# Reaction Driven Convection around a Stably Stratified Chemical Front

J. D'Hernoncourt,[1,*] A. Zebib,[2,†] and A. De Wit[1,‡]

[1]*Service de Chimie Physique et Biologie Théorique CP 231, Université Libre de Bruxelles, 1050 Brussels, Belgium*
[2]*Mechanical and Aerospace Engineering, Rutgers University, Piscataway, New Jersey 08854-8058, USA*

(Received 16 December 2005; published 18 April 2006)

A vertical stratification of a light and hot fluid over a heavy and cold one is expected to be stable with regard to buoyancy-driven convection. Here we show that chemical reactions can trigger convection around chemical fronts even in cases where concentration and heat both contribute to a stable density stratification. The balance between intrinsic thermal and solutal density gradients initiated by a spatially localized reaction zone and double diffusive mechanisms are at the origin of a new convective instability, the mechanism of which is explained by a displaced particle argument. Linear stability analysis of a reaction-diffusion-convection model confirmed by nonlinear simulations delimits the instability region in the parameter space spanned by the thermal and solutal Rayleigh numbers. Experimental systems in which to test our theoretical predictions are proposed.

DOI: 10.1103/PhysRevLett.96.154501 PACS numbers: 47.70.Fw, 47.20.Bp, 47.55.P−, 82.40.Ck

Dynamic instabilities related to compositional and thermal density gradients across the interface separating two miscible fluids are known to affect the Earth's core-mantle boundary [1], lunar core dynamo [2], ocean and atmosphere flows [3], as well as contaminant spreading [4] in aquifers, for instance. Common understanding of the origin of the convection involved in such applications is that typically hot fluids rise and compositionally dense solutions sink. Double-diffusive or thermohaline phenomena can also play a role when compositional and thermal density stratifications are of opposite signs [5,6]. Furthermore, geological, environmental, and industrial flows usually involve chemical reactions, for example, in oil biodegradation, radioactive decomposition, geochemical transformations, or combustion processes. To examine how chemical reactions can affect the onset of convection and trigger new modes of instabilities, we consider the simple model of an autocatalytic reaction-diffusion (RD) front propagating in a porous medium. Chemical fronts are ubiquitous in biological [7], chemical [8], physical [9], and environmental [10] systems. Because of compositional and thermal differences between products and reactants, these fronts are susceptible to intrinsic Rayleigh-Taylor [8,11] and double-diffusive [5,12] instabilities. They thus present an ideal model system to analyze self-organized chemo-hydrodynamic patterns.

We show here that even in the case of a statically stable density gradient across chemical fronts propagating vertically in the gravity field, convection can be triggered by a delicate coupling between the thermal and solutal gradients driven by the reaction and double-diffusive mechanisms. Thanks to a linear stability analysis (LSA) of a simple reaction-diffusion-convection (RDC) model, we identify a new mode of instability of statically stable arrangements and propose a hypothesis based on a displaced particle argument. Nonlinear simulations confirm the prediction of the LSA.

We consider a two-dimensional vertical porous medium or thin Hele-Shaw cell (two glass plates separated by a thin gap width) of infinite extent saturated with reactants. An autocatalytic RD front propagates downward with a velocity $v$ along direction $x$ aligned with the gravity field, $y$ denoting the transverse direction. In a coordinate system ($z = x - vt, y$) moving with the RD speed $v$ and attached to the front located at $z = 0$ (see Fig. 1), the dynamics of the system in the presence of possible flows is described by the following equations:

$$\underline{\nabla} \cdot \underline{u} = 0, \tag{1}$$

$$\underline{\nabla} p = -\frac{\mu}{K}\underline{u} + \rho(c, T)\underline{g}, \tag{2}$$

$$\rho = \rho_0[1 - \alpha_T(T - T_0) - \alpha_c(c - c_0)], \tag{3}$$

$$\frac{\partial c}{\partial t} - v\frac{\partial c}{\partial z} + \underline{u} \cdot \underline{\nabla} c = D_c \nabla^2 c - f(c), \tag{4}$$

$$\frac{\partial T}{\partial t} - v\frac{\partial T}{\partial z} + \underline{u} \cdot \underline{\nabla} T = D_T \nabla^2 T - \frac{\Delta H}{\rho_0 c_p} f(c). \tag{5}$$

The velocity field $\underline{u}$ of the incompressible flow is described by the 2D Darcy's law (2); $p$ is the pressure while $K$ is the permeability of the porous medium (given in a Hele-Shaw cell of gap width $a$ by $K = a^2/12$). The traveling chemical front is the base state of the reaction-diffusion convection Eq. (4) for the concentration $c$ of the solute that affects the density $\rho$ [Eq. (3)]. The exothermic chemical reaction triggers a temperature $T$ distribution also affecting $\rho$ and governed by the energy balance in Eq. (5). The thermal and concentration expansion coefficients, $\alpha_T$ and $\alpha_c$, are taken positive so that the products of the reaction behind the front are lighter than the reactants ahead of it due to both thermal and solutal contributions of $T$ and $c$ to the density. Here $\Delta H$, the heat of the reaction, is

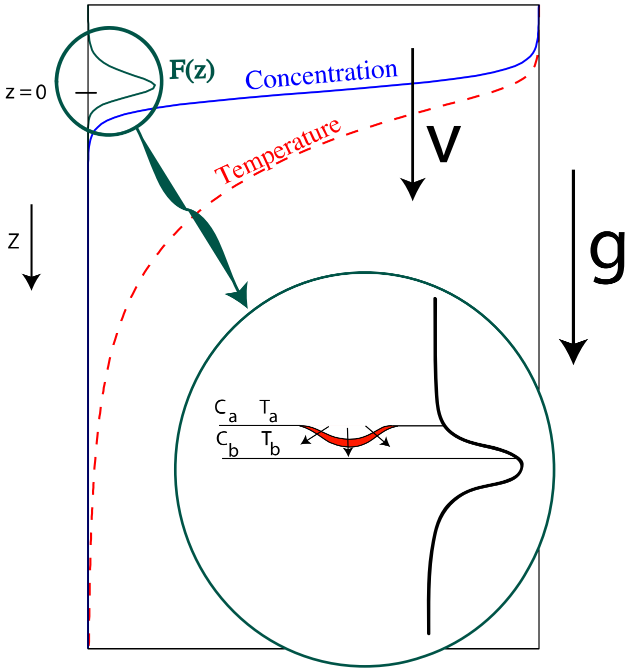

FIG. 1 (color online). Base concentration and temperature profiles of an exothermic reaction front descending in the gravity field with the corresponding zoom on the spatially varying reaction rate function $F(z)$. A physical argument based on the behavior of a displaced particle predicts local instability of the downward propagating exothermic front where $dF/dz > 0$.

negative as we consider an exothermic reaction. The molecular diffusion coefficient $D_c$, the thermal diffusivity $D_T$, the viscosity $\mu$, as well as the reference density $\rho_0$ of the solvant and the specific heat of water $c_p$ are taken constant. Finally let us take $f(c) = \gamma(c - c_0)(c - c_1)(c + c_2)$ as a model dimensional kinetic term known to yield chemical fronts corresponding to a RD solution for which the stable steady state $c_1$ of the kinetics corresponds to the products invading the unstable steady state $c_0$ which stands for the reactants [8,11,13]; $c_2$ is model dependent and $\gamma$ is the kinetic constant.

The diffusive state determines the prevailing concentration gradient, rates of reaction, and propagation and, hence, the important scales of the problem. These are $\Delta c = c_1 - c_0$ for $c - c_0$, $\tau = (\gamma \Delta c^2)^{-1}$ for time, $U = \sqrt{D_c/\tau}$ for velocity, and $l = \sqrt{D_c \tau}$ for length. The initial temperature ahead of the wave is $T_0$, that behind the wave is then the adiabatic value $T_0 + \Delta T$, where $\Delta T = -\Delta H \Delta c/\rho_0 c_p$. We scale $T - T_0$ by $\Delta T$ and incorporate the hydrostatic pressure gradient $\rho_0 \underline{g}$ in the pressure term. The nondimensional equations associated with the problem are then

$$\underline{\nabla} \cdot \underline{u} = 0, \tag{6}$$

$$\underline{\nabla} p = -\underline{u} + (R_T T + R_c c)\underline{i}_z, \tag{7}$$

$$\frac{\partial c}{\partial t} - v\frac{\partial c}{\partial z} + \underline{u} \cdot \underline{\nabla} c = \nabla^2 c + F(c), \tag{8}$$

$$\frac{\partial T}{\partial t} - v\frac{\partial T}{\partial z} + \underline{u} \cdot \underline{\nabla} T = \mathrm{Le}\nabla^2 T + F(c), \tag{9}$$

where $F(c) = c(1 - c)(c + d)$, the Lewis number $\mathrm{Le} = D_T/D_c$, $\underline{i}_z$ is the unit vector in the $z$ direction, and $d = (c_0 + c_2)/\Delta c > 0$. The thermal and solutal Rayleigh numbers are defined as

$$R_T = \frac{-g\alpha_T K \Delta T}{\nu U}, \qquad R_c = \frac{-g\alpha_c K \Delta c}{\nu U}, \tag{10}$$

where $\nu = \mu/\rho_0$ is the kinematic viscosity. In absence of flow ($\underline{u} = 0$), Eqs. (8) and (9) admit a reaction-diffusion traveling front solution with $c, T \sim 0$ as $z \longrightarrow \infty$ and $c, T \sim 1$ as $z \longrightarrow -\infty$.

Linear stability analysis is then employed to study the delicate balance between the thermal and solutal density gradients driven by the reaction and differential diffusion of mass and heat for $\mathrm{Le} > 1$ in the onset of convection. We consider therefore the 2D transverse instability of the basic front solution $c_0(z)$, $T_0(z)$ traveling at RD speed $v$ and of the pressure profile $p_0(z)$ that are the solution of Eqs. (6)–(9) when the fluid velocity $\underline{u} = 0$. We introduce perturbations for the concentration, the temperature, the pressure, and the fluid velocity as $c = c_0(z) + \delta c$, $T = T_0(z) + \delta T$, $p = p_0(z) + \delta p$, $\underline{u} = \delta \underline{u}$, where $\delta \underline{u} = (\delta u, \delta w)$. Inserting these expressions into (6)–(9) and linearizing around the base state, seeking solutions in terms of normal modes, i.e., writing $(\delta c, \delta T, \delta p, \delta u, \delta w) = \{\bar{c}, \bar{T}, \bar{p}, \bar{u}, \bar{w}\}(z)\exp^{(iky+\sigma t)}$, where $k, \sigma$ are the wave number and growth rate of the perturbations, we get

$$\bar{u}' + ik\bar{w} = 0, \tag{11}$$

$$\bar{p}' = -\bar{u} + R_T \bar{T} + R_c \bar{c}, \tag{12}$$

$$ik\bar{p} = -\bar{w}, \tag{13}$$

$$\sigma\bar{c} - v\bar{c}' + c_0'\bar{u} = \bar{c}'' - k^2\bar{c} + \left.\frac{dF}{dc}\right|_{c_0} \bar{c}, \tag{14}$$

$$\sigma\bar{T} - v\bar{T}' + T_0'\bar{u} = \mathrm{Le}\bar{T}'' - \mathrm{Le}k^2\bar{T} + \left.\frac{dF}{dc}\right|_{c_0} \bar{c}, \tag{15}$$

where prime means derivative with regard to $z$. Differentiating (11) and (13) once with regard to $z$ and substracting the two equations after having multiplied the second one by $ik$, gives $\bar{u}'' + k^2\bar{p}' = 0$, which combined to (12) allows us to eliminate $\bar{w}$ and $\bar{p}$ and gives

$$\sigma\bar{c} - v\bar{c}' + c_0'\bar{u} = \bar{c}'' - k^2\bar{c} + \left.\frac{dF}{dc}\right|_{c_0} \bar{c}, \tag{16}$$

$$\sigma\bar{T} - v\bar{T}' + T_0'\bar{u} = \mathrm{Le}(\bar{T}'' - k^2\bar{T}) + \left.\frac{dF}{dc}\right|_{c_0} \bar{c}, \tag{17}$$

$$\bar{u}'' - k^2\bar{u} = -k^2(R_T\bar{T} + R_c\bar{c}), \tag{18}$$

with $\bar{c}, \bar{T}, \bar{u} \sim 0$ as $z \longrightarrow \pm\infty$. The system is unstable towards buoyancy-driven hydrodynamic perturbations as soon as $\mathrm{Re}[\sigma(k)] > 0$ for any given $k$. We solve (16)–(18) using both a pseudospectral Chebyshev method and a spatial discretization method. For each $R_T$, and for each $k$, $R_c$ is calculated so that $\max(\mathrm{Re}\{\sigma(R_c, k, \mathrm{Le}, R_T)\}) = 0$. The critical solutal Rayleigh number $R_{c_{\mathrm{cr}}}$ and the critical wave number $k_{\mathrm{cr}}$ are determined by minimization over $k$. The case where $R_c$ and $R_T$ are both positive corresponds to light and hot (exothermic reaction) products invading heavy and cold reactants *upwards* which is always an unstable situation. The double-diffusive thermohaline mechanisms occur in the two quadrants where $R_c$ and $R_T$ have opposite signs. We focus here on the quadrant where both $R_c$ and $R_T$ are negative, which corresponds to light and hot products invading heavy and cold reactants *downwards* which is a statically stable density stratification from both solutal and thermal points of view. Intuitively, this situation is expected to be always stable allowing only for propagation of planar chemical fronts. Stationary stability boundaries for $R_c \leq 0$, $\mathrm{Le} = 3$ or 10, and $d = 0.0021$ are shown in Fig. 2. The statically stable flow is unexpectedly unstable for $R_c \leq 0$ and $R_T < R_{T_{\mathrm{cr}}} < 0$. To understand this, let us first examine the case $R_c = 0$ for which the concentration jump across the front does not affect the density which varies then only with temperature. One would expect, in that case, the system to be stable when $R_T < 0$, as it corresponds to a light over heavy arrangement due to an exothermic reaction ($\Delta T > 0$). However, according to linear theory the system is unstable with $\mathrm{Le} = 10$ for $R_T < R_{T_{\mathrm{cr}}} = -9.51$. For instance with $R_T = -20$, we find $k_{\mathrm{cr}} = 0.06$ and $\sigma_{\mathrm{cr}} = 0.015$.

A physical explanation of this counterintuitive gravitational instability emerges from an examination of the basic profiles in Fig. 1. Let us consider that, in the region where $F[c(z)]$ increases (i.e., $dF/dz > 0$), a particle at concentration $c_a$ and temperature $T_a$ close to the product region is displaced downward in a more reactive zone, where $c = c_b$ and $T = T_b$ with $c_a > c_b$ and $T_a > T_b$ as the exothermic reaction is more advanced in zone $a$ than in zone $b$. Because $\mathrm{Le} > 1$, i.e., because heat diffuses faster than mass, the particle's temperature quickly tends to the temperature $T_b$ of its surroundings while slower species diffusion allows it to keep its concentration close to $c_a$. Thus the energy source in the displaced particle is smaller than that of the surroundings because $F(c_a) < F(c_b)$. Hence it will not heat up as quickly as its neighborhood (recall $\Delta T > 0$) and is thus cooler; it may continue to sink, driving an instability. This new mechanism of instability finds thus its origin in the existence of a localized zone of reaction and in the differential diffusion of heat and mass. It exists only for $\mathrm{Le} > 1$ as confirmed by the linear stability analysis. Our physical argument also explains the whole $R_c \leq 0$ lower branch of the stability boundary of Fig. 2. In the cases where $R_c < 0$, the system is more statically stable as concentration changes now give an additional solutal contribution to the light over heavy density stratification. Nevertheless, the instability mechanism remains the same but the exothermicity required to trigger convection becomes larger. Therefore, as $-R_c$ becomes larger, larger—in absolute value—and negative $R_T < R_{T_{\mathrm{cr}}} < 0$ are required to make the argument operative. The instability thus magnifies with a larger $-R_T$ and larger $\mathrm{Le} > 1$ since, in dimensionless units, the density jump across the front is $(gK/\nu U)(\rho/\rho_0) = R_T T + R_c c$, and small changes in $T$ are more effective in changing the density at larger negative $R_T$ for a given $R_c$, as is also supported by linear stability calculations. Because the region with $dF/dz > 0$ lies above a region with $dF/dz < 0$, it follows that a region of local stability subdues the region of local instability as is further confirmed by analysis of the critical eigenfunctions of the linear stability analysis. Indeed, as seen in Fig. 3, the critical eigenfunctions (with the infinity norm = 1) show that the disturbance is largest above and ahead of the advancing wave.

Nonlinear simulations of Eqs. (6)–(9) confirm the prediction of this new instability. Figure 4 shows the nonlinear dynamics of an unstable exothermic downward moving front for $\mathrm{Le} = 10$, $R_c = 0$, and $R_T = -20$. For $R_T > -9.51$, the planar front is stable and travels downward

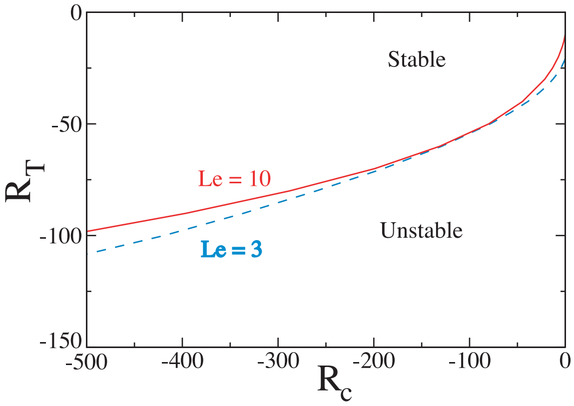

FIG. 2 (color online). Stability boundaries for $d = 0.0021$, $R_c \leq 0$, $R_T \leq 0$, $\mathrm{Le} = 3$ and 10. For $R_c = 0$, the flow is unstable when $R_T < -20.67$ ($\mathrm{Le} = 3$) and $R_T < -9.51$ ($\mathrm{Le} = 10$).

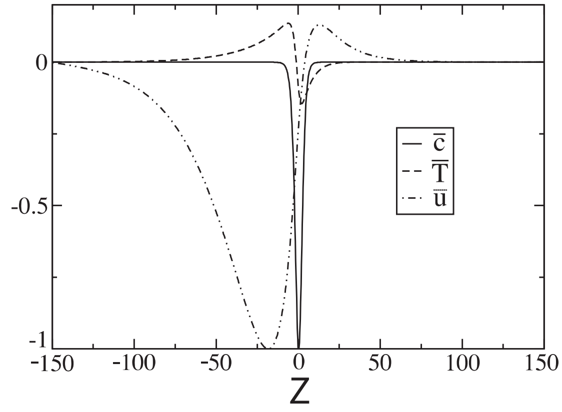

FIG. 3. Most unstable linear eigenfunctions with $R_c = 0$ and $R_T = -20$ ($\mathrm{Le} = 10$).

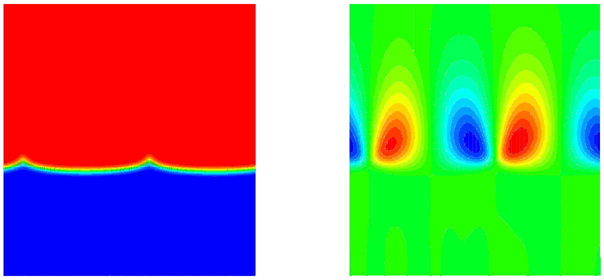

FIG. 4 (color online). Nonlinear simulations of an unstable descending front for Le = 10, $R_c = 0$, $R_T = -20$, $d = 0.0021$ in a system of width 200 with lateral periodic boundary conditions showing the spatially modulated concentration field (left: the products on top at $c = 1$ invading downwards the reactants at $c = 0$) and the stream function (right: light and dark signify, respectively, clockwise and counterclockwise rotations) at time $t = 640$. The wavelength of the pattern is in good agreement with the one predicted by the LSA and the flow is seen to push and deform the isoconcentration lines.

without any deformation. On the contrary, below the critical value $R_{T_{\rm cr}}$, cellular deformations triggered by convective rolls appear, but remain of small and constant amplitude as the buoyancy-driven convection is subdued downwards by the stable region where $dF/dz < 0$. The nonlinear dynamics is therefore quite different from the one observed for Rayleigh-Taylor fingering of chemical fronts [14–16] (when $R_c$, $R_T$ are both positive) but looks analogous to some double-diffusive dynamics previously analyzed numerically for the case where $R_c$ and $R_T$ have opposite signs [12]. To test our theoretical prediction, we propose that a suitable experimental candidate be the downward propagation of exothermic ($R_T < 0$) chemical fronts for which products are lighter than reactants ($R_c < 0$) in insulated Hele-Shaw cells. A classification of the various autocatalytic reactions suggests that reactions such as the iodate-arsenous acid (IAA) [17], iodide-nitric acid [18], and iodate-sulfite [19] systems where the solutal and thermal effects are cooperative could be typical possible candidates. For typical values of parameters of the IAA reaction [11] and taking $\alpha_T = 2.57 \times 10^{-4}$ K$^{-1}$ with $\Delta T = 0.5$ K [20], a gap width $a = 1$ mm, and $\alpha_c \Delta c \sim 1.35 \times 10^{-4}$ [21], we find $R_c = -3.8$ and $R_T = -3.6$. Clearly, the new instability will probably not be effective for such typical experimental conditions in the IAA reaction. However, increase of the absolute value of the Rayleigh numbers can be achieved by increasing the gap width $a$ of the cell, changing initial concentrations and choosing more exothermic reactions. In addition, typically Le $\sim$ 70 for autocatalytic reactions in aqueous solutions [20], a larger value which should facilitate the onset of the instability. Let us note that temperature changes across autocatalytic fronts are typically small enough (of the order of a few K) for our assumption of a temperature independent kinetic constant to hold. The new instability might also be operational in the case of combustion fronts traveling downward in porous media, for which products are hotter and lighter than the heavy and cold fuel. In this case, the effects of the Arrhenius dependence of the kinetic constant on temperature should certainly be evaluated. Eventually, the new proposed instability should now be kept in mind to understand the origin of possible modes of convection around localized reactive zones as encountered in the applications mentioned in the introduction.

J. D. is supported by FRIA (Belgium). A. D. acknowledges ESA, Prodex (Belgium), and the Communauté française de Belgique (ARC programme) for financial support. A. Z. thanks FNRS for a travel grant and ACS-PRF for partial support.

---

*Electronic address: jdhernon@ulb.ac.be

†zebib@rutgers.edu

‡adewit@ulb.ac.be

[1] A. Davaille, Nature (London) **402**, 756 (1999).

[2] D. R. Stegman, A. M. Jellinek, S. A. Zatman, J. R. Baumgardnerk, and M. A. Richards, Nature (London) **421**, 143 (2003).

[3] S. Rahmstorf, Nature (London) **421**, 699 (2003).

[4] I. Dror, T. Amitay, B. Yaron, and B. Berkowitz, Science **300**, 950 (2003).

[5] J. S. Turner, *Buoyancy Effects in Fluids* (Cambridge University Press, Cambridge, England, 1973).

[6] R. W. Schmitt, J. R. Ledwell, E. T. Montgomery, K. L. Polzin, and J. M. Toole, Science **308**, 685 (2005).

[7] J. D. Murray, *Mathematical Biology* (Springer, Berlin, 1993), 2nd ed.

[8] I. R. Epstein and J. A. Pojman, *An Introduction to Nonlinear Chemical Dynamics* (Oxford University, Oxford, 1998).

[9] A. G. Merzhanov and E. N. Rumanov, Rev. Mod. Phys. **71**, 1173 (1999).

[10] P. Ortoleva, *Geochemical Self-Organization* (Oxford University, Oxford, 1994).

[11] A. De Wit, Phys. Rev. Lett. **87**, 054502 (2001).

[12] S. Kalliadasis, J. Yang, and A. De Wit, Phys. Fluids **16**, 1395 (2004).

[13] A. Hanna, A. Saul, and K. Showalter, J. Am. Chem. Soc. **104**, 3838 (1982).

[14] A. De Wit, Phys. Fluids **16**, 163 (2004).

[15] M. Böckmann and S. C. Müller, Phys. Rev. E **70**, 046302 (2004).

[16] T. Bánsági, Jr., D. Horváth, and Á. Tóth, J. Chem. Phys. **121**, 11 912 (2004).

[17] J. A. Pojman, I. R. Epstein, T. J. McManus, and K. Showalter, J. Phys. Chem. **95**, 1299 (1991).

[18] I. P. Nagy, A. Keresztessy, J. A. Pojman, G. Bazsa, and Z. Noszticzius, J. Phys. Chem. **98**, 6030 (1994).

[19] A. Keresztessy, I. P. Nagy, G. Bazsa, and J. A. Pojman, J. Phys. Chem. **99**, 5379 (1995).

[20] B. F. Edwards, J. W. Wilder, and K. Showalter, Phys. Rev. A **43**, 749 (1991).

[21] M. Böckmann and S. C. Müller, Phys. Rev. Lett. **85**, 2506 (2000).