Collective pairing of resonantly coupled microcavity polaritons

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We consider the collective behavior of microcavity polaritons tuned near a bipolariton Feshbach resonance. We show that as well as the regular polariton superfluid phase a “molecular” superfluid phase exists, with (quasi-)long-range order only for pairs of polaritons. We describe the experimental signatures of this phase. Using variational approaches we find the phase diagram (critical temperature, density and exciton-photon detuning). Unlike ultracold atoms, the molecular superfluid phase is not inherently unstable, and our phase diagram suggests it is attainable in current experiments.

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The wealth of physics that has been explored with ultracold atomic gases relies on the ability to tune parameters such as the interaction strength; the crucial tool to enable this is the Feshbach resonance mechanism \cite{Feshbach}. This works by using a magnetic field to vary the detuning $\nu$ between two channels (hyperfine states) of the atoms; a closed channel (bound molecule) and open (scattering) channel. When $\nu$ is large and positive, the closed channel is detuned far above open channel atoms, the formation of molecules is energetically suppressed and atoms scatter with a weakly attractive effective interaction. When $\nu$ is large and negative, atoms are paired into molecules and the effective interaction is weakly repulsive. Near resonance ($\nu \approx 0$), the interaction is very large. This enables tunable pairing and regimes of strong correlations, opening a wealth of interesting possibilities both at few and many-body level.

Ultracold atom experiments are however intrinsically metastable, as opposed to true minima of the free energy. Three-body collisions must be avoided to prevent relaxation to, e.g., a solid phase. Also, Feshbach molecular states are in fact highly rovibrationally excited states, and can relax to lower states via scattering. Exploring regimes of strong interactions while still suppressing such relaxation processes is inherently challenging. For fermionic atoms, Pauli exclusion suppresses scattering rates so strongly interacting regimes can be studied. However for fermions no new phases arise with changing interaction strength: there is instead a smooth crossover between a Bardeen-Cooper-Schrieffer (BCS) condensate of weakly attractive fermions and a Bose-Einstein condensate (BEC) of repulsive molecules \cite{BCS, BEC}.

The situation for bosons near a Feshbach resonance changes substantially: Unlike fermions, both a condensate of molecules and a condensate of unpaired bosons can exist. As discussed below this means that a “molecular” superfluid phase with no off-diagonal long-range order (ODLRO) for the atoms can arise, with a further symmetry breaking phase transition between “atomic” and “molecular” superfluids. Bosonic mixtures have attracted considerable theoretical interest \cite{BosonicMixtures}. However, despite this theoretical interest, experiments have been limited by the stability issue discussed above.

Microcavity polaritons \cite{MCPolaritons}, the quasiparticles resulting from strong coupling between cavity photons and quantum well excitons, do not suffer the metastability problems of cold atoms and so present an ideal opportunity to study bosonic pairing phases. Microcavity polaritons have been observed to form a BEC \cite{MicrocavityBEC}. Furthermore, as recently proposed \cite{BipolaritonResonances, BipolaritonBEC}, the interaction between oppositely polarised polaritons can be enhanced by the resonance with bipolariton states. Various signatures providing evidence for bipolariton states in semiconductor microcavities have been seen \cite{BipolaritonSignatures}. Very recently, Feshbach resonances in a GaAs cavity have been experimentally measured for the very first time \cite{GaAsFeshbach}. Importantly, the bipolariton Feshbach resonance should not suffer from the stability issues which plague cold bosonic atoms: Unlike ultracold atoms, a polariton BEC is not a metastable state, rather it is the minimum free energy state as long as the polariton population is conserved. In addition, there is no deeply bound molecular state below the bipolariton. Microcavity polaritons do have a finite lifetime, however recent experiments have demonstrated a 5–10 fold increase in lifetime \cite{BipolaritonLifetime}, leading to a system very close to thermal equilibrium.

In this Letter we explore the phase diagram of collective paired phases arising from bipolariton resonances in microcavities. We show that by using the cavity-exciton detuning as the interaction tuning parameter \cite{CavityExciton}, a novel phase transition between atomic (i.e. polariton) and molecular (i.e. bipolariton) BEC phases can be realised. We show that temperatures and detunings required for typical materials such as GaAs are attainable, and we discuss experimental signatures for detecting such phases.
FIG. 1. (Color online) Lower (LP) and upper (UP) polariton dispersions $\omega_{k,\mu,\nu}^{LP,UP}$ (thin [black] lines) for GaAs ($\Omega_R=4.4$ meV, $|E_b|=2$ meV [12]), photon mass $m_C = 10^{-4}m_X$, exciton mass $m_X = 0.4m_e$, where the cavity(C)-exciton(X) (dashed [blue] lines) detuning $\delta = \omega_0^C - \omega_0^X = 3.84$ meV is fixed at resonant conditions, $\nu = 0$, i.e. $\omega_0^\mu - \omega_0^X = -|E_b|/2 = -1$ meV (thick [red] line).

Model — The interaction between polaritons with counter rotating polarisations can be dramatically enhanced which is a Feshbach resonance [12, 13]: When the biexciton energy $\omega_{XX} = 2\omega_0^C - |E_b|$ (with $E_b$ the biexciton binding energy) is tuned close to the energy of two lower polaritons (LPs), $2\omega_0^LP$, the interaction between LPs in opposite spin states is resonantly enhanced. The molecular closed channel corresponds to the bipolaron state, while the open channel modes are LPs. This allows the detuning between closed and open channels, $\nu = -(|E_b| - 2\omega_0^LP - \omega_0^X)$, where $2\omega_0^LP = \omega_0^C + \omega_0^X - \sqrt{(\omega_0^C - \omega_0^X)^2 + \Omega_R^2}$, to be controlled by varying the cavity-exciton detuning $\delta = \omega_0^C - \omega_0^X$ (see Fig. 1).

We derive the many-body properties of resonantly coupled polaritons by considering a two-channel model, which includes both LPs in the right- and left-circular polarisation basis, $\psi_{\sigma,\mu}(r) = [\psi_\mu(r) \pm i\psi_\mu^\dagger(r)]/\sqrt{2}$ (x, y are the linear polarisation components) and bipolaron $\psi_m(r)$ fields. Alternatively, one could also work with a single-channel model with no explicit bipolaron field, at the expense of having to introduce a finite range attractive potential $U_{\sigma\tau}(r)$ supporting a resonant bound state [22]. Such an approach unnecessarily complicates the derivation of many-body physics, while a single-channel approach with a model contact interaction cannot describe deeply bound bipolaron states (i.e., biexcitons). Assuming only low momentum LPs are populated and thus approximating $\omega_k^{LP} \approx \omega_0^LP + k^2/2m$, where $k$ is the in-plane (2D) momentum ($h = 1$ throughout), the grand-canonical Hamiltonian then reads:

$$
\hat{H} = \int dr \left[ \sum_{\sigma = \uparrow, \downarrow, \mu, \nu} \left( \hat{\psi}_\mu^\dagger \hat{h}_\sigma \hat{\psi}_\mu + \frac{U_{\sigma\tau}}{2} \hat{\psi}_\mu^\dagger \hat{\psi}_\tau \hat{\psi}_\sigma \right) + U_{\sigma\tau} \hat{\psi}_\mu^\dagger \hat{\psi}_\tau \hat{\psi}_\mu + \frac{\Omega_R^2}{2} \left( \hat{\psi}_\mu^\dagger \hat{\psi}_\mu \right) \right] + \frac{\Delta}{2} \left( \hat{\psi}_m^\dagger \hat{\psi}_m \right) + \text{h.c.}, \tag{1}
$$

where $\hat{h}_\sigma = -\nabla^2/2m_\sigma$, $m_\sigma = m_\mu = m$, is the LP mass, while the bipolaron mass is fixed to twice the exciton mass, $m_m = 2m_X$ (see below). In absence of an external magnetic field which breaks the $\uparrow \leftrightarrow \downarrow$ symmetry, the two spin populations are balanced and the effective chemical potentials are $\mu_\uparrow = \mu_\downarrow = \mu$ and $\mu_m = 2\mu - \nu$, where the detuning $\nu$ is discussed above. The most general case of $\mu_\uparrow \neq \mu_\downarrow$ will be the subject of future study.

The Feshbach coupling $g$ characterises the hybridisation between open and closed channels, i.e., the interconversion of two LPs in opposite polarisations into a bipolaron and vice versa. It is related to an energy scale $\Delta_{LP} = mg^2$, called the resonance width [22]. An estimate of $\Delta_{LP}$ is obtained by including the exciton-photon coupling in the exciton $\hat{f}$-matrix. In agreement with Ref. [13], we find that strong coupling to light only causes a small renormalisation of the scattering resonance properties because of the small polariton to exciton mass ratio $m/m_X$. One thus finds that $g^2 \approx c_0^2\Delta_X/m_X$ [23], where $2c_k^2 = 1 + (\omega_k^C - \omega_k^X)/(\omega_k^C - 2\omega_k^X)^2 + \Omega_R^2$ is the Hopfield coefficient and $\Delta_X \approx 4|E_b|$ [12]. Following the same reasoning, one can also estimate the bipolaron mass, finding that $m_m \approx 2m_X$.

The parameters $U_{\uparrow\uparrow} = U_{\downarrow\downarrow}, U_{\uparrow\downarrow}$, and $U_{mm}$ are the background (i.e., far from the resonance) interaction strengths between the $\psi_{\sigma=\uparrow, \downarrow, m}$ fields. Note that the physical interactions also include terms mediated by the coupling $g$. These background interactions can be written in terms of the corresponding excitonic parameters, $U_{\sigma\sigma'} = U_{\sigma\sigma'}/m = c_0^2U_X^\sigma/m_X$, where, using energy scales appropriate to LPs and excipons, $U_{\sigma\sigma'}$ and $U_{XX}^\sigma$ are dimensionless constants. To fix the parameters to experimental values as given in the caption to Fig. 1, we consider the specific case of GaAs microcavities for which $U_{XX}^\uparrow = U_{XX}^\downarrow = 6$ [12]. Also, we fix $U_{\uparrow\uparrow}^\uparrow = 0$ and $U_{mm} = 4$, though we have checked that our results do not strongly depend on the exact values of these parameters, as long as $U_{XX}^\sigma > 0$ (required for stability) and the correct order of magnitudes are used. Note that, due to the small mass ratio $m/m_X \ll 1$ for $\Delta \lesssim 10\Omega_R$, the polariton fluid is, far from the resonance, much more weakly interacting than the excitonic one, i.e., $U_{\sigma\sigma'} \ll U_{XX}^\sigma$.

Zero temperature — The zero temperature phase diagram found for the GaAs parameters specified above is shown in Fig. 2 with cavity-exciton detuning $\delta$ versus either chemical potential $\mu$ or total density, $n = \int dr (\psi_\uparrow^\dagger \psi_\uparrow + \psi_\downarrow^\dagger \psi_\downarrow + 2\psi_m^\dagger \psi_m)$. In addition to the normal phase (N), $\psi_\uparrow = \psi_\downarrow = \psi_m = 0$, where $\psi_\sigma = (\hat{\psi}_\sigma)$, we can easily predict the two condensed phases compatible with the spontaneous symmetry breaking of the $U(1) \times U(1)$ symmetry of the Hamiltonian (1), $\psi_\uparrow \rightarrow e^{i\phi_\uparrow} \psi_\uparrow, \psi_m \rightarrow e^{i\phi_m} \psi_m$. Condensation of atoms, $\psi_\uparrow = \psi_\downarrow \neq 0$, necessarily implies that of molecules, $\psi_m \neq 0$, a phase we will refer to as atomic and molecular superfluid phase [AMSF]: Here, the $U(1) \times U(1)$ symmetry is completely broken.

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the symmetry of the Hamiltonian is atomic language. For cold atoms, much work focused on correlations would provide unambiguous evidence for the observation of such pair correlations without polarisation. Working in momentum space, suggested by the observation of a locking of the in-plane order lines are separated by tricritical points. Experimentally, identified via spatial correlation functions. In contrast, the MSF phase survives |\psi\rangle = N \exp \left( \sqrt{A} \sum_{\sigma=\uparrow,\downarrow,m} \psi^\dagger_{m\sigma} a_{0\sigma}^\dagger + \sum_k \sum_{\gamma=a,b,m} \tanh \theta_{k\gamma} \hat{b}_{k\gamma}^\dagger \hat{b}_{-k\gamma} \right) |0\rangle.

The operators \( \hat{b}_{ka,b} \) are related to \( \hat{a}_{k\uparrow,\downarrow} \) by:

\[
\frac{\hat{a}_{k\sigma}}{\hat{a}_{-k\sigma}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & \hat{b}_{ka}^\dagger \\ 1 & 1 & \hat{b}_{kb}^\dagger \end{pmatrix},\]

while for the molecular operator \( \hat{b}_{km}^\dagger = \hat{a}_{km}^\dagger \) (note that \( \sigma = \uparrow, \downarrow, m \), while \( \gamma = a, b, m \)). This transformation produces the most general variational ground state with pairing and reflecting the system \( \uparrow \leftrightarrow \downarrow \) symmetry. Minimising the energy \( \langle \hat{H} \rangle \) over the variational parameters \( \psi_\uparrow = \psi_0, \psi_\downarrow, m, \) and \( \theta_{k\gamma} \) we find that \( \theta_{k\gamma} \) has the functional form \( \tanh 2\theta_{k\gamma} = \alpha_\gamma/(\epsilon_{k\gamma} + \beta_\gamma) \), with \( \beta_\gamma > 0, |\alpha_\gamma| \leq \beta_\gamma \), and \( \epsilon_{k\gamma} = k^2/2m_\gamma \) where \( m_a = m_b = m \). The energy can thus be numerically minimised in terms of eight variational parameters \( \alpha_\gamma, \beta_\gamma, \psi_\gamma \), making it easy to determine first order phase boundaries, as well as to find cases where the global minimum energy is not an extremum (zero derivative), but instead occurs at \( |\alpha_\gamma| = \beta_\gamma \).

As \( \tilde{\mu}_{\sigma\sigma'} \ll \tilde{\mu}_{\sigma'\sigma} \sim 1 \) fluctuation corrections to mean field (MF) theory (i.e., \( \theta_{k\gamma} \equiv 0 \)), are expected to be small. At the same time, as bipolaritons have a much larger mass than LPs, closed channel quantum fluctuations give a non-negligible shift. The dashed lines in Fig. 2 show the comparison with MF predictions. Note that, even if fluctuations do quantitatively shift phase boundaries, the phase diagram topology qualitatively matches MF predictions.

The N-MSF transition is second order and occurs for \( \nu = 2\mu \); the AMSF-N and AMSF-MSF transitions can instead be either second or first order, separated by two tricritical points. The MSF phase is characterised by the absence of any order for unpaired polaritons, but the power-law decay of \( g^{(1)}(r) \): The observation of such pair correlations without polariton correlations would provide unambiguous evidence for an MSF pairing phase.

Note that our resonantly coupled spinor polariton fluid corresponds to a bosonic “heteronuclear” mixture in atomic language. For cold atoms, most work focused instead on the homonuclear case, where \( \psi_\uparrow \equiv \psi_\downarrow \). Here, the symmetry of the Hamiltonian is \( U(1) \times Z_2 \), and the residual symmetry in the MSF phase is \( Z_2 \). If we add a spin flip term \( \Omega \psi_\uparrow^\dagger \psi_\downarrow + h.c. \) to the Hamiltonian, as suggested by the observation of a locking of the in-plane polarisation, the initial \( U(1) \times U(1) \) symmetry would again break to \( U(1) \times Z_2 \).

To derive the \( T = 0 \) phase diagram we employ a variational approach. Working in momentum space, \( \psi_\sigma(r) = \sum_k e^{ikr} \tilde{a}_{k\sigma} / \sqrt{A} \), where \( A \) is the system area, we consider a normalised Bogoliubov–Nozières wavefunction [20] including atomic and molecular condensates, as well as pairing terms:

\[
|\psi\rangle = N \exp \left( \sqrt{A} \sum_{\sigma=\uparrow,\downarrow,m} \psi^\dagger_{m\sigma} a_{0\sigma}^\dagger + \sum_k \sum_{\gamma=a,b,m} \tanh \theta_{k\gamma} \hat{b}_{k\gamma}^\dagger \hat{b}_{-k\gamma} \right) |0\rangle.
\]

FIG. 2. (Color online) \( T = 0 \) phase diagram for resonantly paired polaritons in a GaAs microcavity, with cavity-exciton detuning \( \delta \) versus either chemical potential \( \mu \) (left panel) or total density \( n \) (right). The non-condensed (or vacuum) phase N is the white, MSF the light- and AMSF the dark-gray-shaded region. First (thick [red]) and second (thinner [blue]) order lines are separated by tricritical points ([blue] circles), while critical end-points are (red) diamonds. Horizontal dot-dashed lines connect the same chemical potential first-order boundaries in the density phase separated (PS) region. Dashed lines are the boundaries obtained within mean-field, where quantum fluctuations are neglected.

broken. However, the reverse is false [24], and a phase characterised by the absence of atomic ODLRO while molecules do condense (MSF phase) exists [4,6]. A residual \( U(1) \) symmetry (rotations with \( \phi_\uparrow = -\phi_\downarrow \)) survives in the MSF phase.

The different collective paired phases can thus be experimentally identified via spatial correlation functions. In particular, at \( T = 0 \), the AMSF phase is characterised by ODLRO of both unpaired polaritons and bipolaritons. At \( T \neq 0 \), as the system is 2D, this evolves into off-diagonal quasi long-range order, i.e., power-law decay of the correlation functions \( g^{(1)}(r) = \langle \tilde{\psi}_\downarrow^\dagger(r) \tilde{\psi}_\uparrow(0) \rangle \) and \( g^{(1)}(r) = \langle \tilde{\psi}_\downarrow^\dagger(r) \tilde{\psi}_\uparrow(0) \tilde{\psi}_\downarrow(0) \rangle \). In contrast, the MSF phase is characterised by the absence of any order for unpaired polaritons, but the power-law decay of \( g^{(1)}(r) \):

The operators \( \hat{b}_{ka,b} \) are related to \( \hat{a}_{k\uparrow,\downarrow} \) by:

\[
\frac{\hat{a}_{k\sigma}}{\hat{a}_{-k\sigma}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & \hat{b}_{ka}^\dagger \\ 1 & 1 & \hat{b}_{kb}^\dagger \end{pmatrix},\]

while for the molecular operator \( \hat{b}_{km}^\dagger = \hat{a}_{km}^\dagger \) (note that \( \sigma = \uparrow, \downarrow, m \), while \( \gamma = a, b, m \)). This transformation produces the most general variational ground state with pairing and reflecting the system \( \uparrow \leftrightarrow \downarrow \) symmetry. Minimising the energy \( \langle \hat{H} \rangle \) over the variational parameters \( \psi_\uparrow = \psi_0, \psi_\downarrow, m, \) and \( \theta_{k\gamma} \) we find that \( \theta_{k\gamma} \) has the functional form \( \tanh 2\theta_{k\gamma} = \alpha_\gamma/(\epsilon_{k\gamma} + \beta_\gamma) \), with \( \beta_\gamma > 0, |\alpha_\gamma| \leq \beta_\gamma \), and \( \epsilon_{k\gamma} = k^2/2m_\gamma \) where \( m_a = m_b = m \). The energy can thus be numerically minimised in terms of eight variational parameters \( \alpha_\gamma, \beta_\gamma, \psi_\gamma \), making it easy to determine first order phase boundaries, as well as to find cases where the global minimum energy is not an extremum (zero derivative), but instead occurs at \( |\alpha_\gamma| = \beta_\gamma \).

As \( \tilde{\mu}_{\sigma\sigma'} \ll \tilde{\mu}_{\sigma'\sigma} \sim 1 \) fluctuation corrections to mean field (MF) theory (i.e., \( \theta_{k\gamma} \equiv 0 \)), are expected to be small. At the same time, as bipolaritons have a much larger mass than LPs, closed channel quantum fluctuations give a non-negligible shift. The dashed lines in Fig. 2 show the comparison with MF predictions. Note that, even if fluctuations do quantitatively shift phase boundaries, the phase diagram topology qualitatively matches MF predictions. The N-MSF transition is second order and occurs for \( \nu = 2\mu \); the AMSF-N and AMSF-MSF transitions can instead be either second or first order, separated by two tricritical points. At MF level these points are at \( (\mu, \nu) = (0, \Delta_{LP}/(4U)) \) and \( (-\Delta_{LP}/(2W), -\Delta_{LP}/(4U)) \) where \( U = \bar{U}_{\uparrow\uparrow} + \bar{U}_{\uparrow\downarrow} \) and \( \bar{W} = [\bar{U}_{mm}(\bar{U}_{\uparrow\uparrow} + \bar{U}_{\uparrow\downarrow})]^{1/2} \). In between the tricritical points the transition is first order, implying phase separation in density space (Fig. 2, right panel) either between N and AMSF below the critical end-point (diamond [red] symbol) at \( \delta \approx 4.94\text{meV} \), or, above, between MSF and AMSF.

Finite temperature — We have shown that, in GaAs, a polariton MSF phase can be found in the ground state for \( \delta \gtrsim 4.94\text{meV} \). However, to determine whether such a phase is readily accessible, it is important to determine its critical temperature. Since the closed channel mass is the biexciton one, the critical temperature is expected to be much lower than corresponding LP condensation temperatures. It is however important to note that the
MSF phase is not a pure biexciton condensate, because of the hybridisation between channels.

In order to extend our results to finite temperature, we use the variational mean-field theory (VMFT) \cite{27,29}, based on the inequality \cite{28} 
\[ F = -k_B T \ln \text{tr} e^{-H/k_B T} \leq F_{\text{VMFT}} = F_{\text{MF}} + \langle \hat{H} - \hat{H}_{\text{MF}} \rangle_{\text{MF}}. \] 
In a similar spirit to the \( T = 0 \) calculation, \( \hat{H}_{\text{MF}} \) is chosen to allow the same one- and two-point correlation functions and its variational parameters are used to minimise \( F_{\text{VMFT}} \):

\[
\hat{H}_{\text{MF}} = \sum_\gamma \left\{ -2\sqrt{A} \psi_\gamma (\alpha_\gamma + \beta_\gamma) \left( \hat{b}_{\gamma 0} + \hat{b}_{\gamma 0}^\dagger \right) \right. \\
+ \sum_\mathbf{k} \left( \hat{b}_{\mathbf{k} \gamma 0}^\dagger \hat{b}_{-\mathbf{k} \gamma 0} \right) \left( \epsilon_{\mathbf{k} \gamma} + \beta_\gamma \right) \left( \alpha_\gamma + \epsilon_{\mathbf{k} \gamma} + \beta_\gamma \right),
\]

where \( \psi_a = 0 \) and \( \psi_b = \sqrt{2}\psi_0 \). One might have thought that the most general \( \hat{H}_{\text{MF}} \) requires arbitrary functions of \( \mathbf{k} \) in the above matrix, however it can be shown that the optimal functions have the above form. We evaluate \( F_{\text{MF}} \) and averages \( \langle \ldots \rangle_{\text{MF}} \) by standard Bogoliubov diagonalisation \cite{29}. This yields the free energy \( F_{\text{VMFT}} \) as a function of the same eight parameters \( \alpha_\gamma, \beta_\gamma \), and \( \psi_0, \psi_m \), again allowing numerical minimisation. Note that the \( T = 0 \) limit of this approach reproduces the results presented above.

For 2D Bose gases, such as microcavity polaritons, the actual \( T \neq 0 \) transition to a superfluid phase is of the Berezinski-Kosterlitz-Thouless (BKT) type \cite{29}. Nevertheless, the location of phase boundaries predicted by the VMFT are expected to be accurate. In fact, despite the absence of true ODLRO, the quasi-condensate density plays a similar role to the mean-field order parameter \cite{30,31}. This allows Hartree-Fock \cite{29,32} or equivalent approaches (such as VMFT) to reproduce the system equation of state outside the critical region. We have checked that the equation of state of a homonuclear weakly interacting 2D Bose gas found from VMFT closely matches the Monte-Carlo results of \cite{31}, except very close to the critical point. However, while VMFT predicts accurately where the boundaries are, any \( T \neq 0 \) transition to superfluid fluid in 2D calculated via VMFT is first order, as seen in Fig. 3 (the N-MSF transition is very weakly first order due to the small polariton mass). The actual transition will be instead of BKT type, but such critical properties are beyond the reach of the VMFT approach used here. In the 3D homonuclear case, other approaches such as applications of the Nozières-Schmitt-Rink approximation \cite{33} have been considered, predicting second order transitions \cite{6}.

Figure 3 shows the phase diagram both vs \( \delta \) at fixed \( T \) (top panels) and vs \( T \) at fixed \( \delta \) (bottom panels). In the top panels, the main new features introduced by finite \( T = 0.05 \text{ meV} \) are the existence of a finite critical density for the normal state and the extension to arbitrarily large detuning of the phase separated region as discussed above. Because the N-MSF transition is now first order, the critical end-point at \( T = 0 \) is replaced by a triple point. At yet higher temperatures, the triple point moves to higher \( \delta \) and eventually merges with the tricritical point. Of more relevance to experiments, plotting the phase diagram vs temperature one sees that for \( \delta = 25 \text{ meV} \), the MSF phase survives up to \( T = 0.38 \text{ meV} \) (4.4 K). The density dependence of the N-MSF boundary is of the same order of magnitude as the naive expectation \( k_B T_c \sim n/m_m \). At yet larger detunings the MSF phase can extend to higher densities and thus higher temperatures.

Conclusions To conclude, microcavity polaritons appear an ideal system to explore collective pairing phases of bosons. In particular, in addition to the standard polariton superfluid phase, where both polaritons and bipolaritons are characterised by off-diagonal (quasi-)long-range order, we highlight a new phase which displays molecular superfluidity (MSF), i.e., order for bipolaritons but not for polaritons. This phase covers an increasing region of the phase diagram at either larger cavity-exciton detunings or lower temperatures. While for the GaAs parameters considered here we predict the MSF phase to survive up to \( T \sim 4 \text{ K} \) at a cavity-exciton detuning \( \delta = 25 \text{ meV} \), this temperature can be higher for materials with larger Rabi splitting, such as ZnO \( \cite{34} \).

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FIG. 3. (Color online) Finite temperature phase diagrams with the same notation, color scheme and GaAs parameters as in Fig. 2. The critical end-point of Fig. 2 is now replaced by a triple point (purple square). Temperature is fixed to \( k_B T = 0.05 \text{ meV} \) in the top panels, while detuning is \( \delta = 25 \text{ meV} \) in the bottom ones.
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