsilon_0 n_0^2\omega_R}\right]^2, \tag{57}$$

where N is the number of primitive cells. In terms of the dimensionless interaction constant γ, the pair interaction parameter can be rewritten as

$$V_0 = \frac{4\pi^2(c/n_0)^2}{\hbar\omega_R^4}\gamma\frac{c/n_0}{V}. \tag{58}$$

In the optical Kerr effect, the medium possesses an intensity-dependent refractive index: $n = n_0 + n_2 I$, where n_2 is the second-order nonlinear refractive index and I is the intensity of the light traveling through the medium. We consider a self-defocusing Kerr nonlinearity where $n_2 < 0$. By use of the second-order nonlinear refractive index n_2, the pair interaction parameter can also be rewritten as

$$V_0 = \left(\frac{m_e c^2}{\hbar\omega_R}\right)^2 |n_2|\frac{c/n_0}{V}, \tag{59}$$

where m_e is the rest mass of electron. In the integration over photon frequencies ω, the upper limit of the integral is chosen as infinity. In fact, the maximum frequency of photon is $m_e c^2/\hbar$. The prefactor in Eq. (59) accounts for this correction. On comparing Eq. (58) with Eq. (59), the dimensionless interaction constant is immediately acquired as

$$\gamma = \frac{\hbar\omega_R^4}{4\pi^2(c/n_0)^2}\left(\frac{m_e c^2}{\hbar\omega_R}\right)^2 |n_2|. \tag{60}$$

The zero-wave-vector frequency of the Raman-active mode of the diamond crystal is $\omega_R = 2.51 \times 10^{14}$ s^{-1} [11]. The linear and nonlinear refractive indices of the diamond crystal are as follows [13]: $n_0 = 2.42$ and $|n_2| = 1.3 \times 10^{-19}$ m^2 W^{-1}. From Eq. (60) the dimensionless interaction constant is calculated as $\gamma = 0.8592$. According to Eq. (58) in Ref. [7], the transition temperature T_c is a monotonically decreasing function of γ. At $\gamma = 0.8592$ we find that $T_c = 536.8$ K. Because the diamond crystal has the highest melting point (3820 K), $T_c = 536.8$ K is meaningful.

The superconducting theory of solids established by Bardeen, Cooper, and Schrieffer is a striking success of the quantum field theory of solids [14,15]. The basic physical mechanism is that the electron-electron Coulomb repulsion is overcome by the attractive interaction via acoustic phonons, leading to massive electron pairs known as Cooper pairs, which incorporate the acoustic phonons and, hence, propagate without phonon scattering. Many important concepts in this theory have a certain generality and are certain to be applicable to quantum optics. In the present theory, the photon superfluid state is generated by the formation of bare photon pairs. However, there are the following contrasts between the electronic superconducting state and the photon superfluid state. (i) The transition of the electron system from the normal to the superconducting state is connected with a change in the gauge symmetry of the system's state, while the transition of the photon system from the normal to the superfluid state is connected with a change in the phase symmetry

of the system's state. (ii) In the absence of any magnetic field, the superconducting-normal transition of a metal is a second-order phase transition, but the superfluid-normal transition of a Kerr nonlinear blackbody is a first-order phase transition,

To sum up, we have investigated the thermodynamic properties for a blackbody whose interior is filled by a Kerr nonlinear crystal. Below the transition temperature, the photon system in a Kerr nonlinear blackbody is in a superfluid state. We find that the Gibbs free energy of normal and superfluid states is identically equal to zero. Therefore, at the transition temperature, the Gibbs free energy of the two phases is continuous. At the transition temperature, the entropy density of the two phases is discontinuous. Hence, there is a jump in the entropy density and this leads to a latent heat density. The photon system undergoes a first-order phase transition from the normal to the superfluid state. The transition temperature is characteristic of a concrete crystal. The entropy density and specific heat capacity are monotonically increasing functions of the temperature but are monotonically decreasing functions of the Kerr nonlinear coefficient. The predicted properties might be verified in present-day physics laboratories.

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