

Droplet motions fill a periodic table

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Drawing parallels to the symmetry breaking of atomic orbitals used to explain the periodic table of chemical elements; here we introduce a periodic table of droplet motions, also based on symmetry breaking but guided by a recent droplet spectral theory. By this theory, higher droplet mode shapes are discovered and a wettability spectrometer is invented. Motions of a partially wetting liquid on a support have natural mode shapes, motions ordered by kinetic energy into the periodic table, each table characteristic of the spherical-cap drop volume and material parameters. For water on a support having a contact angle of about 60°, the first 35 predicted elements of the periodic table are discovered. Periodic tables are related one to another through symmetry breaking into a two-parameter family tree.

droplet vibrations | sessile drop dynamics | meniscus motions | capillary ballistics | moving contact line

Droplets and droplet motions surround us. Our harvests depend on rain drops. We sweat, we shower, and we drink. Our eyes make tears and our blood splats. Drops enable the protein content of our bodily fluids to be measured (1), our silicon chips to be fabricated (2), and complex parts to be additively sculpted by drop-on-demand processing (3, 4). Water droplets in motion are shaped into objects of beauty by surface tension. Their images have become symbols of purity and cleanliness, selling beer, jewelry, clothing, and automobiles. However, despite more than a century of study, the motions of droplets on a support have resisted systematic classification. This paper introduces the periodic table classification of capillary-ballistic droplet motions.

The capillary-ballistic model assumes an ideal fluid with surface tension acting on the deformable surface (*SI Appendix*). Capillary-ballistic motions are typical of thin liquids like water. Prototypical of dynamics of this kind are free drop vibrations, predicted by Rayleigh to have frequencies (5) λ_{kl} as in

$$\lambda_{kl}^2 = k(k-1)(k+2), \quad k=0,1,2, \dots, \quad 0 \leq l \leq k, \quad [1]$$

where the corresponding deformation is $Y_k^l(\theta, \varphi)$ in spherical coordinates. Here, wavenumber k is the degree and l is the order of the spherical harmonic Y_k^l (6). Frequencies [1] and mode shapes Y_k^l constitute the so-called Rayleigh spectrum, predictions verified experimentally (7, 8). Note that, in [1], different l 's share the same frequency. These degeneracies arise from the perfect symmetry of the spherical free drop. The introduction of a support typically breaks these degeneracies.

Deformations of the supported drop (9), Fig. 1 (*Bottom Row*), break from the $Y_k^l(\theta, \varphi)$ shapes. The number of layers n (*Top Row*, in schematic) and of sectors l [*Bottom Row*: bold lines, rendered shape (*Right*)] characterize modal symmetry. Using $k=l+2(n-1)$, symmetries are alternatively classified “mathematically” by wave-number pairs $[k, l]$. Modes are either “symmetric” (short for axisymmetric), e.g., $[6,0]$ – leftmost, “star,” e.g., $[6,6]$ – rightmost, or “layer” modes (short for layer sector), e.g., $[6,2]$ and $[6,4]$ – middle two modes. Note that the Rayleigh spectrum [1] splits. That is, [1] predicts that all four modes have identical frequencies—since all have $k=6$ —yet, as observed for supported drops, these four modes have distinct frequencies, predicted by our theory. The four modes illustrate symmetry breaking from the axisymmetric shape (leftmost). In this way, introducing the support splits spectra and breaks

modal symmetry. Next, we outline the chemical periodic table analogy, which organizes how such spectra are split and how the corresponding modes mix.

The chemical periodic table, or “chemical PT,” is arguably the most far-reaching design tool of industrial mankind (10, 11). This largely empirical ordering of elements has been rationalized using the *Aufbau*, or building-up, principle of filling of atomic orbitals (12, 13). The more mathematical approach to atomic structure is the spectral theory of classical quantum mechanics built on the Schrödinger equation (14), cited as a triumph of 20th century physics. Predictions of these two approaches are often in agreement, yet they need not be. This paper emphasizes such discrepancies in prediction, for a spectral theory of droplet motions. The theory predicts mixing and splitting of spectral lines which, depending on parameter values, can lead to differences between *Aufbau* and actual spectra, discrepancies historically referred to as “irregularities” in the chemical context (11).

Similar to the chemical PT, the droplet motion PT, or “droplet PT,” derives from a spectral theory built on a Schrödinger-like equation. Capillary waves on a liquid droplet undergoing ideal motion are governed by a wave equation (5). The waves are quantized by confinement at the liquid boundary, much as the box boundary quantizes the particle in a box, the textbook prototype of the quantum concept. The droplet boundary is located where the liquid, gas, and solid support meet, known as the contact line (CL) (15). Quantization occurs whether or not the CL is pinned or moving. The resulting droplet wave theory leads to a PT wherein droplet motions are ranked according to energy levels with periods and groups arising from symmetries of mode shapes generated by the standing waves. Note that this phenomenon is physically distinct from “pilot wave hydrodynamics,”

Significance

Droplets and their motions surround us—in art, science, and technology. Yet, droplet motions have resisted classification. Here, we reveal a periodic table (PT) classification of droplet motion that is profound in implication and refreshing in originality. The classical PT of chemical elements is a synthesis of knowledge of monumental stature. This paper provides a parallel PT synthesis of ballistic droplet motions, demonstrates the techniques by which one can identify “motion elements,” and introduces the wettability spectrometer, all enabled by a recent spectral theory of meniscus motions. In the realm of pedagogy, the simplicity of the droplet motion PT provides unique perspective on the chemical PT making concepts like chemical bonding and atomic orbitals more accessible.

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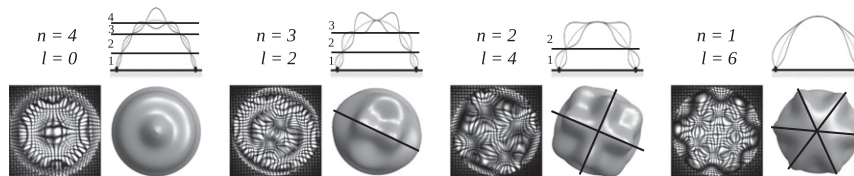


Fig. 1. Supported drop modes: numbers of layers n (side view, *Top Row*) and sectors l [top view, *Bottom Row*; photo (*Left*), rendered (*Right*)] give modal symmetry. Wavenumber k depends on n as $k = l + 2 (n - 1)$. See *SI Appendix* for discussion of alternative (n, l) and $[k, l]$ wavenumber classifications.

whose analogy to quantum-mechanical concepts has recently been developed (16, 17).

For our droplet motions, the ordering is according to kinetic energy, proportional to the square of the frequency of oscillation. For atoms, the energy arises from the arrangement of electrons in their orbitals, yet for multielectron atoms, because of electronic interactions, shielding, and relativistic effects, it remains an open challenge to predict ordering by energy from quantum-mechanical first principles (18). Textbooks typically rationalize the ordering of the elements by invoking the Pauli exclusion, Hund, and *Aufbau* principles (often with Madelung rule) (19–21). These three principles are essentially empirical guides—none has been derived from the principles of quantum mechanics—and actual energy ordering deviates (22). In contrast, the relative simplicity of droplet motions means that their energy levels can be readily computed from a Schrödinger-like equation. This simplicity enables as yet undiscovered “motion elements” to be predicted, the wettability spectrometer to be invented, and the PT to be contextualized among droplet worlds.

Mode Shapes and Droplet PT

A drop of low-viscosity liquid can be excited to yield nearly ideal motions, as happens for water drops on a horizontal plate vertically shaken from below (9, 23). Fig. 2*A* shows the experiment in schematic. At rest, a small enough droplet on a plate (hatched) exhibits a spherical-cap shape (dashed). On excitement by periodically forcing (double arrow), a volume-preserving deformed shape (blue) is the response (Fig. 2*A*).

Vertical shaking can break the symmetry of the rest shape. See *Movie S1* for a time-periodic response. During up- or down scans in driving frequency, mode shapes are those exhibiting resonance

and corresponding frequencies are identified as the natural frequencies (18). Spatial symmetries of the spherical cap are polar and azimuthal in nature. Breaking polar but not azimuthal symmetry yields axisymmetric shapes while breaking azimuthal necessarily breaks polar symmetry yielding fully 3D shapes.

In the droplet PT, modes are organized into periods and groups, Fig. 2*B*. Periods are distinguished by the first wavenumber k , or principal quantum number, and groups are distinguished by the second wavenumber l , or second quantum number. The leftmost group consists of star modes. The rightmost group is a merger of the $l = 0$ and $l = 1$ modes. The other groups in Fig. 2*B* also represent mergers into single groups of even- and odd-layer modes.

The $l = 1$ modes are distinguished as rocking modes because a single peak rocks from side to side, pointing first to one side, then retracting and sweeping to point to the opposite side. The only rocking mode with star symmetry is the $[1, 1]$ mode. This mode turns out to be the only unstable mode. It translates along the support while rocking, the so-called walking droplet (24) (*SI Appendix*). This instability might be likened to the reactivity of the hydrogen atom.

An abbreviated chemical PT is shown in Fig. 2*C* and, as with the droplet PT, energies increase left to right and top to bottom. Colored blocks in the chemical PT represent the s -, p -, and d orbitals, which, when filled, have 2 (green), 6 (blue), and 10 (red) groups each.

Corresponding blocks of the chemical and droplet PTs are colored similarly to emphasize the common symmetry-breaking origin of groups within these blocks. Relative to the droplet PT, colored blocks of the chemical PT are wider because of additional (third and fourth) quantum numbers. Additionally, the droplet PT has a purple block taking on the role of the f orbitals (lanthanides) in a long-form version of the chemical PT.

For the chemical PT, the building-up “principle” is really a guide (22), as mentioned, since violations or irregularities do occur. The first irregularity arises in building from *Ar* to *K* and persists through *Ca* and *Sc* [Fig. 2*C* (circled)]. It arises because the energy- (actual atoms) and symmetry-ordering (imagined orbitals) begin to deviate. For the droplet PT, irregularity corresponds to the mixing of spectral lines, as discussed below.

Capillary-Ballistic Model

The dynamically deforming meniscus is a free boundary with its own free boundary, the CL, yielding a nested free-boundary-value problem. The Schrödinger-like wave equation governing meniscus dynamics assumes ideal vorticity-free liquid motions beneath the surface. The bulk liquid inertia is countered by surface tension at the deformable meniscus, according to the Young–Laplace interfacial condition. A boundary integral approach maps the problem to the surface domain and a CL drag model closes the formulation. See also *SI Appendix*.

After invoking normal modes, proportional to $e^{i\omega t}$, the governing equation on the domain $\Gamma \cup \gamma$ (Fig. 2*A*) is

$$\rho \Omega^2 M[\eta] = \sigma K[\eta], \quad [2]$$

where M and K are mass (inertia) and capillarity (curvature) integrodifferential operators, operating on deformations $\eta(\theta, \varphi)$. Dirichlet conditions on η correspond to a pinned CL. For the

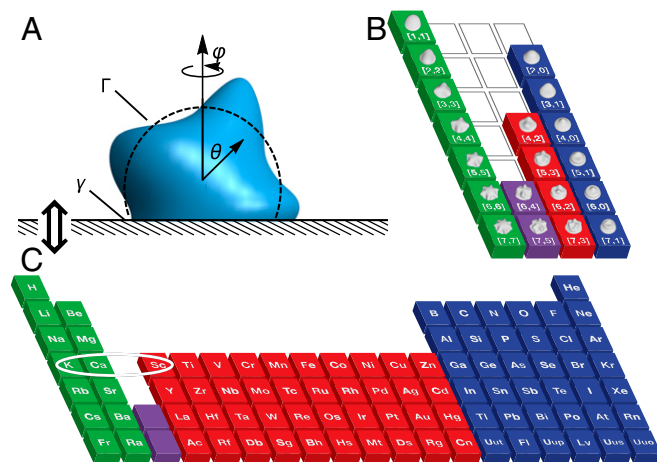


Fig. 2. Mode shapes and PTs. (*A*) sketch of disturbance (rendered, blue) to rest state (dashed, black); (*B*) sample droplet PT with energy increasing left to right and top to bottom, with symmetry-related groups of modes: star (green), 4,5-layer (purple), 2,3-layer (red), and symmetric and rocking (blue). (*C*) Chemical PT with blocks of groups distinguished by color, and with the first irregularity in *Aufbau* ordering circled.

free drop of radius R , modes are $\eta = RY_k^l$, yielding via evaluation, $\rho\Omega^2 M[\eta] = -\rho R\Omega^2 Y_k^l$ and $\sigma K[\eta] = -(\sigma/R^2)k(k-1)(k+2)Y_k^l$, which put into [2] yield Rayleigh spectral lines [1], after scaling $\lambda^2 \equiv (\rho R^3/\sigma)\Omega^2$. For supported drop motions, more broadly, solutions of the spectral eigenvalue problem (2) with specified CL conditions yield frequencies Ω_{kl} and shapes η_{kl} , which together constitute the spectrum. These must be obtained computationally. To summarize, our capillary-ballistic model is classical hydrodynamically with one exception—a CL drag coefficient is introduced to account for the resistance to liquid CL movement along the solid support. Spectra will depend on this CL line drag, and that modeling is now briefly described.

Control Parameters, Contact Angle, and Mobility

Resonant frequencies and associated mode shapes make up a spectrum, which depends on droplet volume and the material system (liquid/solid/gas), viewed here as controllable (Fig. 3A). Two parameters characterize this system: contact angle (CA) α and CL resistance Λ (25, 26), called the “line drag” (Fig. 3B). For simplicity, we shall refer to $\alpha < 90^\circ$ systems as hydrophilic, or “philic” for short, $\alpha > 90^\circ$ as hydrophobic, or “phobic.” The two-parameter family of spectra leads to a two-parameter family of droplet PTs.

Mobile drops have movable CLs. Fully mobile drops have a fixed CA ($\Delta\alpha = 0$) without regard to CL displacement $\Delta\eta$ (or speed) (Fig. 3C, *Left*), while a pinned drop (fully immobile) has fixed displacement ($\Delta\eta = 0$) without regard to CA deviation $\Delta\alpha$ (Fig. 3C, *Right*). The fully mobile and pinned CL behaviors are ideal extremes that span actual behavior. For actual CL motion, there is always some finite resistance (nonzero and noninfinite) to the driving force agent, $\Delta\alpha$, which limits the CL speed, $\Delta\eta/\Delta t \equiv U_{CL}$ (Fig. 3B, dashed line), according to $\Delta\alpha = \Lambda U_{CL}$. The line drag Λ is also known by its reciprocal, the mobility. Note that our linearized theory does not account for CA hysteresis but

approximates it. For our purposes, Λ may be viewed as a phenomenological parameter. It should be noted that Λ is well defined, has been measured experimentally, and has been related to CL dissipation, independent of any theory (27).

For both pinned and fully mobile CLs, motions predicted by the capillary-ballistic governing system [2] are dissipationless. In these cases, the system is Hamiltonian and the sum of potential and kinetic energies is an invariant—all motions are oscillatory. Nonoscillatory motions only occur away from the ideal extremes, that is, for $\Lambda \neq 0, \infty$. Moreover, these extremes imply that a maximum of CL dissipation must occur somewhere between.

In summary, supported drops have spectral lines, $\lambda_{kl}(\alpha, \Lambda)$, and mode shapes that depend on two parameters. Varying (α, Λ) samples this two-parameter family of PTs and irregularities arise whenever mixing of spectral lines occurs (24).

Spectral Lines, Splitting, and Mixing

The free (unsupported) drop is an important comparison case. The Rayleigh spectrum [1] has already been introduced and has been related to the more general spectral problem [2]. According to [1], frequency λ increases asymptotically as $\lambda^{3/2}$ for large wavenumber, as for purely capillary dispersion (29). The fact that higher wavenumbers have higher frequencies is referred to as “standard order.”

The first symmetry-breaking consequence of introducing the support is the restriction $k+l=\text{even}$, owing to the condition of no liquid penetration at the plate (zero normal fluid velocity). Already for the mobile hemisphere $(\alpha, \Lambda) = (90^\circ, 0)$, the evenness condition must be invoked, eliminating half the Rayleigh modes and leaving only those with mirror symmetry across the equator. Varying to any $(\alpha, \Lambda) \neq (90^\circ, 0)$ breaks this mirror symmetry and splits the spectral lines. In Fig. 3D, spectral splitting from the mobile hemisphere by varying Λ is illustrated for three frequencies, λ_{5l} for $l=1,3,5$. From

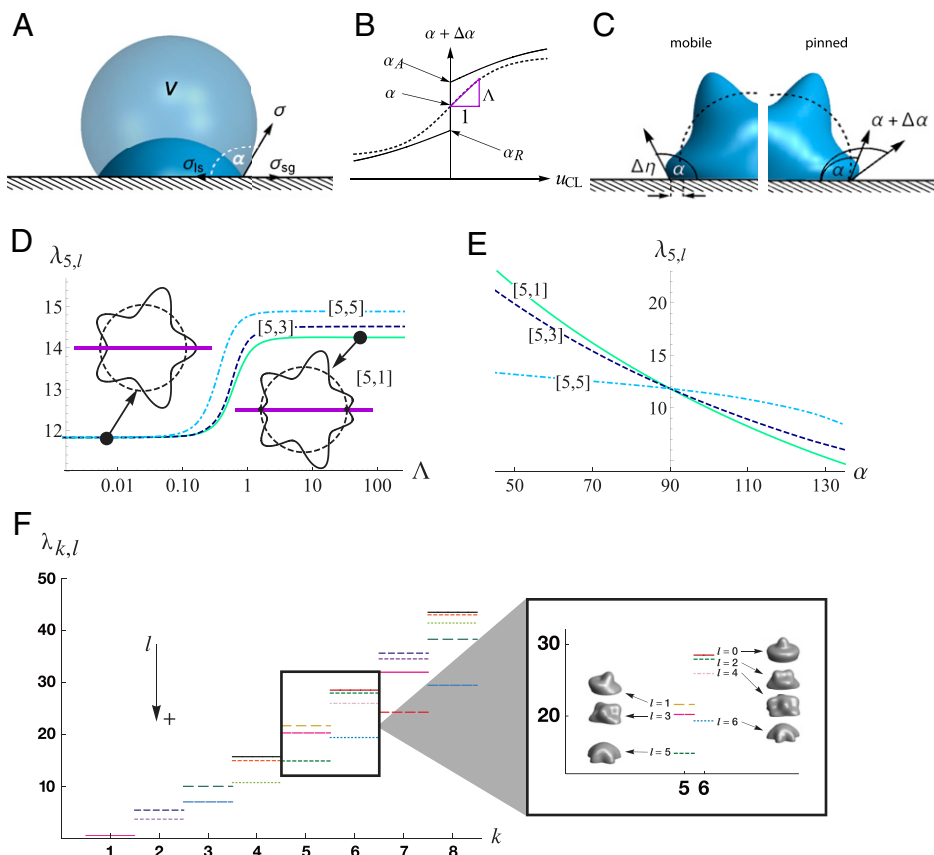


Fig. 3. Spectra depend on α and Λ . (A) Rest-state contact angle α or, equivalently, spherical-cap volume V ; and (B) CL mobility Λ , which relates CL speed, U_{CL} , to CA deviation from rest, $\Delta\alpha$ (CL kinetic property); (C) Limiting behaviors of CL motion correspond to (C, *Left*) no resistance $\Lambda = 0$ ($\Delta\alpha = 0$), a “fully mobile” CL with time-dependent displacement $\Delta\eta_l$, and to (C, *Right*) infinite resistance $\Lambda = \infty$ ($\Delta\eta_l = 0$), an immobile or “pinned” CL with time-dependent deviation $\Delta\alpha$. In between, $0 < \Lambda < \infty$, are “partially mobile” CLs. (D and E) Spectral splitting (D) by CL mobility Λ and (E) by CA α . (D) Splitting of frequency $\lambda_{5,l}$ for hemisphere ($\alpha = 90^\circ$) by mobility $\Lambda \neq 0$. (D, *Inset*) Broken shape symmetry is illustrated for the [5,1] mode by reflection across the equatorial plane, contrasting mobile and pinned modes. (E) Splitting of frequencies $\lambda_{5,l}$ for mobile modes $l = 1, 3, 5$, in α -dependence; (F) For $(\alpha, \Lambda) = (60, 0)$, splitting and mixing of spectral lines (frequencies $\lambda_{k,l}$) with explicit k dependence and with l increasing (+) downward (arrow), and (*Inset*) illustrating shapes corresponding to spectral lines breaking downward with l , for phobic PTs ($\alpha < 90^\circ$). (F, *Inset*) Illustration of an irregularity: the [6,6], has lower energy than the [5,1] and [5,3] modes, breaking standard order.

mobile to pinned, modewise, there is a monotonic increase in frequency that amounts to a net 25% overall. The insets illustrate how profile symmetry is broken. In Fig. 3E, for $\Lambda = 0$, the same three frequencies are shown in dependence on α . For the same footprint, phobics have lower frequency than philic drops because of larger volumes. Modal monotonicity (28) is also exhibited in this α -dependence.

For $(\alpha, \Lambda) = (60^\circ, 0)$, Fig. 3F illustrates in a stairstep spectral plot how the first 8 Rayleigh degeneracies split into 24 lines, akin to the Balmer and Lyman spectral series for the hydrogen atom. Only the so-called Noether mode $k=1$ does not split. Remarkably, breaking the mirror symmetry by geometry imperfection ($\alpha \neq 90^\circ$ with $\Lambda = 0$) destroys the time independence of the Noether mode (compare *SI Appendix*), much as does breaking full mobility by introducing some line drag ($\Lambda \neq 0$ with $\alpha = 90^\circ$). In summary, imperfection $(\alpha, \Lambda) \neq (90^\circ, 0)$ by either geometry or mobility can break the Noether time independence.

Non-Rayleigh spectral lines beyond $k=1$ split into multiple steps with corresponding mode shapes distinguished by azimuthal structure (Fig. 3F, *Inset*). For $k=5$, for instance, splitting leads to three distinct lines having the shapes of [5,1], [5,3], and [5,5]. Mode [5,1] has the highest frequency (Fig. 3F, *Inset*). For $k=6$, splitting leads to four modes, [6,0], [6,2], [6,4], and [6,6]. For philic drops with the same k , the shape with greatest symmetry ([5,1] or [6,0]) has the highest frequency. In other words, for philic drops, splitting occurs downward with increasing

asymmetry l while, for phobic drops, splitting occurs upward with increasing l , as already seen in Fig. 3E. A similar splitting occurs for the atomic spectral lines (30, 31).

Mixing of spectral lines upsets the standard order by breaking monotonicity. That is, mixing corresponds to a lower k having a higher frequency. For $(\alpha, \Lambda) = (60^\circ, 0)$, mixing first occurs at $k=4$ where the [5,5] mode has $\lambda_{55} < \lambda_{42}$ (Fig. 3D). Mixing also occurs among the $k=5,6$ bands of spectral lines (Fig. 3D, *Inset*). Spectral mixing leads to irregularities in the PT. The $(\alpha, \Lambda) = (60^\circ, 0)$ PT follows the standard order up until the sixth element, mode [4,4], according to Fig. 3F, after which it deviates, exhibiting irregularity; compare Fig. 4, bottom row, near left, in contrast to top row, left (or Fig. 2C).

Breaking Symmetry, PTs, and Irregularities

Symmetry is broken by breaking mobility and/or geometry, as noted, with an influence on the PT as summarized in Fig. 4. Breaking mobility is illustrated in the bottom row and breaking geometry in the top row. The top row exhibits two standard orderings, referred to as the philic ($\alpha < 90^\circ$) and the phobic ($\alpha > 90^\circ$) standards. These orderings split differently on increasing shape asymmetry l . For phobic drops, splitting occurs upward to higher energies while for philic drops, splitting occurs downward to lower energies, as in Fig. 3D, discussed above. For example, for philic modes with the same k , star shapes have

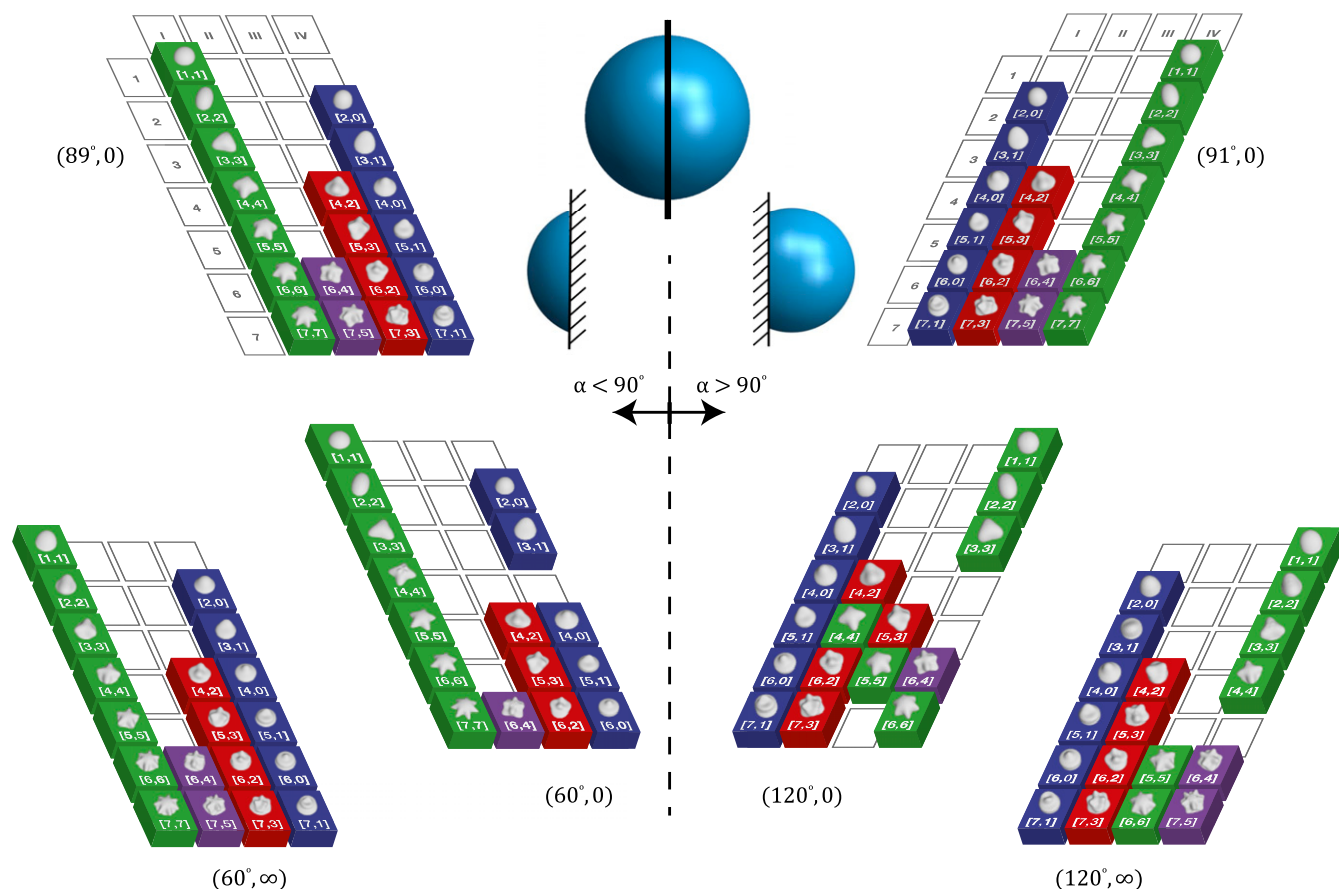


Fig. 4. Symmetry breaking from spherical shape with corresponding PTs in stadium view (colored, symmetry groups). Hemispherical drops (*Top Center*, blue) provide the symmetry center for a two-parameter family (α, Λ) of symmetry breaking. Breaking left ($\alpha < 90^\circ$) and right ($\alpha > 90^\circ$) correspond to philic and phobic rest shapes (blue), while breaking down and away correspond to decreasing mobility. Elements within each PT are ordered by kinetic energy, increasing left to right and top to bottom. First break (*Top Row*) occurs to slightly philic (*Left*) and to slightly phobic (*Right*) mobile drops, defining two standard orders. Second break (*Bottom Row*) occurs to mobile ($\Lambda = 0$, near center) and to pinned ($\Lambda = \infty$, far from center) drops. Groups, colored by mode type, illustrate irregularities (mixing colors) to standard orders that develop with greater symmetry breaking and higher-order elements.

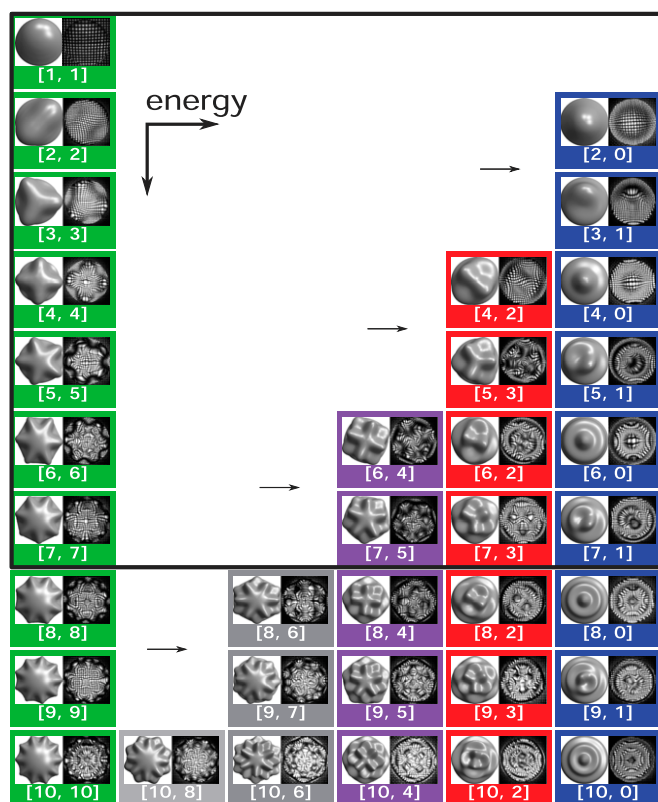


Fig. 5. Droplet PT discovery for $(\alpha, \Lambda) = (60^\circ, \infty)$ with panels showing rendered shape by theory (Left) against corresponding observed shape (Right). The first 35 modes have been experimentally observed. The extension to 35 modes of the truncated 19 mode set (boxed), the PT of Fig. 2B, illustrates how groups build out the droplet PT. Kinetic energy increases left to right and top to bottom. Thin arrows indicate continuation of the period.

lower energy than symmetric shapes while the reverse holds for phobic modes.

We adopt terminology to parallel that used for the chemical PT. Groups are vertical columns and periods are horizontal rows. The principal wavenumber k plays the role of the principal quantum number and defines the period, labeled 1–7, Fig. 4 (Top Row). Modes are atoms and mode number is atomic number. Secondary wavenumbers l are orbital types (s, p, d, f), and so forth. For any principal wavenumber k , there are $l \leq k$ orbital types, subject to $k + l = \text{even}$. Note that in the droplet PT metaphor there is only one mode per orbital type. That is, in contrast to the chemical PT where s -, p -, d -, and f orbitals can accommodate multielectrons so that groups and blocks differ, for our PT, every group consists of one single block. And, in our rendering of the PTs, star modes ($k = l$) are colored green, symmetric ($l = 0$) and rocking modes ($l = 1$) are blue, 2,3-layer-sector modes ($l = 2, 3$) are red, and 4,5-layer-sector modes ($l = 4, 5$) are purple. In the standard order, these symmetries define the groups, labeled I, II, III, and IV, Fig. 4 (Top Row).

The phobic and phobic standard PTs (Fig. 4, Top Row) can be built up in mode number Z by prescription. From a mode number Z with wavenumber k , one builds to $Z + 1$ as follows. For the phobic (phobic) case, add (subtract) to (from) the secondary wavenumber l until $l = k$ (until $l = 0$), subject to $k + l = \text{even}$, at which point the period is full. In both phobic and phobic cases, if the period of mode Z happens to be full, first increase the wavenumber to $k + 1$ and then proceed as just prescribed. This building up has been carried out up to $Z = 19$ for the standard PTs in Fig. 4 (Top Row), corresponding to seven periods and

four groups. Clearly, this *Aufbau* procedure can continue without end, leading to an unlimited number of periods and groups. For most droplet PTs, this *Aufbau* procedure has limited usefulness, however, because of the occurrence of irregularities. Just as in the case of the chemical PT, irregularities tend to accumulate with increasing mode number and greater symmetry breaking.

In Fig. 4 (Bottom Row), the four PTs illustrate four different irregularities. PTs are always constructed by ordering modes according to increasing energy, left to right and top to bottom. Consider the phobic case. Comparing $(\alpha, \Lambda) = (60^\circ, 0)$ with the phobic standard $(89^\circ, 0)$, one observes that the standard ordering applies through the [4,4] mode. Thereafter, the [5,5] jumps ahead of the [4,2] mode, effectively punching a hole in the PT and pushing the groups II, III, and IV downward one unit. As the standard ordering is broken and the periods mix, the *Aufbau* principle fails. In contrast, comparing the $(\alpha, \Lambda) = (60^\circ, \infty)$ case to the standard phobic PT, one observes that the ordering is maintained. The imperfection of a pinned CL is enough to bring the PT back into registry with the standard PT. In this sense, pinning stabilizes the PT.

In summary, the spectrum for the fully mobile hemispherical drop serves as the organizing center or mother spectrum from which bursts a two-parameter family of daughter spectra, by symmetry breaking. Each family member is represented by its own PT, and these members are related one to another by a family tree of PTs, illustrated in Fig. 4, where CA varies leftward and rightward away from the hemisphere and the line drag increases downward.

Results

Fig. 5 gives the predicted and to-date discovered PT for water drops with CLs pinned on a circle of 25-mm radius, having volumes that give a rest CA of 60° . Rendered shapes (Left) are paired to observed mode shapes (Right). The dynamic surface topography of shapes is observed in the top-view snapshot, whereby light from below passes a fixed grid before being refracted at the deformable interface (23). The first 35 modes have been discovered, guided by the frequency predictions of our capillary-ballistic spectral theory.

Dynamic Wettability Spectrometer

The idea of the wettability spectrometer is to measure frequency shifts against the Rayleigh standard, to infer the line drag from our spectral theory predictions. Shifts are easily measured using frequency scans, much as with traditional spectrometers (e.g., IR and UV). In our case, instead of probing molecular or atomistic modes, we probe droplet vibratory modes using line drag as a metric for dynamical wettability (32–35). With the great proliferation of “designer supports”—chemically and mechanically conditioned surfaces tailored for desired properties (36)—there is a growing need to characterize dynamical wetting.

The practicability of our spectrometer depends on the sensitivity of spectral lines to wettability changes. Fast-moving CLs occur at small spatial scales, making line drag challenging to quantify. Spectral sensitivity is currently being tested on the International Space Station, taking advantage of the spatial and temporal amplification provided by microgravity (37). Further Earth-based testing is planned, taking advantage of a new class of fast digital holographic microscopes (38). Spectral theories of meniscus motions, like that presented here, but differing in details of constraint, are of broad applicability to drop-on-demand printing and to capillarity-driven atomization, among other forming processes that rely on rapid shaping by surface tension.

Our Chemical World, as One of Many Worlds

If one could set up a parallel between the chemical and droplet PTs, one might use the droplet perspective to imagine worlds with chemistries different from ours. A first step in this direction determines whether our chemical PT belongs on the phobic or

phobic side of Fig. 4. If one associates spherical symmetry of atomic orbitals with cylindrical symmetry of droplet modes, then the answer must be “the philic side,” since energy breaks toward less stable (downward) for philic drops just as higher orbitals make atoms less stable typically. A next step is to scale based on the rate of accumulation of irregularities. Of the six droplet PTs in Fig. 4, three exhibit irregularities and two of these occur for phobic drops. Hence, moving from the center, there are different rates of irregularity accumulation, philic and phobic. This is expected in view of the asymmetric spectral splitting away from the hemispherical drop (Fig. 3E). A simplest such parallel scales the first occurrence of irregularity between the PTs. For the chemical PT, this corresponds to the intersection of groups I–III and period 4; that is, the K , Ca , and Sc progression (Fig. 2D), as discussed above. For the droplet PTs, the corresponding intersection yields the $(60^\circ, 0)$ world (Fig. 4), where the $[5,5]$ mode has lower energy than the $[4,2]$ and $[4,0]$ modes. In this way, it may be claimed that the $(60^\circ, 0)$ droplet world parallels our chemical world, all the while being surrounded by neighboring worlds.

Discussion

From the semiconductor chips in our cell phones, fabricated by immersion lithography, to the water spray hitting our shower walls, droplets with moving CLs feature indirectly and directly in our daily lives. Here we have framed a spectral theory of capillary-ballistic droplet motions in terms of symmetry breaking from the free spherical drop and here introduced a two-parameter family of PTs of mode shapes, each PT ordered by energies and subordered by symmetries into periods and groups, much like the chemical PT.

On one hand, the droplet PT is much simpler than the chemical PT. On the other hand, each droplet PT possesses a richer context, being surrounded by a doubly infinite family of neighboring PTs. This richer context stimulates our imagination about other chemical worlds—different elements might combine

in different ways to make different molecules. Motion elements from the droplet PT already have been observed to combine as motion molecules, with some elements superposing linearly and others clinging together nonlinearly, as judged by the hysteresis they exhibit during mutual joining and parting (9). Of course, the nonlinear behavior of all droplet motions is governed by the same set of rules, the nonlinear Navier–Stokes equations. The nonlinear behavior of combining elements is largely unexplored while the influence of viscous effects on droplet spectra has received some attention (39). Both extend our ballistic motions.

Inspired by Helmholtz’s discovery of the permanence of vortical motions in an ideal fluid (40), Lord Kelvin proposed vortex atoms as a basis for matter (41). Vortex atoms were long forgotten by the time that Bohr introduced the old quantum theory (12), a theory which successfully explained the observed spectral lines of hydrogen and thereby provided the first substantial framework for understanding the chemical PT. It is with some irony, then, that droplet PTs based on the motions of ideal fluids can provide a perspective on the chemical PT, broader than that provided by the old quantum theory. We offer this paper as homage to those of the past centuries who have labored in the realm of ideas, enabling more encompassing perspectives.

Materials and Methods

The experimental methods (9, 23) and the capillary-ballistic model with its solution method (24) have been previously reported. In *SI Appendix*, following the order of the main text, we provide some detail for better understandability.

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