PHYSICAL REVIEW B **109**, 045125 (2024)

# Cavitation in electron fluids and the puzzles of photoemission spectra in alkali metals

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(Received 30 July 2023; revised 19 November 2023; accepted 19 December 2023; published 12 January 2024)

Angle-resolved photoemission spectra of alkali metals exhibit a puzzling, nondispersing peak in the apparent density of states near the Fermi energy. We argue that the holes left behind a significant fraction of photoejected electrons are not wavepacketlike objects used to describe excitations of an equilibrium Fermi liquid, but instead, are relatively localized entities resulting from a photon-induced cavitation in the electron fluid. At the same time, these special localized holes can be thought of as vacancies in a transient Wigner solid. The corresponding contribution to the photoemission current is nondispersive and is tied to the Fermi level; it exhibits certain similarities to photoemission from localized core orbitals such as the presence of recoil currents. Calculated spectra are consistent with experiment. We briefly discuss the present findings in the context of quantum measurement.

DOI: 10.1103/PhysRevB.109.045125

Angle-resolved spectra of sodium and potassium exhibit a distinct, peculiar peak near the Fermi energy, within a substantial range of photon energies [1–3]. This peak does not move with the photon's energy and is narrower than the momentum-conserving, dispersing peak. The intensity of the nondispersing peak is substantial even when the initial state of the electron for a *vertical* transition would be above the Fermi energy. Furthermore, in potassium, it is the dispersing peak that is often hard to resolve [2], while the anomalous peak is clearly visible. The Fermi surfaces in Na and K are particularly simple—nearly spherical in fact—and fully contained within the first Brillouin zone [4]; thus, no sharp features in the density of states are expected. Surface states do not seem to be at play either, since the resulting peaks, if any, would not be strictly tied to the Fermi energy.

Mahan and coworkers [5,6] argued that the peculiar photoemission peak is a wing of the dispersing peak when the latter is centered at electron energies above the Fermi surface; the broadening is due to interactions and their interplay with the free surface. Detailed estimates [5,6] yield photoemission spectra that are qualitatively similar to some of those observed in sodium for photon energies corresponding to the $(1, 1, 0) \rightarrow (3, 3, 0)$ transitions, but lack the anomalous "balcony peaks" seen in the adjacent range of photon energies that correspond to the $(1, 1, 0) \rightarrow (-4, -4, 0)$ transitions [7]. The situation with potassium is even less conclusive [8].

Overhauser [9] proposed, alternatively, that the anomalous peak results from a static charge-density wave (CDW) [10]. Sodium does become close packed at sufficiently low temperatures, thus implying, potentially, a structural instability. Still, experimental studies [11] decisively rule out the presence of a static CDW, consistent with recent studies [12] according to which the Fermi surface of sodium is relatively insensitive to the detailed structure of the crystal. A detailed review of previous work can be found in Ref. [3].

Here we argue that the puzzling photoemission peak is caused by nonadiabatic effects that are not amenable to perturbative expansions around the equilibrium state of the electron assembly. The frequency $\omega_{\mathrm{ph}}$ of the incoming photon is much greater than the typical rates of electronic motions $\omega_{\mathrm{ph}} \gg v_F/a$, where $v_F$ and $a$ are the Fermi velocity and lattice spacing, respectively. Thus, one expects a response similar to giant resonances seen in nuclear spectra [13], though spanning a relatively narrow spectral range because the plasma oscillations are in their ground state at the energies in question. To quantify the photocurrent one must compute the one-particle density function $\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)$ of the electron. The momentumlike argument $\boldsymbol{k}$ of the Wigner transform of the latter density matrix $\rho(\boldsymbol{r}, \boldsymbol{k}) = \int d^3(\boldsymbol{r}_2 - \boldsymbol{r}_1)\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)e^{-i\boldsymbol{k}(\boldsymbol{r}_2 - \boldsymbol{r}_1)}$ essentially corresponds to the momentum $\boldsymbol{k}$ of the electronic wavepacket, while the dependence of the latter Wigner transform on the center-of-mass variable $\boldsymbol{r} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$ reflects the spatial variation of the corresponding charge density. Landau's Fermi-liquid theory corresponds to

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the limit of this spatial variation being very slow and describes the quasiequilibrium response of the electron fluid [14]. Conversely, high-frequency motions of the electron fluid $\omega > v_F/a$ are heavily hybridized with the plasmons via Landau damping [15,16], whereby the charge density varies on length scales comparable to the lattice spacing. This, then, suggests a possibility that in addition to extended electron wavepackets characteristic of the equilibrium, Fermi-liquid behavior, the fast photons can also knock out individual electrons in the form of localized entities.

In fact, just this latter possibility is the only one that could be realized classically. For concreteness, we consider a setup in which a compact region of a Newtonian fluid changes its velocity instantaneously from zero to $v_0$, as it would in response to a sudden perturbation applied to the region. Specifically for a spherically shaped region of radius $R$, the reactive force of the surrounding fluid depends on time in the following manner, per the solved problem 24.9 from Ref. [17]:

$$F(t) = 6\pi\eta R v_0[1 + R\sqrt{\rho/t\pi\eta}] + \frac{2\pi}{3}\rho R^3 v_0 \delta(t), \tag{1}$$

where $\eta$ and $\rho$ are the viscosity and density, respectively, of the fluid. The intensity of dissipation is given by $v_0 F(t)$. Of interest here is the nonadiabatic contribution $\propto t^{-1/2}$ to the viscous part of the response, which represents a characteristic hydrodynamic tail and, tellingly, scales with the area of the sphere. The corresponding loss spectrum amounts to an inverse-square root peak $\omega^{-1/2}$, which diverges at low energies. The latter low energies would correspond to the vicinity of the Fermi energy in an electron fluid.

This notion prompts us to inquire whether a classical-like photoemission from localized electronic states can occur—as a bulk phenomenon—in quantum fluids made of electrons. It would suffice for such localization, if any, to be only transient, because of the short duration of photoemission events. Localization of particles in the bulk simply means the particles have formed a solid. A solid is a state of broken translational symmetry in which the particles are each assigned to specific sites in space; the particles perform vibrational motions around their respective sites [18]. The notion of a solidlike component to the wavefunction of an electron fluid may seem surprising, at first. We recall, however, that the electric current, if any, is exclusively due to the electrons' ability to tunnel through classically forbidden, internuclear regions. One may associate the time spent in classically forbidden regions with the liquid component of the wavefunction. The remaining time electrons perform bound motions within the classically allowed regions, each region assigned to a corner of a lattice. These motions correspond to a solidlike component of the overall wavefunction and lower translational symmetry, even if transiently.

Let us construct the solidlike component for a monovalent solid, which houses one electron per site. Begin with a Wigner solid of the jellium, whereby the electrons are sufficiently far apart and the positive charge is uniformly distributed [13]. Imagine a process where we uniformly compress the system. To compensate for the concomitant increase in the kinetic energy of the electrons, we redistribute the positive charge so as to create a local excess of positive charge at the lattice sites of the original Wigner solid; the sites will become the actual atomic nuclei at the end of the compression process. (The number of sites remains constant during the process. The pertinent Wigner solid does not have to be strictly periodic [19], thus allowing for vibrational displacements of the nuclei and a variety of cell shapes.) Since the barriers in the crystal field that separate distinct lattice sites are finite, a fluid component to the electronic wavefunction will appear eventually. Because the number of electrons per site remains constant, the "compression construct" represents a continuous process; thus the solidlike and the liquidlike components of the electron assembly coexist, when both are present. The two phases remain in mutual equilibrium, while their respective mole fractions depend on the extent of the compression. This effective coexistence of two distinct phase behaviors in the very same region of space is analogous to what happens during the crossover to activated transport in liquids [18,20], when metastable structures begin to form. Translational symmetry is broken on time scales shorter than the lifetimes of the metastable structures but is restored on longer times. Note a coexistence of liquid and solid behaviors, respectively, has been reported for Hartree-Fock solutions in jellium [21].

Within a single-electron picture, the localized states can be thought of as bound states that individual electrons transiently create for each other on short times. (This is in addition to the potentials due to the ionic cores, of course). The corresponding energy levels are, however, not well defined because the electrons are not static. The resulting line broadening is analogous to what happens during spectral diffusion [22,23], since the leading contribution of local charge fluctuation to the shift of on-site energies is dipole-dipole, owing to charge conservation. An electron moves from site to site at rate $v_F/a$, while inducing a local dipole moment change $ea$. These effective dipoles are uniformly distributed at concentration $n \sim 1/a^3$. Contributions of individual dipoles to the overall spectral shift are roughly $\sim(ae)^2/r^3 \equiv A/r^3$, each fluctuating at rate $\gamma \sim v_F/a$. The width of the corresponding spectral line increases with time [22,23] at the rate $\sim nA\gamma = (e^2/a)(v_F/a) \simeq E_F(v_F/a)$. The broadening on the time scale $\pi/\omega_{\text{ph}}$ of a photoemission event is, then, roughly $E_F(v_F/a\omega_{\text{ph}}) \sim 10^{-1}E_F$, consistent with experiment. The solidlike response will be progressively diminished for slower experimental probes, the overall response ultimately approaching that of a Fermi liquid.

The liquidlike and solidlike contributions to the wavefunction correspond to two distinct, nonoverlapping components of the overall wavefunction characterized by pronounced localization in the momentum and direct space, respectively. Indeed, already the ground state of an electron fluid in the presence of a scattering potential is orthogonal to the ground state in the absence of the potential [24]. Very generally, a solid must be separated by a discontinuous transition from the fluid state [18,25,26]. Consequently, the two phases occupy disconnected portions of the phase space. Because of this lack of overlap between the liquidlike and solidlike contributions to the overall wavefunction, we may present the total intensity of the photocurrent as a weighted sum of the respective intensities of those two contributions:

$$I(E) = x_{\text{liq}} I_{\text{liq}}(E) + x_{\text{sol}} I_{\text{sol}}(E), \tag{2}$$

where $E$ is the energy of the detected electron and $x_{\text{liq}} + x_{\text{sol}} = 1$, by construction.

To estimate the solidlike contribution $I_{\rm sol}(E)$ to the photocurrent, we first note that in the spectral range in question [1–3], no plasmons are produced. Indeed, the plasmon frequency in Na, 5.7 eV [27], is significantly greater than the Fermi energy, 2.8 eV [1]. In other words, our transient electron solid recoils as a whole. We will approximate this solid as harmonic. The coordinates of any lattice fragments thus obey the Gaussian distribution [28]; denote the corresponding variance with $\delta r^2$. The probability for the solid to recoil as a whole, after the fragment absorbs or emits momentum $q$, is given by $e^{-q^2(\delta r)^2}$, a notion used in Mössbauer spectroscopy [29]. Conversely, the expression $e^{-q^2(\delta r)^2}$ can be viewed, up to a multiplicative factor, as the probability distribution for a local harmonic degree of freedom $\delta r$ that is compatible with a zero-phonon recoil of the lattice at momentum $q$. The corresponding ground-state wavefunction is $\psi_q(\boldsymbol{r}) = (q^2/\pi)^{3/4}\, e^{-q^2r^2/2}$, where $q$ represents a parameter. We thus estimate the photocurrent $I_{\rm sol}(E)$, due to localized initial states, by first evaluating the current using the function $\psi_q(\boldsymbol{r})$ as the initial state, for a given value of $q$, and then averaging over a pertinent distribution of $q$. The set of recoil values $q$, due to emitting a localized electron, should be consistent with the rate of spatial variation of the valence electrons. At values $k_f$ of the momentum of the outgoing electron pertinent to Plummer *et al.*'s experiment $k_f \sim 3k_F$, the valence wavefunction can be largely approximated by the frontier atomic orbital $\psi_{\rm fr}$ on an individual center. (For Na, this would be the 3$s$ orbital.) Thus we use the magnitude squared of the normalized Fourier transform $|\widetilde{\psi}_{\rm fr}(q)|^2$, times $4\pi q^2$, as the probability distribution for the parameter $q$.

The (zero-plasmon) recoil due to the transient-solid component of the electron assembly causes a negligibly small shift of the photoemission spectrum, as does the recoil due to the pertinent nuclei. If it were not for the recoil due to the electron fluid, localized electrons would be all extracted near the Fermi energy, the latter nominally corresponding to a quiescent fluid devoid of currents, consistent with the classical limit considered above. This notion can be also formulated quantum mechanically, in an effective single-electron picture: Single-particle states for the extended and localized states tend to mutually repel [30,31], while the extended states form a continuous band. Our effective localized states—which note are not tied to lone pairs, impurity levels, or surface states etc.—are thus "pushed" outside of the continuous band. At the same time, there should be no gap between the delocalized and localized states either, because the two sets of states correspond, respectively, to a liquid and solid that coexist, as already mentioned. Consequently, the chemical potentials of the phases are mutually equal, which pegs the emission line for localized electrons near the Fermi energy of the electron liquid. Conversely, no such matching of the chemical potentials is expected in nonmonovalent metals, because there is no continuous process that converts a Wigner solid into a lattice with more than one electron per site. The resulting mismatch in the chemical potentials actually corresponds to the recoil energy of the electrons sharing the site with the photoejected electron. Thus we predict that in nonmonovalent metals, there will *also* be a photocurrent due to localized sources, but the energy of the outgoing electron will be down shifted, relative to the Fermi level, by the said recoil energy.

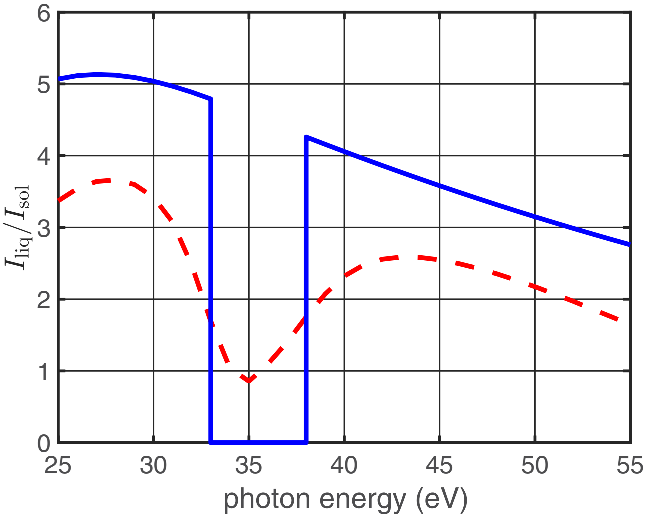

FIG. 1. The ratio of the integrated photocurrents from Eq. (3) as a function of the photon frequency without (solid line) and with (dashed line) line-broadening effects included.

The dispersing part of the photocurrent is, likewise, largely determined by the Fourier transform of the wavefunction of the atomic valence shell, but within a near vicinity of the momentum of the outgoing electron, according to a standard calculation [32–39] detailed in Supplemental Material [40]. When the broadening of the dispersing peak is neglected, one obtains a rather simple expression for the relative intensity of the liquid- and solidlike contributions to the photocurrent, at a given value of the photon frequency

$$\frac{I_{\rm liq}}{I_{\rm sol}} = \frac{\pi^{1/2}}{2}\,\frac{k_{f,\rm liq}^3}{k_{f,\rm sol}^3}\,\frac{|\widetilde{\psi}_{\rm fr}(k_{f,\rm liq})|^2}{\int_0^\infty \frac{dq}{q}\, e^{-k_{f,\rm sol}^2/q^2}\, |\widetilde{\psi}_{\rm fr}(q)|^2}. \tag{3}$$

Here, $k_{f,\rm liq}$ and $k_{f,\rm sol}$ denote the momentum for the outgoing electron extracted as a wavepacket and localized object, respectively. The two momenta are rather close numerically because the photon frequency is much greater than $E_F$. According to Eq. (3), the contribution of the localized electrons is distributed over a broad momentum range and, thus, should be suppressed but only several fold, relative to the momentum-conserving transitions, except when the latter transitions fall into the spectrally forbidden region. The result of the calculation, shown in Fig. 1 with the solid line, is consistent with this expectation.

The peak due to localized sources of photocurrent is intrinsically broadened owing to the short-lived nature of the effective confining potential due to the transient electronic solid, as already discussed. Smaller in magnitude, but significant methodologically is the broadening of the Fermi-energy peak due to recoil currents of the electron fluid. These currents must arise because a spatially uniform fluid is not the ground state of the electron assembly in the presence of a bounding potential due to the (photo-induced) localized hole. The recoil currents are entirely analogous to those arising during photoemission from a deep localized state. Under the latter circumstances, a sharp absorption line will broaden to become a skewed peak, the low-energy side of which is an integrable power divergence [41,42]:

$$I_{\mathrm{sol}}(E) \propto \frac{1}{(E-E_f)^{1-\alpha}}, \tag{4}$$

where

$$\alpha = 2\sum_l (2l+1)(\delta_l/\pi)^2 \tag{5}$$

and $\delta_l$ is the phase shift for scattering, due to the aforementioned local potential, at value $l$ of the angular momentum. As alluded to already, the majority of scattering in alkali metals occurs at $l=0$. If we assume, for simplicity, that the scattering is exclusively in the $l=0$ channel and that the Friedel sum rule [43] $1=(2/\pi)\sum_l(2l+1)\delta_l$ applies, we obtain $\delta_0=\pi/2$, thus yielding $\alpha=1/2$. This is the same exponent for the loss spectrum as in the classical limit of the Newtonian liquid considered earlier. Consistent with this notion, the phase shift $\pi/2$ corresponds to a purely viscous response, whereby for an oscillating signal $e^{i\omega t}$ the momentum transfer rate goes as $\eta(d/dt)e^{i\omega t}=\eta\,\omega\,e^{i(\omega t+\pi/2)}$. Still, one should generally expect scattering at $l>0$ as well, which will amount to deviations from the hydrodynamic result in Eq. (1).

Although the localized electron is extracted near the absorption edge, the present situation is distinct from the x-ray edge problem. There, the excited electron (hole) scatters from a core orbital right into the continuum perturbed by the excess local potential created by the excitation; thus the electron (hole) itself contributes to the recoil currents and, in turn, the overall response of the fluid [42,44]. Here, instead, the outgoing electron—which had been localized in the first place—does not itself contribute to the recoil currents. Thus, in contrast with the conventional edge problem, the recoil always results in a divergence at the spectrum's edge.

We estimate the weights $x_{\mathrm{liq}}$ and $x_{\mathrm{sol}}$ in Eq. (2) by comparing the times valence electrons spend in classically forbidden and allowed regions, respectively,

$$\frac{x_{\mathrm{liq}}}{x_{\mathrm{sol}}} \approx 4D\frac{t_{\mathrm{forbidden}}}{t_{\mathrm{allowed}}}, \tag{6}$$

where we have also included the transmission coefficient $D$ for the tunneling so as to account only for successful tunneling attempts. Because the occupied portion of the valence band in alkali metals is comparable in width to that of a free electron gas at the same density, one may assume that the potential energy barrier separating two nearest-neighbor sites is sufficiently narrow so that the shape of the potential energy maximum separating two nearest-neighbor ionic cores can be well approximated by an inverted parabola. Thus the time the electron travels one way under the barrier is given by $t_{\mathrm{forbidden}}=\pi/\omega^{\ddagger}$, where $\omega^{\ddagger}$ is the frequency of the motion within the parabola. We estimate the frequency $\omega^{\ddagger}$ by using the curvature of the Thomas-Fermi potential at distances corresponding to the midpoint between two nearest atoms in the lattice. The residence time in the classical region is determined by the plasmon frequency itself, $t_{\mathrm{allowed}}=\pi/\omega_p$, since this is the pertinent frequency for charge oscillations even on small lengthscales $\sim a$, in view of the dispersion $\omega_p(k)$ being relatively weak. We qualitatively estimate the transmission coefficient as the ratio of the band width for the electrons in the metal and free electrons: $D=m/m^*$. (We adopt $m^*/m=1.28$ for the effective mass of the electron relative to its free-particle value [45,46].) Indeed, the band width scales with the tunneling matrix element, while one should recover $D=1$ for free electrons. The factor 4 reflects that there are 4 internuclear spaces separating closest neighbors in the bcc lattice per nucleus. This yields $x_{\mathrm{liq}}/x_{\mathrm{sol}}\approx 1.85$.

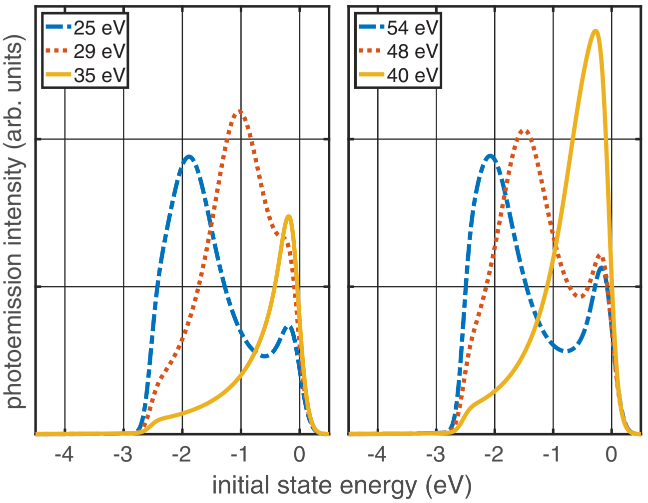

FIG. 2. Photoemission spectra from Eq. (2) data for sodium in the (1, 1, 0) direction for select values of photon frequencies indicated in the legend, to be compared with Fig. 2 from Ref. [1]. The electron energy is relative to the Fermi level. We set $\alpha=1/2$ in Eq. (4).

Thus we have argued that a substantial contribution to the overall electronic wavefunction is due to localized electrons. The photocurrent due to this contribution, per absorbed photon, is comparable to that stemming from the Fermi liquid. Spectrally, the photocurrent due to localized sources is tied to the Fermi level, apart from some broadening. Put together, the above notions then rationalize the puzzling Fermi-energy photoemission peak in alkali metals. We evaluate the photoemission spectra for sodium, shown in Fig. 2, to be compared with Fig. 2 of Ref. [1]. (Experimental spectra also contain a background due to a variety of processes [36], not considered here.) The extent of broadening of the dispersive line was chosen by hand to be similar to that seen in the experiment; the breadth is nonetheless consistent with the electron's mean free path [47–49]. The integrated intensity of the Fermi peak is less than that for the dispersive peak, when the latter is allowed, but the Fermi peak is also sharper near the top and remains visible within a substantial range of photon energies. This is qualitatively consistent with experiment. Incidentally we note that the narrowness of the anomalous peak, relative to the dispersive peak, is consistent with the former stemming from nonitinerant electrons. Because the dispersive peak is broadened, its total intensity is somewhat diminished in the spectrally allowed range. Conversely, even when the center of the dispersive peak is in the spectrally forbidden region, its wings generally extend into the occupied region of the valence band, as in Refs. [5,6]. The intensity ratio from Eq. (3)

corrected for these broadening effects is shown in Fig. 1 with the dashed line. For the anomalous peak, we adopt the parametrization from Ref. [50].

To avoid ambiguity, we note the present analysis pertains exclusively to the bulk physics. Effects of the free surface are not included. Also, strictly speaking, on the short time scales of photoemission, plasmons should be regarded as a symmetry-lowering perturbation to the Fermi liquid. These effects can be visualized and contribute to the background [32,51], see Supplemental Material [40].

Photoemission out of a localized state exhibits classical features, consonant with the infrared catastrophe [24] accompanying the recoil currents. (Similar catastrophes, leading to a classical-like localization of a quantum motion, take place as part of the Kondo effect or, for instance, the localization of a particle interacting with a bath [52].) The photon's momentum and energy are initially imparted to the material within a localized region, before they are passed on to the rest of the electrons and the nuclei. The density of the grand-canonical free energy ($V =$ const, $T =$ const) is equal to the negative pressure [53]. Thus a photon impinging on a volume $V$ effectively creates an excess negative pressure $-\hbar\omega_{\text{ph}}/V$, the corresponding forces being much greater than the characteristic electronic forces when $V \lesssim a^3(\hbar\omega/E_F) \simeq 10^1 a^3$. This negative pressure is, in fact, the driving force behind the decrease in local density caused by photoemission. This negative pressure will persist until the hole is filled by the recoil currents. When creating a localized hole, we are bringing in physical contact two distinct phases thus incurring a mismatch penalty. (If the interface is thin, the penalty amounts to a conventional surface tension [53].) Thus, the formation of the hole is a *nucleationlike* process. Nucleation of a low-density phase caused by local excess of negative pressure is a well-known phenomenon called "cavitation," hence the title of the article. Nucleation, of course, is a strongly nonlinear phenomenon; *homogeneous* nucleation furthermore represents a breaking of spatial symmetry.

As a dividend of the present analysis, we note that the metal acts as a transmitter of electrons, during photoemission, the final state of the particle being a plane wave. Conversely, one may consider the reciprocal process, in which the metal is the receiver. Hereby, the electron is initially a plane wave and eventually enters the metal in the form of a localized object while filling a localized vacancy, whose concurrent formation is accompanied by recoil currents. This reciprocal process can be thought of as a detection event for the received electron, so that its location becomes known to the extent determined by the size and shape of the hole. As the measurement proceeds, the single-particle density matrix progressively deviates from its initial, nearly free-electron value. Thus the present scenario is an explicit example of how a measurement event is a result of a strongly nonlinear, many-body phenomenon but can be profitably thought of as a "collapse" of a one-particle wavefunction, if the full density matrix of the system is unavailable. Because the event is an instance of symmetry breaking, its outcome is history dependent. This is analogous to how the precise magnetization pattern in a magnet below the Curie point or, to give another example, the detailed structure of a glass below the glass transition [18], depend on the preparation protocol. Other, arguably simpler, scenarios can be imagined. For example, consider a dilute gas or a set of deep core orbitals in a metal such that the photon's wavelength is much greater than the spatial separation between pertinent orbitals. An electron to be photoemitted is automatically localized within an orbital whose eventual identity will have emerged as a result of a symmetry-lowering process and, thus, depends on the history. The nonlinear phenomenon is whatever the process that causes individual orbitals not to form a band in the first place, such as a metal-insulator transition [54]. Likewise, receiving orbitals are also automatically localized.

We thank E. Ward Plummer (now deceased) and Gerry Mahan (now deceased) for inspiring conversations and Peter G. Wolynes and Eric Bittner for helpful insight. We gratefully acknowledge the support by the NSF Grants No. CHE-1465125 and No. CHE-1956389, the Welch Foundation Grant No. E-1765, and a grant from the Texas Center for Superconductivity at the University of Houston. We gratefully acknowledge the use of the Maxwell/Opuntia Cluster at the University of Houston. Partial support for this work was provided by resources of the uHPC cluster managed by the University of Houston and acquired through NSF Grant No. ACI-1531814.

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