Chapter 27

When Liquid Rays Become Gas Rays: Can Evaporation Ever Be Non-Maxwellian?

Gilbert M. Nathanson

Abstract A rare mistake by Otto Stern led to a confusion between density and flux in his first measurement of a Maxwellian speed distribution. This error reveals the key role of speed itself in Stern's development of "the method of molecular rays". What if the gas-phase speed distributions are not Maxwellian to begin with? The molecular beam technique so beautifully advanced by Stern can also be used to explore the speed distribution of gases evaporating from liquid microjets, a tool developed by Manfred Faubel. We employ liquid water and alkane microjets containing dissolved helium atoms to monitor the speed of evaporating He atoms into vacuum. While most dissolved gases evaporate in Maxwellian speed distributions, the He evaporation flux is *super*-Maxwellian, with energies up to 70% higher than the flux-weighted average energy of $2 RT_{\text{liq}}$. The explanation of this high-energy evaporation involves two beautiful concepts in physical chemistry: detailed balancing between He atom evaporation and condensation (starting with gas-surface collisions) and the potential of mean force on the He atom (starting with He atoms just below the surface). We hope that these measurements continue to fulfill Stern's dream of the "directness and simplicity of the molecular ray method."

1 Introduction: J. C. Maxwell and Otto Stern

Otto Stern's first publication, in 1920, described an ingenious Coriolis measurement of the root-mean-square (rms) speed of a Maxwellian distribution of silver atoms emitted from a hot oven ("gas rays") [1]. It is remarkable that this distribution had not been measured before, but even more remarkable was the correction to Stern's article later in 1920. Stern's postdoctoral advisor, Albert Einstein, pointed out to Stern that he had calculated the rms speed, $\langle c^2 \rangle_{\text{density}}^{1/2} = (3RT/m)^{1/2}$ using the density weighting $n(c)$ instead of the flux (velocity) weighted average $\langle c^2 \rangle_{\text{flux}}^{1/2} = (4RT/m)^{1/2}$, where the

G. M. Nathanson (✉)

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA

e-mail: nathanson@chem.wisc.edu

© The Author(s) 2021

B. Friedrich and H. Schmidt-Böcking (eds.), *Molecular Beams in Physics and Chemistry*, https://doi.org/10.1007/978-3-030-63963-1_27

631

flux $J(c) = c \cdot n(c)$. Stern immediately published a correction that agreed more closely with his measured value [2], and 27 years later published a measurement of the full distribution [3]. It is heartening to know that even the great Otto Stern made mistakes, although it took someone of the stature of Einstein to correct him! (See Chap. 5 for more history.) In a sense, this chapter starts with Stern's mistake by exploring the nature of speed distributions, but with a focus on the speeds of evaporating gases dissolved in liquid microjets in vacuum ("liquid rays"). Our discussion of non-Maxwellian evaporation weaves a tale that involves two beautiful concepts in physical chemistry, namely detailed balancing between condensation and evaporation and the potential of mean force for a dissolved gas in solution.

The Maxwellian properties of number-density and flux distributions are thoroughly summarized by David and Comsa, a review article I highly recommend [4]. These two distributions can be imagined using the fingers on one hand. Cup the air within your fist: the molecules trapped inside have a Maxwellian speed distribution given by $n(c) \sim c^2 e^{-mc^2/2RT} n_{\text{gas}}$. Here $n(c)dc$ is the number of molecules per unit volume in a narrow speed interval dc . Now make an "O" with your thumb and forefinger: the speed distribution of molecules passing through the "O" is instead the flux (speed-weighted) distribution, $J(c, \theta) \sim c^3 e^{-mc^2/2RT} \cos\theta n_{\text{gas}}$, where θ is the polar angle. In this case, $J(c, \theta) \sin\theta d\theta d\phi dc$ is the number of molecules passing through a unit area per second per unit speed and solid angle interval. This distribution is shifted toward higher speeds (c^3 vs. c^2) because faster molecules traverse the area of the "O" more frequently than do slower molecules. $J(c, \theta)$ is also weighted by $\cos\theta$ because the normal velocity, $c_z = c \cdot \cos\theta$, is the component that transports the gas molecule to the surface formed by the "O", such that the integrated gas-surface collision frequency with a unit area is given by $(RT/2\pi m)^{1/2} n_{\text{gas}}$ [5]. Next situate your "O" over the surface of a glass of water: the flux of water vapor or other gas molecules striking the surface, as pictured as in Fig. 1, is just the same $J(c, \theta)$. This review addresses how the probabilities of dissolution and evaporation vary with the translational energy of the gas molecule, and what this dependence tells us about the mechanisms of solvation.

Maxwell's seminal 1860 article derived the number-density speed distribution of molecules that bears his name and often that of Boltzmann [6]. In a later 1879 article, Maxwell included comments on collisions of molecules with surfaces [7]. He categorized gas molecules striking a surface in two distinct ways: adsorption, which refers to the trapping of molecules at the surface (bound in a physisorption or chemisorption well), and reflection, which corresponds to an immediate, direct bounce from the surface. The fact that not all gases stick upon collision with a surface was in fact proved by Estermann and Stern in their celebrated study of the diffraction of helium atoms from the surface of crystalline lithium fluoride in 1930 [8]. Maxwell's and Stern's paths intersected more than once!

Fig. 1 Condensation and evaporation are reverse processes. Water molecules strike the surface in a cosine angular distribution and velocity(flux)-weighted Maxwellian distribution of translational energies. When every approaching water molecule sticks, the evaporation distribution is also cosine and Maxwellian. The simulation snapshot of the surface of water is adapted with permission from P. Jungwirth, Water's wafer-thin surface, *Nature*, **474**, 168–169 (2011)

2 Condensation and Evaporation as Reverse Processes

We now know that molecules colliding with a surface interact in numerous ways, as summarized in recommended reviews [9–18]. During a single or multi-bounce nonreactive collision, these pathways include not only translational energy exchange but also vibrational, rotational, and electronic transitions (including spin-orbit) in the gas-phase molecule and in the surface and subsurface molecules within the collision zone. The range of energy exchange can vary from zero (elastic collisions such as occurs in diffraction) through production of “hot” adsorbed species to complete energy equilibration at the substrate temperature (also called thermalization) and momentary trapping within the gas-surface potential (often called sticking if the species remains on the surface for long times, often longer than the measurement). It is often said that the trapped molecule “loses memory” of its initial trajectory after its microscopic motions are scrambled through numerous interactions with surface atoms [19, 20]. These adsorbed molecules may subsequently desorb back into the gas phase (trapping-desorption [21, 22]) at rates that are determined by the surface temperature but by not its initial trajectory or internal states.

We also know that, when the gas-solid or gas-liquid system has come to equilibrium, the outgoing and incoming fluxes of each species must be equal. Langmuir stated this criterion in 1916 with extraordinary prescience: “Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail.” [23] In modern terms, a molecular dynamics simulation of gas-solid or gas-liquid collisions can be run backward to simulate the reverse

process for every internal [20, 24–26] and velocity component [4, 20] (see water movie at nathanson.chem.wisc.edu by Varilly and Chandler [27]). This microscopic reversibility, a detailed balancing of every molecular process, has an astonishing implication at equilibrium: because the flux of molecules arriving at a surface is Maxwellian and cosine, the flux of molecules leaving the surface must be Maxwellian and cosine too. If the trapping probability depends on incident energy or angle, then the flux of just the desorbing molecules will be non-Maxwellian and non-cosine, with the difference made up by the molecules that directly scatter from the surface! Only the sum of all scattering and desorbing molecules must be Maxwellian and cosine. Thus, if one could observe just the desorbing molecules, one might measure a distribution that is non-Maxwellian and non-cosine, and then infer from it the energy and angular distribution of incoming molecules that undergo trapping and solvation.

A measurement of the desorption distribution can indeed be made in a vacuum experiment (where there is almost no impinging flux) if one assumes that the distribution out of equilibrium in the vacuum chamber is the same as at equilibrium. The history of these concepts for gas-solid interactions is told with great clarity and suspense by Comsa and David [4] and by Kolasinski [20]. I have also learned much from several original references [28–30].

3 Rules of Thumb for Gas-Surface Energy Transfer and Trapping

Three key concepts and examples from gas-surface scattering can be used to appreciate the implications of detailed balancing, as summarized below.

1. The kinematics of the collision govern energy transfer: light gas atoms or molecules bounce off heavy surface atoms or molecules, transferring just a fraction of their translational energy upon collision [31]. Conversely, gas species that are heavier than the surface species (often the case for liquid water) will undergo multiple collisions that lead to efficient energy transfer. For an incoming sphere colliding head-on with an initially stationary sphere (zero impact parameter), the energy transfer is given by $\Delta E/E_{\text{inc}} = 4\mu/(1 + \mu)^2$, where $\mu = m_{\text{gas}}/m_{\text{surf}}$ and $E_{\text{inc}} = 1/2 m_{\text{gas}} c_{\text{inc}}^2$. This equation also models an atom striking a flat cube in a perpendicular direction. When $\mu = 1/4$, 64% of the incident kinetic energy of the gas atom is transferred to the surface atom, while it rises to 89% for $\mu = 1/2$. Numerous experiments verify that energy transfer indeed increases with heavier gas and lighter surface molecules [13, 32–34]. Further studies show that grazing collisions (large impact parameter) transfer less energy, and thermal motions generally decrease the overall energy transfer as well. Sophisticated models of energy transfer have been developed that take into account the shape of molecules [35] and surface and their internal excitation, including the development of a “surface Newton diagram” [18, 36].

Fig. 2 Two-step mechanism for the dissolution of a gas atom or molecule. In general, high translational energies and grazing collisions lead to direct scattering from the surface, while lower incident energies and more perpendicular collisions lead to energy loss and momentary trapping. This trapping is typically followed by desorption back into the gas phase or diffusion and solvation in the bulk

- Attractive forces create gas-surface potential energy wells that can momentarily trap the incoming molecule once it has dissipated its excess energy after one or several bounces, as pictured in Fig. 2. For the simple model above, the minimum initial translational energy required to escape the potential energy well is

$$E_{\min} = 4\mu/(1 - \mu)^2 \cdot \varepsilon \quad (1)$$

where ε is the well depth [11, 30]. This expression neatly separates into kinematic (mass) and potential energy terms. For $\mu = 1/4$ and $\varepsilon = 20$ kJ/mol (a hydrogen bond between gas and liquid), $E_{\min}$ is 36 kJ/mol or $14 RT_{\text{liq}}$ at 300 K—only gases with higher energy will escape thermalization and momentary trapping. Again, experiments verify that heavy gas atoms/light surface atoms and strong attractive forces enhance trapping via the strength of the reagent or product desorption signal [13, 33, 37]. We note the inherent distributions of attractive forces and impact parameters arising from bumpy surfaces, molecular orientation, varying approach angles, and multiple collisions, along with thermal motions of the surface atoms, will broaden the sharp cutoff imposed by Eq. 1. The value of $E_{\min}$ might then be taken as midway along the trapping probability curve [20, 30].

- The Maxwellian flux distribution in terms of translational energy E is given by $J(E) = E/(RT)^2 e^{-E/RT}$. This function peaks at $E = RT = 2.5$ kJ/mol at

300 K and has an average value of $2 RT = 5.0$ kJ/mol (not $3/2 RT$, which is the average energy of the number-density distribution). In the example above, only 1 in 120,000 molecules at 300 K have translational energies greater than 36 kJ/mol (only 1 in 160 have energies greater than 18 kJ/mol and 1 in 8 have energies greater than 9 kJ/mol). This is a general result: while even heavy gases will often scatter directly from a surface at high collision energies of many 10s to 100s of kJ/mol, these energies have vanishingly low probabilities in a room temperature Maxwellian distribution. Full energy dissipation and trapping (adsorption) is the rule rather than the exception for most molecules on most surfaces near room temperature.

4 Implications of Detailed Balance

The three rules above have immediate implications for the evaporation of gases from solids and liquids. By detailed balancing, the desorption flux J_{des} is equal to the flux of impinging molecules J_{trap} that are momentarily trapped in the interfacial region. The trapping probability $\beta(E, \theta)$ then connects the desorbing and impinging fluxes via [30]

$$\begin{aligned} J_{\text{des}}(E, \theta) &= J_{\text{trap}}(E, \theta) = \beta(E, \theta) \cdot J_{\text{inc}}(E, \theta) \\ &= \beta(E, \theta) \cdot \frac{E}{(RT)^2} e^{-E/RT} \cdot \frac{\cos \theta}{4\pi} \cdot n_{\text{gas}} \end{aligned} \quad (2)$$

such that $\beta(E, \theta)$ may be considered both the trapping probability ($J_{\text{trap}}/J_{\text{inc}}$) and the evaporation probability ($J_{\text{des}}/J_{\text{inc}}$). The rules of thumb above suggest that $\beta(E, \theta)$ will be constant and close to one for most gases, especially when the liquids are made of light molecules such as water (where μ often exceeds one) and where dispersion, dipolar, and hydrogen bonding interactions occur. Thus, most gas molecules should evaporate in a distribution that is close to Maxwellian and cosine at room temperature from water and organic liquids, but perhaps not from solid or liquid metals [30, 38].

Deviations from the typical rules for trapping can reveal underlying mechanisms. One deviation occurs when $\beta(E, \theta)$ changes significantly over the energies in a Maxwellian distribution (0 to $\sim 7 RT_{\text{liq}}$) or at grazing angles, most likely because of light gas/heavy surface masses (small μ) and weak attractions ε . In these cases, collisions at low energy should lead to trapping while the molecules will scatter at higher energies (as predicted by Eq. 1). Detailed balancing then requires that the adsorbate will desorb in a speed distribution tilted toward lower translational energies because $\beta(E, \theta)$ steadily declines from high to low values as E increases. Rettner and coworkers indeed show this behavior for argon atoms desorbing from hydrogen-covered tungsten, whose sub-Maxwellian desorption matches the distribution of incoming Ar atoms that are momentarily trapped at the surface [30]. This study is mandatory reading for its clarity and precision.

Conversely, imagine an H_2 molecule dissociating upon collision with a metal surface, such as copper. It must have enough translational energy to overcome the ~ 20 kJ/mol barrier in order to break the H–H bond and form surface Cu–H bonds. High energies along the surface normal facilitate this dissociative adsorption. In the reverse associative desorption, the two adsorbed H atoms come together to generate an H_2 molecule that suddenly finds itself repulsively close to the surface and leaves the surface at high energies, preferentially along the surface normal, that match the incoming energies that lead to dissociation. This detailed balancing of dissociative adsorption and recombinative desorption is observed in pioneering experiments by Cardillo and coworkers and by others [4, 28].

5 Maxwellian Evaporation and a Two-Step Model for Solvation

Now we come to the question in this chapter. Are there also deviations in Maxwellian evaporation from liquids and solutes dissolved in them? During 30 years of observation, we have monitored the vacuum evaporation of liquids such as glycerol, ethylene glycol, alkanes and aromatics, fluorinated ethers, and water from sulfuric acid and pure and salty water itself [39–43]. We have also recorded the evaporation of solute atoms and molecules such as Ar, N_2 , O_2 , HCl, HBr, HI, Cl_2 , Br_2 , BrCl, N_2O_5 , HNO_3 , CO_2 , SO_2 , HC(O)OCH_3 , CH_3OCH_3 , CH_3NHCH_3 , and butanol from one or more of the solvents listed above and others [39, 40, 42, 44–48]. We observed Maxwellian speed distributions in every case (except when the vapor pressure is so high that the gas expands supersonically [41, 49]). This observation is in accord with the arguments above, so we were not surprised. For solvent evaporation and condensation, the mass of the evaporating solvent is necessarily equal to the mass of the surface molecules ($\mu = 1$). In this case, there is very efficient energy transfer (just like billiard balls) and the attractive forces that cohere the molecules into a liquid also trap the gaseous solvent molecule upon collision with the surface. For hydrogen-bonding gases, the attractive forces are also very strong and lead to significant trapping.

We also find, however, that even Ar and N_2 evaporating from salty water evaporate in Maxwellian distributions (within our signal to noise) [42, 43, 50]. By detailed balancing, this Maxwellian evaporation implies that collisions of Ar and N_2 at energies populated in a Maxwellian distribution must thermally equilibrate upon collision. This nearly complete thermalization is likely promoted by the soft nature of surfaces composed of water and organic molecules (it is not true for liquid metals) and weak attractions of a few RT_{liq} .

Separate studies provide insights into the mechanism of dissolution and reaction. Reactive scattering experiments probe $\text{HCl} \rightarrow \text{DCl}$ exchange in collisions of HCl with liquid $\text{D}_2\text{O}/\text{D}_2\text{SO}_4$ and of $\text{Cl}_2 \rightarrow \text{Br}_2$ exchange and $\text{N}_2\text{O}_5 \rightarrow \text{Br}_2$ oxidation in NaBr/glycerol [39, 45, 46]. In all three cases, the product DCl or Br_2 evaporates in a Maxwellian distribution at the temperature of the liquid. The measurements reveal

that the ratio of the desorbing product to trapping-desorption (TD) component of the reactant ($J(\text{product})/J_{\text{TD}}(\text{reactant})$) is independent of reactant collision energy from near-thermal to hyperthermal energies. These observations suggest a two-step process for dissolution and reaction (as illustrated in Fig. 2): [39] (1) incoming molecules either directly scatter from the surface or dissipate their excess translational energy, becoming momentarily trapped within the gas-surface potential energy well and losing memory of their initial trajectory, and then (2) these trapped molecules either evaporate or dissolve into the bulk at rates that are determined by gas and liquid properties and temperature, but not by their initial trajectory. In this two-step process, reaction occurs after thermalization within the interfacial region or deeper in the bulk. For the reversible solvation of a non-reacting gas (such as Ar or CH_3OCH_3), evaporation occurs along the reverse pathways, starting with the solute molecule diffusing from the bulk to the surface and then being jettisoned in a Maxwellian distribution into the vacuum by numerous energy-exchanging encounters with surface molecules. This two-step mechanism likely applies to the dissolution and evaporation of most gaseous solutes, but are there exceptions?

6 Non-Maxwellian Evaporation Discovered!

Faubel and Kisters first observed the non-Maxwellian evaporation of acetic acid dimers from a water microjet in 1988, which they attributed to repulsive ejection of the hydrophobic dimer at the surface of water [51]. This single observation persisted until we recorded the non-Maxwellian evaporation of helium atoms in 2014 [50]. Our measurements came about by accident: we were generating microjets [42, 50, 52] of alkane solutions to mimic evaporation of jet fuel in vacuum, which were created by pressurizing a sealed reservoir of the liquid with Ar or N_2 (as first developed by Manfred Faubel [53, 54] and described in Chap. 26). As shown in Fig. 3, the pressurized liquid then emerges from a glass tube with a tapered hole as narrow as $10\text{ }\mu\text{m}$ in diameter. We found that, by vigorously shaking the reservoir, gas can be dissolved into the liquid, which then evaporates as the thin liquid stream exits the nozzle and passes through the vacuum chamber. We have exploited the Maxwellian evaporation of dissolved Ar atoms as “argon jet thermometry” because the Ar speed distribution yields the instantaneous temperature of the jet.

Helium may also be used as a pressurizing gas to create microjets. To our astonishment, we found that He evaporation is non-Maxwellian for every solvent tested, including octane, dodecane, squalane, jet fuel, ethylene glycol, and pure and salty water (as shown in Fig. 4 for 7 M LiBr and 7 M LiCl in water) [42, 43, 50]. Importantly, its behavior is opposite to expectations: instead of evaporating in a slower, sub-Maxwellian distribution, as predicted by argon desorbing from tungsten mentioned above, the He atoms evaporate in a distinctly faster, *super-Maxwellian* distribution! The extent of non-Maxwellian behavior can be gauged by the average translational energy of the exiting He atoms: $1.14 \cdot (2RT_{\text{liq}})$ for dodecane at 295 K, $1.37 \cdot (2RT_{\text{liq}})$

Fig. 3 Vacuum evaporation of helium from pure and salty water microjets. The microjet is a fast-moving thin stream of solvent typically thinner than a strand of hair. When the jet radius is significantly smaller than the He-water mean free path, nearly all He atoms avoid collisions with evaporating water molecules in the vapor cloud surrounding the jet. The jet diameters range from 10 to 35 μm and travel at ~ 20 m/s. The breakup lengths vary from less than 1 mm for pure water at 252 K to 7 mm for 7 M LiBr/H₂O at 235 K

for pure supercooled water at 252 K, and $1.70 \cdot (2RT_{\text{liq}})$ for 7 M LiBr/H₂O at 255 K, which are 14, 37, and 70% higher than expected [42, 43].

Detailed balancing provides a fascinating interpretation: the super-Maxwellian evaporation of He atoms implies that the reverse process of He dissolution must also be super-Maxwellian.¹ The translational energies of He atoms that dissolve are shifted to higher values, such that the solvation probability, the analog of the trapping probability, increases with increasing collision energy. This result may be interpreted to mean that some He atoms dissolve by “ballistic penetration”, pushing water molecules slightly aside as they pass through the interfacial region and enter the liquid! The measured, relative evaporation probabilities $\beta(E)$ for 7 M LiCl and LiBr in water are shown in Fig. 4, which by detailed balance are also the relative solvation

¹We note that the reverse scattering experiments of He from liquids is complex, involving at least four pathways: direct recoil, trapping-desorption, trapping-dissolution-evaporation, and “ballistic” entry and evaporation. Our attempts to separate the processes have not been successful, as the TOF spectra are dominated by direct recoil. Dissolution appears to be a rare event.

Fig. 4 Examples of helium evaporation from salty water. (a) TOF spectra of He atoms evaporating from 8 molal (7 M) LiBr (232 K) and LiCl (237 K), which peak at significantly shorter arrival times (higher speeds and kinetic energies) than the dashed Maxwellian distributions at each temperature. (b) The corresponding translational energy distributions of the He atoms, again in comparison to Maxwellian distributions (dashed lines, here called P_{MB}). The relative solvation probabilities $\beta(E)$ (dot-dash) each rise steadily with kinetic energy (see Footnote 2). Panel c shows the excellent agreement between the Skinner/Kann simulations and measurements. This figure is reproduced from Ref. [43]

probabilities for He atoms.² Both curves rise steadily with increasing evaporation energy (which is also the collision energy for the reversed trajectories). Many of these He atoms therefore circumvent the two-step trapping-dissolution mechanism

²Because we measure only relative He fluxes in the experiments, not absolute fluxes, $J_{\text{des}}(E)$ and $J_{\text{inc}}(E)$ are each area-normalized in Fig. 4, only ratios of $\beta(E)$ at different E are meaningful. The angular average over $\beta(E, \theta)$ for the cylindrical microjet is described in Refs. [42, 43].

described above as they pass through the interfacial region. But why? Helium atoms have the lowest polarizability of any atom in the periodic Table ($0.2 \text{ \AA}^3$). In turn, the He-surface potential energy may be so shallow (less than RT_{liq}) that the attractive forces cannot capture He atoms at the surface for the time needed for He atoms to dissolve—thermal motions of the surface molecules instead immediately kick most of the He atoms back into the gas phase. In this case, a substantial fraction of the He atoms cannot enter the liquid via the adsorbed state because the shallow well cannot trap them. We know that the high-energy evaporation of He does not originate from its low mass because the opposite behavior is observed for the evaporation of H_2 from water. For this even lighter gas, evaporation is indeed sub-Maxwellian, as predicted kinematically: energy transfer between H_2 and water is inefficient ($\mu = 0.11$), and only the low energy H_2 molecules lose enough energy to be trapped in the H_2 -water potential energy well (H_2 is 4 times more polarizable than He). We also note that the only other gas we have observed that displays super-Maxwellian behavior is neon, which is also weakly polarizable ($0.4 \text{ \AA}^3$).

7 A View from the Interior

Detailed balancing arguments are beautiful and rigorous and in accord with experiments, but they leave us yearning to know more. How do the dissolved He atoms “know” to evaporate in the same super-Maxwellian distribution that leads to dissolution? It must be so because a single (but complex) potential energy function for all He-water and water-water interactions governs the reverse evaporation and condensation processes [29]. Comsa and David [4] quote an early pioneer, Peter Clausing, who described the detailed balancing requirement of the cosine angular distribution for condensation and evaporation as an “incomprehensible wonder machine”, but this statement could apply to the speed distribution as well. My theory colleague Jim Skinner and his student Zak Kann set out to make helium evaporation from water comprehensible, but their explanation is still full of wonder.

Skinner and Kann first performed classical molecular dynamics simulations of He atoms dissolved in pure liquid water [43]. Their simulations indeed show that dissolved He atoms possess a Maxwellian speed distribution right up to the top one to two layers of water, where the He atom is then accelerated into vacuum during the final few collisions of He with H_2O molecules moving outward. My students and I had hoped that the measured He speed distributions would reveal new features of gas-water interactions, but the agreement between simulation and measurement was excellent! Skinner and Kann then went a step further, calculating the Potential of Mean Force (PMF) on the He atom. This potential is equal to the free energy of the He atom as it is dragged infinitely slowly through the interface and into the bulk, sampling all configurations of the water molecules along the way. The free energy curve (PMF) of He in pure water calculated at 255 K is shown in Fig. 5. It starts high in bulk water and decreases to the gas phase value: the difference between the asymptotes is equal to the (very positive) free energy of solvation of approximately

Fig. 5 Potential of Mean Force (PMF) description of an He atom being expelled from water at 255 K. The black curve is the liquid water density, for which the 0 distance is the Gibbs dividing surface. The blue curve is the calculated helium PMF (free energy of solvation), and the green curve is the mean force (negative derivative of the PMF), which spikes in the interfacial region. The grey curve is the resulting helium atom kinetic energy. For these curves, the PMF spans 0 to 10 kJ/mol, the He density-averaged KE spans $(3/2)RT = 3.2$ kJ/mol to $\sim 1.5 \times (3/2)RT = 4.7$ kJ/mol, and the mean force spans -0.5 to $+2.3$ kJ/mol/Å. The small drop in He kinetic energy after 1 Å reflects the weak attractive force between He and surface water molecules decelerating the He atom as it leaves. This figure is adapted from Ref. [43]

9.5 kJ/mol at the supercooled 252 K temperature of the 10 μm diameter microjet. Accordingly, helium has the lowest solubility of any gas in water, equal to $n_{\text{water}}/n_{\text{gas}} \sim 1/100$ at 252 K. The free energy curve may possess a small barrier (<0.5 kJ/mol) between the surface and bulk regions, but displays at most a very shallow minimum at the surface. This is unlike even N_2 or O_2 , which are also weakly soluble but whose attraction to H_2O generate weak adsorption wells (>2 kJ/mol) [55].

Why then do He atoms emerge at higher than Maxwellian translational energies? The negative derivative of the free energy curve is just the “mean force” associated with the PMF—it is the repulsive force acting on the He atom itself as it moves infinitely slowly through the liquid! Figure 5 shows this mean force spikes right at the interface where the He atoms are accelerated [43]. Here is the key point: if the He atom indeed moved slowly through the interfacial region, it would undergo enough energy-exchanging collisions with water molecules at each point to maintain a Maxwellian distribution. But the He atoms do not move slowly, and at some point they stop equilibrating as the interfacial density becomes sparser (as in Fig. 5) and there are insufficient He– H_2O collisions to absorb the extra He atom energy. In this case, the He atom “detaches” from the PMF and exits into vacuum, carrying its excess energy with it imparted by the repulsive forces. In a sense, the water molecules “squeeze” the interloping He atom into vacuum as the water–water hydrogen bonds “heal” to their native structure.

We note that the PMF only describes the force perpendicular to the surface. Skinner and Kann have also investigated the angular distributions of evaporating atoms, and deduce that the perpendicular component is even more super-Maxwellian but is partially canceled by sub-Maxwellian parallel components [56]. This study includes

a wide-ranging investigation of the effects of solute mass and solute-solvent attractive forces on solute evaporation, including confirmation that H_2 is sub-Maxwellian and Ne is super-Maxwellian. Parallel simulations by Williams, Patel, and Koehler of He evaporation from dodecane lead to a fascinating “cone and crater” mechanism by which He atoms are expelled in an exposed cone at the surface whose walls may crater inward, accelerating the He atom from the cone [57, 58].

One rule of thumb emerges from these investigations: the more insoluble the gas, the steeper the PMF, the greater the force on the evaporating gas atoms, and the more likely that the He atom will emerge in a non-Maxwellian distribution. Thus, higher He atom exit energies should accompany lower solubilities in different solvents, a trend that we observe experimentally [43]. This correlation is not quantitative, however, because the PMF describes a slowly moving solute atom that fully equilibrates as it moves through solution and samples all configurations of the water molecules—it is the breakdown of this picture arising from insufficient He-water collisions in the outermost region that gives rise to an excess kinetic energy. A focus on the mean force and interfacial collisions instead provides an exquisite statistical framework that can guide future investigations.

8 Future Non-Maxwellian Adventures

What are some potential new directions for helium evaporation experiments? The demonstration of super-Maxwellian He evaporation is the closest we have come to He atom diffraction from periodic solid surfaces. The question of what can be learned from He scattering from liquids was one my students and I asked when we began in 1988, and it took until now to address it: super-Maxwellian He evaporation from liquids reflects the forces acting on the He atom in the outermost layers of the liquid. Skinner’s and Kann’s successful simulations [43] suggest that He evaporation from pure and salty water may not contribute to a refined picture of gas-water interactions because they were already so successful in replicating the energy distributions. But water is almost never pure or even just salty. Oceans, lakes, aerosol particles, and tap water contain numerous organic species, many of which are surface active [59–61]. We hope in future studies to investigate surfactant-coated microjets prepared with soluble ionic species such as tetrabutylammonium bromide and neutral ones such as butanol or pentanoic acid [47]. Helium evaporation from these surfactant solutions may reveal how gases move through loosely to tightly packed alkyl chains, depending on their bulk-phase concentration, and thus provide information on the mechanisms of gas transport through monolayers [62]. It will also be intriguing to mimic the seminal studies of the Cardillo and Comsa groups [4, 28], who investigated H_2 permeation and desorption through metals. We can monitor the parallel evaporation of He atoms through thin polymer films of functionalized organic polymers and even self-assembled monolayers over a wide range of exit angles. It is inspiring to imagine that Stern might have enjoyed these studies, an extension of his “method of

molecular rays” to liquids in vacuum, “for which I [Stern] consider the directness and simplicity as the distinguishing property.”

Acknowledgements This work was supported by the National Science Foundation (CHE-1152737) and the Air Force Office of Scientific Research. I thank the many contributions of my students working on the projects described here, including Alexis Johnson, Diane Lancaster, Jennifer Faust, Christine Hahn, and Tom Sobyra, who all became masters of microjets and committed untold hours to making these experiments work. I am also indebted to Zak Kann and Jim Skinner for a bountiful collaboration and for teaching us the extraordinary insights that statistical mechanics can provide. I am grateful to Dudley Herschbach for introducing me to the life of Otto Stern and to Dudley and Peter Toennies for being Honorary Chairpersons of the Otto Stern conference. My special thanks go to Bretislav Friedrich and Horst Schmidt-Böcking for organizing and directing every aspect of the conference, which spanned science, history, philosophy, music, science outreach, and a dazzling excursion on the Rhein River. Otto Stern leapt off the page through loving tributes, history lessons, and the astonishingly manifold applications of the molecular ray technique that he founded. We all glimpsed a multidimensional human being—a fantastically insightful and fearless scientist and outstandingly moral mentor in dark times. His words and deeds have become a constant companion.

References

1. O. Stern, A direct measurement of thermal molecular speed. *Z. Phys.* **2**, 49–56 (1920)
2. O. Stern, Addition to my work “a direct measurement of thermal molecular speed”. *Z. Phys.* **3**, 417–421 (1920)
3. I. Estermann, O.C. Simpson, O. Stern, The free fall of atoms and the measurement of the velocity distribution in a molecular beam of cesium atoms. *Phys. Rev.* **71**, 238–249 (1947)
4. G. Comsa, R. David, Dynamical parameters of desorbing molecules. *Surf. Sci. Rep.* **5**, 145–198 (1985)
5. A.H. Persad, C.A. Ward, Expressions for the evaporation and condensation coefficients in the Hertz-Knudsen relation. *Chem. Rev.* **116**, 7727–7767 (2016)
6. J.C. Maxwell, Illustrations of the dynamical theory of gases—Part I. On the motions and collisions of perfectly elastic spheres. London, Edinburgh Dublin Phil. Mag. J. Sci. **19**, 19–32 (1860)
7. J.C. Maxwell, VII. On stresses in rarified gases arising from inequalities of temperature. *Phil. Trans.* **170**, 231–256 (1879)
8. I. Estermann, O. Stern, Diffraction of molecular beams. *Z. Phys.* **61**, 95–125 (1930)
9. J.A. Barker, D.J. Auerbach, Gas-surface interactions and dynamics; thermal energy atomic and molecular beam studies. *Surf. Sci. Rep.* **4**, 1–99 (1985)
10. S.T. Ceyer, New mechanisms for chemical at surfaces. *Science* **249**, 133–139 (1990)
11. C.T. Rettner, D.J. Auerbach, J.C. Tully, A.W. Kleyn, Chemical dynamics at the gas-surface interface. *J. Phys. Chem.* **100**, 13021–13033 (1996)
12. G.M. Nathanson, Molecular beam studies of gas-liquid interfaces. *Ann. Rev. Phys. Chem.* **55**, 231–255 (2004)
13. J.W. Lu, B.S. Day, L.R. Fiegand, E.D. Davis, W.A. Alexander, D. Troya, J.R. Morris, Interfacial energy exchange and reaction dynamics in collisions of gases on model organic surfaces. *Prog. Surf. Sci.* **87**, 221–252 (2012)
14. H. Chadwick, R.D. Beck, Quantum state resolved gas-surface reaction dynamics experiments: a tutorial review. *Chem. Soc. Rev.* **45**, 3576–3594 (2016)
15. M.A. Tesa-Serrate, E.J. Smoll, T.K. Minton, K.G. McKendrick, Atomic and molecular collisions at liquid surfaces, in *Ann. Rev. Phys. Chem.*, vol. 67, ed. by M.A. Johnson, T.J. Martinez (2016), pp. 515–540

16. C.H. Hoffman, D.J. Nesbitt, Quantum state resolved 3D velocity map imaging of surface scattered molecules: incident energy effects in HCl plus self-assembled monolayer collisions. *J. Phys. Chem. C* **120**, 16687–16698 (2016)
17. F. Zaera, Use of molecular beams for kinetic measurements of chemical reactions on solid surfaces. *Surf. Sci. Rep.* **72**, 59–104 (2017)
18. W.A. Alexander, Particle beam scattering from the vacuum-liquid interface, in *Physical Chemistry of Gas-Liquid Interfaces*, ed. by J.A. Faust, J.E. House (Elsevier, The Netherlands, 2018), pp. 195–234
19. C.T. Rettner, D.J. Auerbach, Distinguishing the direct and indirect products of a gas-surface reaction. *Science* **263**, 365–367 (1994)
20. K.W. Kolasinski, *Surface Science: Foundations of Catalysis and Nanoscience*, 3rd edn. (Wiley, United Kingdom, 2012). Ch. 3
21. J.E. Hurst, C.A. Becker, J.P. Cowin, K.C. Janda, L. Wharton, D.J. Auerbach, Observation of direct inelastic scattering in the presence of trapping-desorption scattering—XE ON Pt(111). *Phys. Rev. Lett.* **43**, 1175–1177 (1979)
22. M.E. Saecker, G.M. Nathanson, Collisions of protic and aprotic gases with hydrogen-bonding and hydrocarbon liquids. *J. Chem. Phys.* **99**, 7056–7075 (1993)
23. I. Langmuir, The constitution and fundamental properties of solids and liquids part I solids. *J. Am. Chem. Soc.* **38**, 2221–2295 (1916)
24. D.F. Padowitz, S.J. Sibener, Sublimation of nitric oxide films—rotation and angular distributions of desorbing molecules. *Surf. Sci.* **217**, 233–246 (1989)
25. H.A. Michelsen, C.T. Rettner, D.J. Auerbach, R.N. Zare, Effect of rotation on the translational and vibrational energy dependence of the dissociative adsorption of D₂ on Cu(111). *J. Chem. Phys.* **98**, 8294–8307 (1993)
26. M.J. Weida, J.M. Sperhac, D.J. Nesbitt, Sublimation dynamics of CO₂ thin films: a high resolution diode laser study of quantum state resolved sticking coefficients. *J. Chem. Phys.* **105**, 749–766 (1996)
27. P. Varilly, D. Chandler, Water evaporation: a transition path sampling study. *J. Phys. Chem. B* **117**, 1419–1428 (2013)
28. M.J. Cardillo, M. Balooch, R.E. Stickney, Detailed balancing and quasi-equilibrium in adsorption of hydrogen on copper. *Surf. Sci.* **50**, 263–278 (1975)
29. J.C. Tully, Dynamics of gas-surface interactions: thermal desorption of Ar and Xe from platinum. *Surf. Sci.* **111**, 461–478 (1981)
30. C.T. Rettner, E.K. Schweizer, C.B. Mullins, Desorption and trapping of argon at a 2H–W(100) surface and a test of the applicability of detailed balance to a nonequilibrium system. *J. Chem. Phys.* **90**, 3800–3813 (1989)
31. E.K. Grimmelmann, J.C. Tully, M.J. Cardillo, Hard-cube model analysis of gas-surface energy accommodation. *J. Chem. Phys.* **72**, 1039–1043 (1980)
32. M.E. King, G.M. Nathanson, M.A. Hanninglee, T.K. Minton, Probing the microscopic corrugation of liquid surfaces with gas-liquid collisions. *Phys. Rev. Lett.* **70**, 1026–1029 (1993)
33. M.E. Saecker, G.M. Nathanson, Collisions of protic and aprotic gases with a perfluorinated liquid. *J. Chem. Phys.* **100**, 3999–4005 (1994)
34. B.G. Perkins, D.J. Nesbitt, Quantum-state-resolved CO₂ scattering dynamics at the gas-liquid interface: Incident collision energy and liquid dependence. *J. Phys. Chem. B* **110**, 17126–17137 (2006)
35. T.Y. Yan, W.L. Hase, J.C. Tully, A washboard with moment of inertia model of gas-surface scattering. *J. Chem. Phys.* **120**, 1031–1043 (2004)
36. W.A. Alexander, J.M. Zhang, V.J. Murray, G.M. Nathanson, T.K. Minton, Kinematics and dynamics of atomic-beam scattering on liquid and self-assembled monolayer surfaces. *Faraday Discuss.* **157**, 355–374 (2012)
37. T.B. Sobyra, M.P. Melvin, G.M. Nathanson, Liquid microjet measurements of the entry of organic acids and bases into salty water. *J. Phys. Chem. C* **121**, 20911–20924 (2017)
38. M. Manning, J.A. Morgan, D.J. Castro, G.M. Nathanson, Examination of liquid metal surfaces through angular and energy measurements of inert gas collisions with liquid Ga, In, and Bi. *J. Chem. Phys.* **119**, 12593–12604 (2003)

39. J.R. Morris, P. Behr, M.D. Antman, B.R. Ringeisen, J. Splan, G.M. Nathanson, Molecular beam scattering from supercooled sulfuric acid: collisions of HCl, HBr, and HNO₃ with 70 wt % D₂SO₄. *J. Phys. Chem. A* **104**, 6738–6751 (2000)
40. A.H. Muentert, J.L. DeZwaan, G.M. Nathanson, Collisions of DCl with pure and salty glycerol: enhancement of interfacial D → H exchange by dissolved NaI. *J. Phys. Chem. B* **110**, 4881–4891 (2006)
41. S.M. Brastad, G.M. Nathanson, Molecular beam studies of HCl dissolution and dissociation in cold salty water. *Phys. Chem. Chem. Phys.* **13**, 8284–8295 (2011)
42. D.K. Lancaster, A.M. Johnson, K. Kappes, G.M. Nathanson, Probing gas–liquid interfacial dynamics by helium evaporation from hydrocarbon liquids and jet fuels. *J. Phys. Chem. A* **146**, 14613–14623 (2015)
43. C. Hahn, Z.R. Kann, J.A. Faust, J.L. Skinner, G.M. Nathanson, Super-Maxwellian Helium evaporation from pure and salty water. *J. Chem. Phys.* **144** (2016)
44. B.R. Ringeisen, A.H. Muentert, G.M. Nathanson, Collisions of HCl, DCl, and HBr with liquid glycerol: gas uptake, D → H exchange, and solution thermodynamics. *J. Phys. Chem. B* **106**, 4988–4998 (2002)
45. L.P. Dempsey, J.A. Faust, G.M. Nathanson, Near-interfacial halogen atom exchange in collisions of Cl₂ with 2.7 M NaBr–glycerol. *J. Phys. Chem. B* **116**, 12306–12318 (2012)
46. M.A. Shalowski, J.R. Gord, S. Staudt, S.L. Quinn, T.H. Bertram, G.M. Nathanson, Reactions of N₂O₅ with salty and surfactant-coated glycerol: interfacial conversion of Br[−] to Br₂ mediated by alkylammonium cations. *J. Phys. Chem. A* **121**, 3708–3719 (2017)
47. T.B. Sobyra, H. Pliszka, T.H. Bertram, G.M. Nathanson, Production of Br₂ from N₂O₅ and Br[−] in salty and surfactant-coated water microjets. *J. Phys. Chem. A* **123**, 8942–8953 (2019)
48. T. Krebs, G.M. Nathanson, Reactive collisions of sulfur dioxide with molten carbonates. *Proc. Natl. Acad. Sci. U.S.A.* **107**, 6622–6627 (2010)
49. D.K. Lancaster, A.M. Johnson, D.K. Burden, J.P. Wiens, G.M. Nathanson, Inert gas scattering from liquid hydrocarbon microjets. *J. Chem. Phys. Lett.* **4**, 3045–3049 (2013)
50. A.M. Johnson, D.K. Lancaster, J.A. Faust, C. Hahn, A. Reznickova, G.M. Nathanson, Ballistic evaporation and solvation of helium atoms at the surfaces of protic and hydrocarbon liquids. *J. Phys. Chem. Lett.* **5**, 3914–3918 (2014)
51. M. Faubel, T. Kisters, Non-equilibrium molecular evaporation of carboxylic acid dimers. *Nature* **339**, 527–529 (1989)
52. J.A. Faust, G.M. Nathanson, Microjets and coated wheels: versatile tools for exploring collisions and reactions at gas–liquid interfaces. *Chem. Soc. Rev.* **45**, 3609–3620 (2016)
53. M. Faubel, S. Schlemmer, J.P. Toennies, A molecular beam study of the evaporation of water from a liquid jet. *Z. Phys. D* **10**, 269–277 (1988)
54. M. Faubel, Photoelectron spectroscopy at liquid surfaces, in *Photoionization and Photodetachment: Part I*, vol. 10A, ed. by C.-Y. Ng (World Scientific, Singapore, 2000), pp. 634–690
55. R. Vácha, P. Slavíček, M. Mucha, B.J. Finlayson-Pitts, P. Jungwirth, Adsorption of atmospherically relevant gases at the air/water interface: free energy profiles of aqueous solvation of N₂, O₂, O₃, OH, H₂O, HO₂, and H₂O₂. *J. Phys. Chem. A* **108**, 11573–11579 (2004)
56. Z.R. Kann, J.L. Skinner, Sub- and super-Maxwellian evaporation of simple gases from liquid water. *J. Chem. Phys.* **144**, 154701 (2016)
57. S.V.P. Koehler, M.A. Williams, MD simulations of He evaporating from dodecane. *Chem. Phys. Lett.* **629**, 53–57 (2015)
58. E.H. Patel, M.A. Williams, S.P.K. Koehler, Kinetic energy and angular distributions of He and Ar atoms evaporating from liquid dodecane. *J. Phys. Chem. B* **121**, 233–239 (2017)
59. R.E. Cochran, O. Laskina, J.V. Trueblood, A.D. Estillore, H.S. Morris, T. Jayarathne, C.M. Sultana, C. Lee, P. Lin, J. Laskin, A. Laskin, J.A. Dowling, Z. Qin, C.D. Cappa, T.H. Bertram, A.V. Tivanski, E.A. Stone, K.A. Prather, V.H. Grassian, Molecular diversity of sea spray aerosol particles: impact of ocean biology on particle composition and hygroscopicity. *Chem* **2**, 655–667 (2017)
60. T.H. Bertram, R.E. Cochran, V.H. Grassian, E.A. Stone, Sea spray aerosol chemical composition: elemental and molecular mimics for laboratory studies of heterogeneous and multiphase reactions. *Chem. Soc. Rev.* **47**, 2374–2400 (2018)

61. K. Jardak, P. Drogui, R. Daghrir, Surfactants in aquatic and terrestrial environment: occurrence, behavior, and treatment processes. *Environ. Sci. Pollut. Res.* **23**, 3195–3216 (2016)
62. G.T. Barnes, Permeation through Monolayers. *Colloids Surf. A* **126**, 149–158 (1997)

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.