1. Supercool Water - How the Gibbs Free Energy Explains Metastability in Classical Nucleation Theory

It is well known that purified water can remain in a metastable liquid state well below its freezing point[1]. This seems to contradict common phase diagrams, like figure 1A, which show for a given pressure and temperature which phase has the lowest Gibbs free energy. To explain why the phase transition still does not occur spontaneously, it is necessary to condsider the *process* of ice formation, from which one finds a separate contribution to the Gibbs free energy giving rise to a local minimum. Our analysis is based on classical nucleation theory (CNT) and in particular [5].

We consider an homogenous[2] system of water undergoing quasistatic cooling, such that the liquid is isothermal at short time-scales. We neglect hydrostatic variation to consider the fluid approximately isobaric at small length-scales. For the water to undergo a macroscopic phase transition into ice, a tiny ice crystal formed from microscopic fluctuations must be allowed to grow spontaneously; by the given assumptions, it is in contact with an isothermal, isobaric reservoir and will spontaneously minimize the Gibbs free energy.

Consider such a microscopic spherical ice crystal, referred to as a nucleus, with radius[3] r. For constant pressure p and a given temperature $T < T_m$, where $T_m(p)$ is the melting point of water, the ice phase will be preferred to the liquid phase by a free energy differnence $\Delta G_{ph}(T)$ per volume, which is known to be approximately proportional to the supercooling $\Delta T = T_m - T$:

$$\Delta G_{ph} = \frac{\Delta H_f \Delta T}{V_m T_m}, \quad [5] \tag{1}$$

where ΔH_f is the enthalpy of fusion and V_m is the molar volume. Hence the bulk of the ice crystal in supercooled water will carry a relative negative free energy

$$\Delta G_v(T, r) = -\Delta G_{ph} \frac{4}{3} \pi r^3$$

driving the phase transition to occurr.

However, the surface tension σ introduces an energy cost of creating a new surface for the nucleus, adding the positive surface term

$$\Delta G_s(r) = \sigma 4 \pi r^2.$$

Summing these terms gives the Gibbs free energy of the nucleus $\Delta G = \Delta G_s + \Delta G_v$ from CNT.

Interestingly, the surface term grows as r^2, while the volume term grows as r^3. This means that a small nucleus will spontaneously melt, as the surface term will dominate. Furthermore, there is a critical radius r^* at which the volume term gains dominance, such that any nucleus exceeding this size will grow to encompass the whole system. The situation is shown in figure 1B. We proceed by finding the stationary points of the Gibbs free energy difference:

$$0 = \left(\frac{\partial \Delta G}{\partial r} \right)_{T,\, p} = (8\pi\sigma - 4\pi \Delta G_{ph} r) r$$

[1] A video demonstration can be found in [6], the newest from Henry Reich at minutephysics, which inspired this choice of topic.

[2] That is, without impurities and in contact with no external surfaces.

[3] Note that for liquids and solids, the radius is related to the number of particles $N \propto r^3$ through the only weakly temperature and pressure-dependent density-coefficient ρ, and can be considered to play a similar role to N in the ideal gas system, being the extensive parameter in G.

giving a local minimum around $r = 0$, and a peak at $r^* = 2\sigma/\Delta G_{ph}$, see figure 1B. The corresponding critical Gibbs energy is

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_{ph}^2} = \frac{16\pi\sigma^3 V_m^2 T_m^2}{3\Delta H_f^2}\frac{1}{\Delta T^2} = \eta k T_m/\Delta T^2 \quad \text{with} \quad \eta = \frac{16\pi\sigma^3 V_m^2 T_m}{3k\Delta H_f^2},$$

where we used (1).

Now as we quasistatically cool water, it is always in thermal equilibrium, and so it is natural to assume for any given temperature T that the probability per volume of a nucleus of radius r forming is proportional[4] to the Bolzmann factor like in the canonical ensemble, as the system needs to find a balance between maximizing entropy and minimizing the Gibbs energy. This motivates the formation rate of a critical radius nucleus per volume from CNT

$$J = J_0 e^{-\frac{\Delta G^*}{kT}}, \quad [5]$$

where we here take J_0 to be approximately constant. We can then model the nucleus formation as a poisson process with rate $\lambda = JV$, where V is the total water volume. The expected survival time is then $\lambda^{-1} = (JV)^{-1}$, or, for low supercooling $T \approx T_m$, proportional to $e^{\eta/\Delta T^2}$.

This is exponentially inverse-qubic related to the supercooling, from which we can draw two conclusions: Firstly, water at low supercooling will persist essentially forever, unless a nucleation is sparked by external factors like impurities in the water or an external force to the container[5]. Secondly, there will be a sharp critical temperature where the expected time of stability will suddenly fall to the order of less than a second.

We have hence shown that for freezing to occur spontaneously, thermodynamic fluctuations must give rise to an ice crystal of radius greater than some critical radius which grows smaller as the supercooling increases. Furthermore, we have seen that in homogenous water without any external nucleation cites, this is extremely unlikely when the supercooling is small, explaining the observed effect of supercooled water.

[4]We will not concern ourselves with the kinetic prefactor, seeking only approximate scaling properties of the stability of supercooled water; the full expression is not more illuminating, involving the Zeldovich factor, the monomer attatchment frequency and the nucleation cite concentration as seen in equation 8 in [5].

[5]This gives rise to some very cool demonstrations, as in [6].

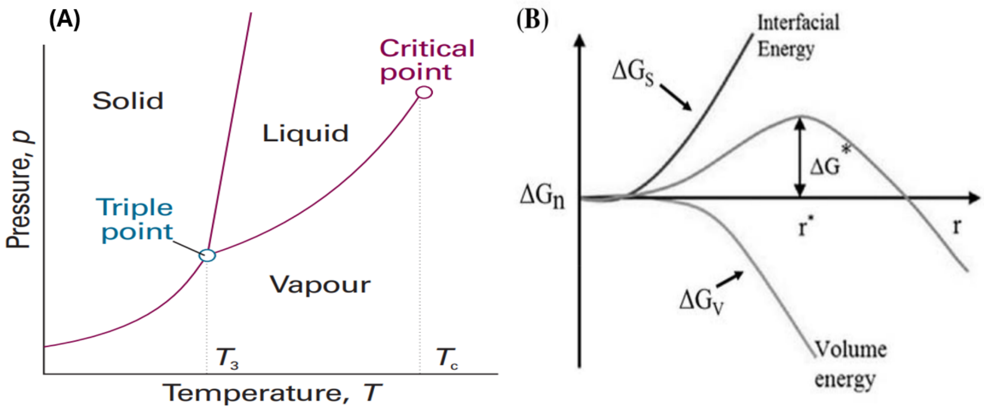

Figure 1: A) Phase diagram for water, indicating which phase is Gibbs-energetically favourable for the given pressure and temperature. The figure is a resized version of figure 4.1 in [1]. B) The free energy of the nucleus ΔG_n shown as a sum of a positive quadratic surface term and a negative cubic volume term giving a metastable supercooled state where thermodynamic fluctuations must create a nucleus exeeding the critical radius r^* for freezing to occur spontaneously. The figure is taken from [5].

2. A Note on Black Hole Entropy

Theorem (Bekenstein-Hawking entropy)**.** *The entropy of a black hole with mass M, charge Q and angular momentum L is given by*

$$S_{BH} = \frac{8\pi^2 kGU^2}{hc^5}, \tag{2}$$

where G is the gravitational constant, c is the speed of light and $U = M_{ir}c^2$, where

$$M_{ir}^2 = \frac{1}{2}\left(M^2 - \frac{Q^2}{2} + \sqrt{M^4 - L^2 - QM^2}\right) \tag{3}$$

denotes the irreducible mass (given here in natural units).

We will not consider quantum effects, and will only seek to prove this theorem up to an undetermined proportionality constant α (which turns out to be $\frac{\pi}{2}$), utilizing some results from the literature without proof. The hard part of our proof will be to establish the lemma below, starting from the following facts given in the excersise description:

Lemma. *The entropy of a black hole is proportional to its area, $S_{BH} = \xi A$.*

Fact 1 (No hair theorem)**.** *A black hole is fully characterised by three properties: Its mass M, charge Q, and angular momentum L.*

Fact 2 (Thermodynamic variables for a black hole)**.** *For the black hole system, M, Q and L play respectively the analagous roles of E, V, N in an ideal gas system. Introducing intensive conjugate variables Φ for the horizon electric potential and Ω for the horizon angular momentum we specifically get $dM = TdS + \Phi dQ + \Omega dL$.*

Fact 3 (The Schwarzschild radius)**.** *A Schwarzschild black hole is spherical with radius $R = \frac{2GM}{c^2}$.*

Our proof of the lemma will follow the general approach in [3], though we deviate in several details wherever I felt there was a more natural approach (perhaps at the expense of rigour). We start by reducing to the Schwarzschild case ($M = M_{ir}, Q = 0, L = 0$) by means of Penrose processes, establishing also that the entropy depends only on the area of the black hole. We then deduce the black hole temperature by thermodynamical arguments, and use the gravitational redshift in Schwarzschild geometry to get a formula for local temperature measurments close to the black hole. From this expression, we will deduce the lemma.

Proof of theorem. Before digging into the hard part, we deduce the theorem up to a proportionality constant α given the lemma and the fact that the problem reduces to the Schwarzschild case with $M = M_{ir}$. Dimensional analysis gives

$$[S] = [\xi][A] = [k],$$

and noting that[6] $[m^{-2}] = [c^3G^{-1}h^{-1}]$ we get

$$\xi = \alpha\frac{kc^3}{Gh}. \tag{4}$$

By Fact 3, $A = 4\pi R^2$, where $R = 2GMc^{-2}$, which gives

$$S_{BH} = \xi A = \alpha\frac{kc^3}{Gh}4\pi(\frac{2GM_{ir}}{c^2})^2 = \alpha\frac{16\pi kG}{hc^5}M_{ir}^2c^4 = \frac{2\alpha}{\pi}\frac{8\pi^2 kGU^2}{hc^5}$$

where we used (4) and $U = Mc^2$, which is simply the Einstein mass-energy relation applied to the Schwarzschild black hole. □

[6]This is unique, since the natural units $c = G = h = k = 1$ are clearly independent.

Proof of lemma. We adopt natural units $c = G = h = k = (4\pi\epsilon_0)^{-1} = 1$, where ϵ_0 is the vacuum permittivity; they are clearly independent. By the No hair theorem, we know that the entropy depends only on M, Q and L, so we will calculate the entropy for an arbitrarily given black hole with parameters M_0, Q_0, L_0.

From thermodynamic analogy to the ideal gas system, we see that to decrease L and Q to zero without changing the entropy of the black hole (that is, in a reversible process), we need $\mathrm{d}S = 0$, hence every infinitesimal change must satisfy

$$\mathrm{d}M = \Phi \mathrm{d}Q + \Omega \mathrm{d}L.$$

I assume that a description of the actual idealised methods for doing this are beyond the scope of the excercise, so we will simply refer to [3] and [2] to confirm that such reversible processes ideed are possible given that the black hole area remains constant.[7] Since we can thusly vary all parameters of the black hole without changing the entropy, S must be a function only of the black hole area. We are then free to reduce to the Scwarzschild case $M = M_{ir}, Q = L = 0$, where $M_{ir}(M_0, Q_0, L_0)$ is the mass which gives the same surface area for the Scwarzschild case as for the original black hole.

To determine the area of a charged, spinning black hole is also presumably beyond the scope of this course, so I simply state the results as given in [3] (combining equations 1.7, 1.9 and 1.10):

$$A = 4\pi R_{ir}^2 \quad \text{where} \quad R_{ir}^2 = 2M^2 - Q^2 + 2\sqrt{M^4 - L^2 - Q^2M^2}$$

is the squared radius of the resulting Schwarzschild black hole after the reversible transformation. Fact 3 then gives $M_{ir}^2 = R_{ir}^2/4$, which is easily seen to be the expression for the irreducible mass (equation 3) in the theorem, and gives

$$A = 16\pi M_{ir}^2, \tag{5}$$

which is confirmed by equation 4 in [2]. As we treat the reduced case, we will denote by M the irreducible mass from here on out.

The first law of thermodynamics (Fact 2) gives for the static Schwarzschild case of constant spin and charge[8]

$$\mathrm{d}M = T\mathrm{d}S = T\frac{\mathrm{d}S}{\mathrm{d}A}\mathrm{d}A = TS' \cdot 32\pi M \mathrm{d}M,$$

where we used (5) to compute $\mathrm{d}A$, and where $S' = \frac{\mathrm{d}S}{dA}$. Hence

$$T = \frac{1}{32\pi M S'} = \frac{M}{2AS'} \tag{6}$$

is the black hole temperature. It is worth discussing briefely what 'the temperature of a black hole' might mean. A black hole is a perfect black body, so assuming it radiates at all, it is natural to expect that it might radiate like a black body. Then the temperature is associated with the *strongest radiated frequency ν as observed from far away*, according to Wien's law[9] $T \propto \nu$. This was indeed shown by Hawking to be true (quantum derivation, of course, as classical black holes emit nothing), see [4].

Since we are in Scwarzschild geometry, it is then easy to find the temperature measured locally by a shell observer. Recall that the line element is

$$\mathrm{d}s^2 = \chi^2 \mathrm{d}t^2 - \frac{\mathrm{d}r^2}{\chi^2} - r^2\,\mathrm{d}\phi^2,$$

[7] Note that we take a more foundational route than thorugh the area theorem, which was mentioned in the excercise description, though we discuss its implications after the proof. This was approved by professor Jamieson.

[8] The result for T can be derived without the case reduction, as in [3], but I want to avoid the general expressions for tidyness.

[9] The derivation should also be possible from the Stefan-Bolzmann law, but one must be more careful then as multiple parameters are transforming due to the curved geometry. But since the Planck spectrum is uniformly redshifted, the ν-proportionality should hold also locally, so we might as well keep things simple.

where $\chi(r) = \sqrt{1 - \frac{2M}{r}}$ and we work in two spatial dimensions in polar coordinates r, ϕ. Letting Δt be the time step between succesive wave tops in the strongest radiation, we get $\nu = 1/\Delta t$ and so by Wien's law

$$\frac{T_{shell}}{T} = \frac{\nu_{shell}}{\nu} = \frac{\Delta t}{\Delta t_{shell}} = \frac{1}{\chi},$$

where we used $\Delta t_{shell} = \chi \Delta t$, which follows immediately from the line element when $dr = \mathrm{d}\phi = 0$ for a pure time displacement. Hence we can express the local temperature as

$$T_{shell} = \frac{T}{\chi}. \tag{7}$$

As we assumed that T_{shell} is a truly local measurement[10], it can only depend on the local curvature, or the gravitational pull at the shell radius. This is the geodesic devaiation, and we will not give a rigorous disposition[11], but we can give a very loose motivation for the expression: The redshift factor χ measures how light stretches in the curved space around the shell observer. The gradient $\mathrm{d}\chi/\mathrm{d}r$ measures how this stretching changes with position, so one might think that in order to stay fixed, one must in some sense accelerate against this gradient. Indeed, equation 2.11 in [3] confirms that

$$g_\chi = -\frac{\mathrm{d}\chi}{\mathrm{d}r} = \frac{M}{\chi r^2} \approx \frac{M}{\chi R^2}.$$

where we differentiated χ and chose a shell very close to the horizon, $r^2 \approx R^2$.

Inserting into (7) and using (6) we get

$$T_{shell}(g_\chi) = \frac{T}{\chi} = \frac{M}{2AS'}\frac{R^2}{M}g_\chi = \frac{1}{8\pi S'}g_\chi.$$

This should be true for any black hole, and in particular, there can be no area dependence in T_{shell} (the black hole area is not locally visible), so $S'(A) = \xi$ for some constant ξ. Solving this elementary differential equation under the boundary condition that empty space ($A = 0$) should have no entropy, we finally get

$$S_{BH} = \xi A.$$

□

This results warrants some qualitative discussion. First of all, one might ask whether this entropy is reasonable in the sense of the second law. Indeed, Hawking showed the so-called Area theorem ([8]); that the black hole area may never decrease (in classical general relativity). In light of our derivation, we get the second law of (classical) black hole thermodynamics: The entropy of a black hole may never decrease. This indicates that the thermodynamic perspective on black holes has some real physical significance.

Secondly, one may note that for a Schwarzchild black hole (or equivalently, in the limit where L and Q goes to zero), the irreducible mass is just the black hole mass, by (3), hence the temperature, which goes like $1/M_{ir}$ by the first equality in (6), depends only on the mass[12]. By analogy to an ideal gas system, this means that the temperature depends only on the energy parameter. This might be reminiscent of the photon gas[13],

[10] We will not prove this; arguments can be found in [3].

[11] The derivation is not hard, but I don't want to introduce covariant derivatives with Schwarzchild Christoffel symbols here. Details can be found 15 minutes into 'Lecture 09 - Acceleration' published on the LMS for PHYC90012 with professor Melatos, where he computes the four acceleration; our results follows from this by contracting to get the proper acceleration.

[12] This is essentialy trivial by the no hair theorem, but the inverse proportionality is due to our derivation.

[13] There is no volume term for the black hole; in fact, it is holographic in the sense that all information is contained at its surface.

$E/V = aT^4$, which is not too surprising, since we modeled the black hole as a black body in our derivation. More interestingly, the reciprocal relationship $T \propto 1/M$ implies a negative heat capacity $\mathrm{d}M/\mathrm{d}T$; quantum mechanically, as the black hole radiates mass, it grows hotter, hence it constantly counteracts thermal equilibrium with its surroundings. Thus, the canonical ensemble might be inappropriate for black hole thermodynamics. This peculiarity is discussed briefly in section 5 in [7].

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