Evaporation Wave Model for Superheated Liquids

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Summary

Experiments with rapid decompression of superheated liquids and droplets exploding near the superheat limit reveal the existence of steady evaporation waves. An idealized model for steady evaporation waves has been analyzed. A evaporation wave is treated as a jump or discontinuity between metastable liquid and an equilibrium vapor or liquid–vapor mixture.

Numerical solutions of the jump conditions have been obtained using Starling's equation of state to represent the thermodynamics of equilibrium and metastable states of hydrocarbon fluids. For simple fluids (small specific heat), only solutions with two-phase downstream states exist. Single-phase downstream states (complete evaporation waves) are predicted for complex fluids with a specific heat comparable to or greater than octane, given a sufficiently superheated initial state. Possible wave velocities range between zero and a maximum value determined by a Chapman-Jouguet condition.

This wave model is combined with a simple similarity description of liquid and vapor motion to predict the rates of steady spherical bubble growth in superheated liquids. The Chapman-Jouguet hypothesis is used to fix the evaporation rate and the results are compared with observations in bubble column experiments.

Introduction

Metastable liquids can spontaneously and rapidly change phase under adiabatic conditions. Metastable liquid states (shown in Fig. 1) can be experimentally reached from equilibrium states through processes of adiabatic depressurization and/or isobaric heating. The region of metastable liquid states is bounded by the equilibrium or saturation boundary on one side and the superheat limit on the other. The superheat limit is the temperature at which phase change is initiated by homogeneous nucleation; this temperature lies close to but below the absolute limit of thermodynamic stability, $(\partial p/\partial v)_T = 0$, known as the *spinodal*.

Superheated liquids and associated rapid phase changes appear in a variety of physical phenomena. A simple laboratory experiment is to heat a small droplet of fluid by immersing it in a column of denser fluid which is heated at the top and cooled at the bottom, a "bubble column". When the droplet temperature approaches the superheat limit, the droplet rapidly vaporizes (in less than 100 μs for a 1 mm diameter hydrocarbon droplet) with an audible pop. Detailed investigations (Shepherd and Sturtevant [1], Frost and Sturtevant [2]), have shown that under certain conditions (low ambient pressure, large superheat) the vaporization has an explosive character. In explosive

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boiling, the liquid is converted to a liquid-vapor mixture by a traveling wave which sweeps through the liquid at a velocity of 5-15 m/s. While this wave moves with a constant mean velocity, the surface is rough and unsteady, indicating violent instability and fragmentation processes occurring at the interface between liquid and liquid-vapor mixture.

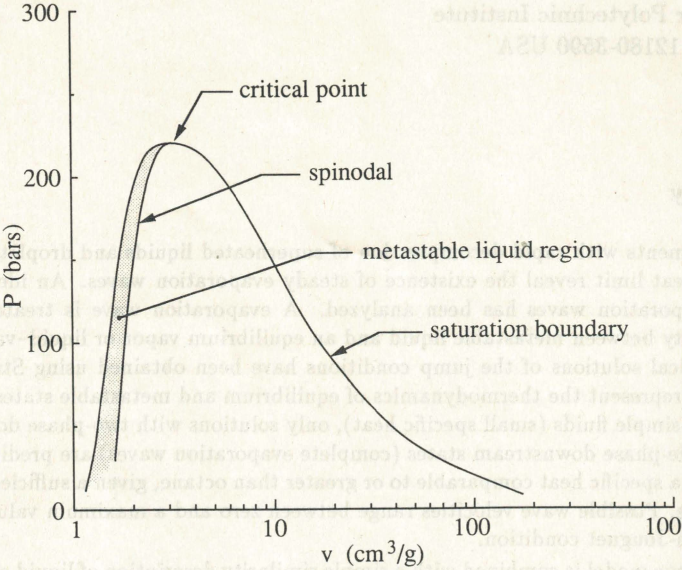

Figure 1. Pressure-volume diagram of a fluid showing the region of liquid metastable states bounded by the saturation line σ and the spinodal $(\partial p/\partial v)_T = 0$.

Evaporation waves are also observed in other laboratory experiments such as rapid depressurization of liquid-filled containers. Experiments, reviewed by Hill and Sturtevant [3] in this symposium, reveal that following the expansion wave created by depressurization, a much slower (0.5-25 m/s) evaporation wave follows. The wavefront moves at a constant mean velocity, but is highly disturbed and produces fine liquid fragments in the downstream flow.

The examples quoted above involve very low-speed waves but higher velocity evaporation waves may also exist. Molten metal-water interactions, often known as steam explosions, can result in quite violent interactions involving transient evaporation waves with velocities of up to 500 m/s. While the evidence for such high-speed waves is limited, numerous industrial accidents and large-scale experiments (see the references in Frost *et al.* [4] of this symposium) have demonstrated the destructive nature of these events.

These experimental observations of high and low speed waves have naturally led to the suggestion that evaporation waves are analogous to combustion waves and both subsonic (deflagration) and supersonic (detonation) waves may exist in superheated liquids. Indeed, as we discuss below, this analogy is exact in that two such solution branches do exist for steady waves in superheated liquids. This analogy has further suggested the special role of solutions with sonic (relative to the wave) flow downstream;

these are the Chapman-Jouguet (CJ) solutions of combustion. Frost [5] has estimated sound speeds in the liquid-vapor mixtures downstream of the evaporation wave observed in bubble growth and finds that the CJ condition appears to be satisfied. Chaves [6] investigated the same hypothesis for evaporation waves created in depressurization experiments and also obtained good agreement with the CJ hypothesis. It is not possible to obtain a CJ solution for a high-speed wave in a pure liquid (see the discussion in Fowles [7], this symposium) but wave speeds between 300 and 500 m/s have been predicted for supersonic waves which satisfy the CJ condition in liquid metal/liquid water/vapor water mixtures (Board and Hall [8]). Note that the water downstream of the wave in these "thermal detonations" is in a single fluid, supercritical state.

Analysis of Planar Steady Waves

The experimental and theoretical evidence reviewed above indicates that there are at least two classes of evaporation waves. In a variety of situations, these waves appear to be steady in an average, macroscopic sense, although violently unstable at a microscopic level. This suggests that a steady wave analysis, identical to that used for waves in inviscid reacting flow, can be used to explore the admissible solutions for steady evaporation waves in superheated liquids.

Consider a control volume surrounding a portion of a steady evaporation wave (Fig. 2); superheated liquid (labeled state 1) flows in from the left, vapor or liquid-vapor mixture (labeled state 2) flows out to the right. We suppose that the control volume can be chosen so that even if the wave is curved, it can locally be considered planar and any possible flow divergence will be neglected. In this frame of reference, the wave is at rest and the fluid moves into the wave with velocity w_1, density ρ_1, pressure p_1, enthalpy h_1 and entropy s_1 and leaves with corresponding quantities at state 2. We assume that there is no storage within the control volume, the flow is effectively inviscid, and the control volume has been chosen so that energy transport by heat conduction is negligible.

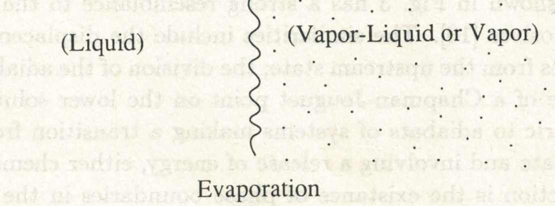

Figure 2. Control volume surrounding an steady evaporation wave. Upstream states (1) are superheated liquid; downstream states (2) can be either equilibrium liquid-vapor mixtures, pure liquid, or pure vapor.

Under the restrictions outlined above, upstream (1) and downstream (2) states are related by the jump conditions across an interface:

$$\rho_1 w_1 = \rho_2 w_2 \tag{1}$$

$$p_1 + \rho_1 w_1^2 = p_2 + \rho_2 w_2^2 \tag{2}$$

$$h_1 + \frac{w_1^2}{2} = h_2 + \frac{w_2^2}{2} \tag{3}$$

$$s_2 \geq s_1 \tag{4}$$

which are identical to the conditions used to describe inviscid gasdynamic discontinuities. These relations are supplemented by the equations of state $p(\rho, T)$, $h(\rho, T)$; we have used Starling's equations for hydrocarbons and Kennan and Keyes equations for water. Equations and parameter values were taken from Reynolds [9] compilation. Solutions for downstream states are obtained as a function of a single parameter such as wave speed or downstream pressure once the upstream state is specified. A variety of upstream states have been explored, these states are usually metastable liquid near the superheat limit. For a specified initial temperature and pressure, the initial enthalpy, density, and entropy are computed by extrapolating the equations into the metastable region. Inspection of property values estimated in this fashion show that reasonable results, *i.e.*, smooth extrapolation of equilibrium properties, no singularities near the spinodal, are obtained.

The downstream fluid is considered to be an equilibrium state, which could be either liquid, a liquid-vapor mixture, or pure vapor depending on the solution branch and fluid type. For single-phase downstream states, the jump equations (1-3) must be solved numerically by an iterative procedure. This is most conveniently performed by combining equations 1-3 to obtain the Rankine-Hugoniot equation,

$$h_2(p_2, v_2) - h_1 = \frac{1}{2}(p_2 - p_1)(v_2 + v_1) \tag{5}$$

which yields the locus of possible downstream states as a pressure-volume (p_2, v_2) curve known as the Hugoniot or shock adiabat. The adiabat can be obtained by direct computation without iteration when the downstream state is a mixture state, since the final pressure and temperature must lie on saturation curve σ. A complete adiabat curve for water with an initial state on the spinodal at $p_o = 2.89$ MPa, $T_o = 600$ K is shown in Fig. 3.

The adiabat shown in Fig. 3 has a strong resemblance to the adiabats predicted for chemical explosives [10]. The similarities include the displacement of the locus of downstream states from the upstream state; the division of the adiabat in two branches; and the existence of a Chapman-Jouguet point on the lower solution branch. These features are generic to adiabats of systems making a transition from a metastable to an equilibrium state and involving a release of energy, either chemical or thermal. An important distinction is the existance of phase boundaries in the superheated liquid case, these can result in slope discontinuities or *kinks* in the adiabat. Such features can give rise to wave instabilities or *shock splitting* [11] when constructing simple wave solutions to initial value problems.

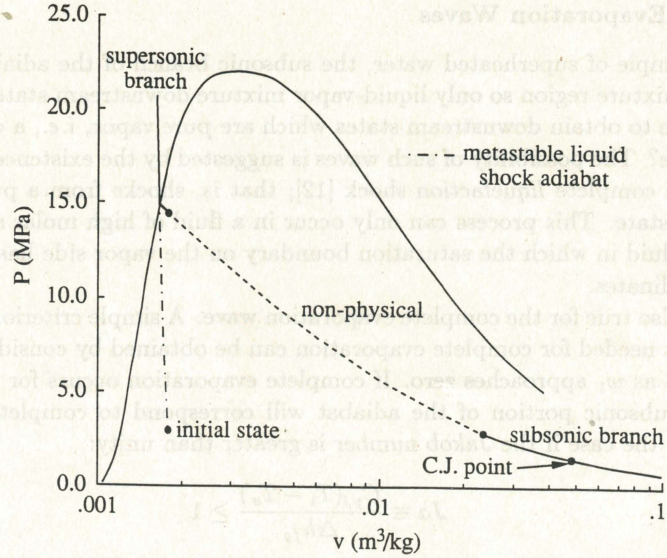

Figure 3. Complete adiabat solution for water with a superheated liquid initial state starting on the spinodal at $p_o = 2.89$ MPa, $T_o = 600$ K. The dashed branch marked nonphysical represents solutions to the adiabat which have imaginary steady wave velocities. The dot-dashed line from the initial state up to the saturation curve is the isentrope in the metastable liquid.

The lower ($p_2 \leq p_1$) branch represents subsonic waves, for a given wave velocity $0 \leq w_1 \leq w_{max}$ there are usually two solutions for the downstream state. Using combustion terminology, this is known as the *deflagration* branch of the adiabat. There is only one solution at the *Chapman-Jouguet* point, where the wave has the maximum velocity and the downstream flow is sonic relative to the wave. In the case shown in Fig. 3, the CJ deflagration speed is 9.8 m/s. For solutions above the CJ point downstream flow is subsonic; below the CJ point, supersonic. The deflagration branch terminates at a point where the entropy inequality, Eqn. 4, is violated. This occurs when the downstream pressure becomes sufficiently small.

The upper ($p_2 \geq p_1$) branch represents supersonic waves. As shown in Fig. 3, a kink occurs in the adiabat where it crosses the phase boundary, this results in two solutions for the downstream state for given wave velocity $\infty \geq w_1 \geq w_{min}$. Using combustion terminology, this is known as the *detonation* branch of the adiabat. The solution passing through the kink has the minimum wave velocity (520 m/s) but unlike chemical explosives, this is not a CJ solution since the downstream flow is not sonic. States on the small portion of the adiabat accessible within the saturation region have supersonic downstream flow as discussed by Fowles [7]. No CJ point exists further up the adiabat from the kink since these states are simply a continuation of the shock adiabat in the metastable liquid.

Complete Evaporation Waves

For the example of superheated water, the subsonic branch of the adiabat terminates inside the mixture region so only liquid-vapor mixture downstream states are possible. Is it possible to obtain downstream states which are *pure* vapor, *i.e.*, a complete evaporation wave? The possibility of such waves is suggested by the existence of the inverse process, the complete *liquefaction* shock [12]; that is, shocks from a pure vapor to a pure liquid state. This process can only occur in a fluid of high molar specific heat, a *retrograde* fluid in which the saturation boundary on the vapor side has positive slope in T-s coordinates.

This is also true for the complete evaporation wave. A simple criterion for the molar specific heat needed for complete evaporation can be obtained by considering the limit of Eqns. 1-3 as w_1 approaches zero. If complete evaporation occurs for this case, then the entire subsonic portion of the adiabat will correspond to complete evaporation. This will be the case if the *Jakob number* is greater than unity:

$$Ja \equiv \frac{C_{p,l}(T_1 - T_\sigma)}{\Delta h_{fg}} \geq 1 \tag{6}$$

Using the simple rules of thumb for the superheat limit $T_1 \sim 0.9T_c$, the normal boiling point $T_\sigma \sim 0.6T_c$, and the latent heat $\Delta h_{fg} \sim 10RT_\sigma$ this implies that $C_p(T_\sigma)/R > 33$ for complete evaporation of a liquid at the superheat limit and one atmosphere initial pressure. The simplest molecule that meets this criterion is octane, C_8H_{18}.

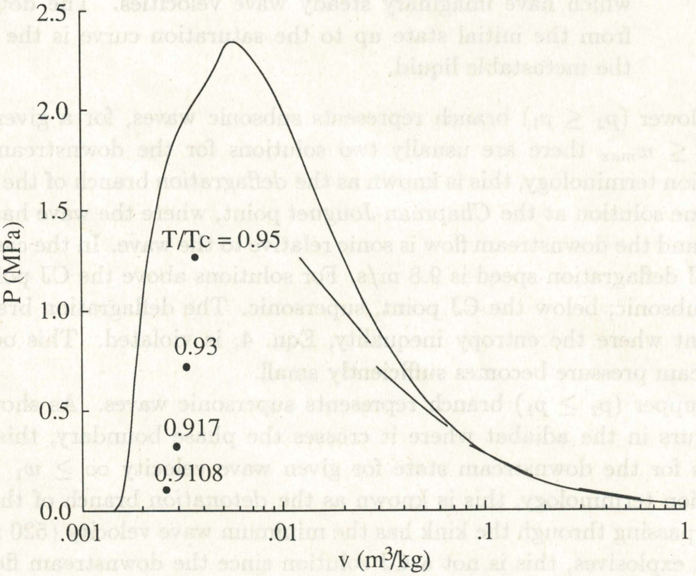

Figure 4. Portion of subsonic adiabats for n-octane with upstream states on selected spinodal points and subsonic downstream states. Initial states are labeled by the reduced temperature $T_r = T/T_c$. Downstream states are mixtures for initial points of $T_r = 0.95$ and 0.93; the adiabat crosses the saturation curve for $T_r = 0.917$; the adiabat lies completely in the vapor region for $T_r = 0.9108$.

Numerical solution of the jump conditions for octane [13] verifies this simple estimate. The subsonic-subsonic portion of the adiabats are shown in Fig. 4 for four upstream states on the spinodal. As the upstream pressure is decreased, the adiabat moves toward and across the saturation boundary. At an initial pressure of one atmosphere ($T = 0.91\ T_c$), the subsonic adiabat lies completely in the vapor state. Computations [13] with lower hydrocarbons in the alkane series, butane and pentane, show only mixture downstream states.

Bubble Growth Model

Subsonic evaporation waves can be combined with a simple similarity solution to the radial continuity and momentum equations to obtain [13] an idealized model for rapid bubble growth in superheated liquids. This model is based on the experimental observations [1,2,5] that the bubble radial velocity and evaporative mass flux are approximately constant for the explosive boiling mode of evaporation near the superheat limit.

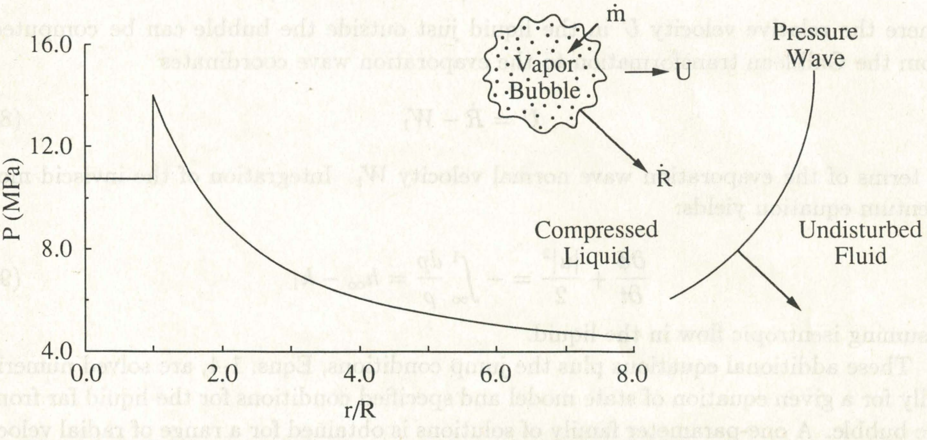

Figure 5. Schematic of the postulated similarity flowfield for the steady growth of a liquid-vapor mixture bubble within a superheated liquid. Radial variation of pressure is shown for a bubble radial velocity of 147.1 m/s in water superheated to the spinodal point of 600 K and 2.89 MPa. The bubble velocity corresponds to an evaporation wave velocity of 72.85 m/s, slightly above the CJ velocity of 67.7 m/s but below the maximum velocity of 78.5 m/s.

In our idealized model, shown in Fig. 5, a single spherical bubble of radius $R(t) = \dot{R}t$ grows in a superheated liquid of infinite extent. A steadily-moving evaporation wave separates the liquid from a stagnant liquid-vapor mixture within the bubble. As shown in Fig. 5, the pressure within the bubble is much higher than the ambient pressure at large distances from the bubble but lower than liquid pressure just outside the bubble due to the pressure decrease across the evaporation wave. The pressure drops off rapidly with increasing radial distance from the bubble due to the divergence of the streamlines, *i.e.*, the $1/r^2$ dependence of the fluid velocity. At a distance $r/R = c/\dot{R} \approx 10$, where c is the metastable liquid sound speed, the pressure wave terminates in a weak shock front, beyond which the liquid is undisturbed. This shock can be located and its' strength determined by the nonlinearization technique of Whitham [14].

The entire flow field outside the bubble has been constructed as a similarity solution, in which the similarity parameter is r/t. Our solution is a simple extension of Taylor's original similarity solution [15] for the flow outside of a sphere (or nonevaporating bubble) expanding at a constant radial velocity. Taylor showed that for small radial Mach numbers, the acoustic approximation to the full Euler equations yielded a good approximation to the exact solution obtained by numerical methods. In the present study, an alternative approximation of an almost incompressible liquid (used in most bubble growth analyses) has been used. We have compared our approximate solutions (in the limit of vanishing evaporation mass flux) with Taylor's exact results and find good agreement for low (less than 0.2) interface Mach numbers.

Using the incompressible flow approximation for the radial motion outside the bubble, the velocity u can be derived from a potential function ϕ:

$$u = \nabla\phi; \qquad \phi = -\frac{R^2(t)U}{r}; \qquad u = \frac{R^2(t)U}{r^2} \tag{7}$$

where the relative velocity U in the liquid just outside the bubble can be computed from the Gallilean transformation to the evaporation wave coordinates

$$U = \dot{R} - W_1 \tag{8}$$

in terms of the evaporation wave normal velocity W_1. Integration of the inviscid momentum equation yields:

$$\frac{\partial\phi}{\partial t} + \frac{|u|^2}{2} = -\int_{\infty}^{1} \frac{dp}{\rho} = h_\infty - h_1 \tag{9}$$

assuming isentropic flow in the liquid.

These additional equations plus the jump conditions, Eqns. 1-4, are solved numerically for a given equation of state model and specified conditions for the liquid far from the bubble. A one-parameter family of solutions is obtained for a range of radial velocities, $0 \leq \dot{R} \leq \dot{R}_{max}$. The maximum velocity is limited by the entropy inequality, Eqn. 4. Solutions for the liquid at the bubble surface and the liquid-vapor mixture within the bubble are shown in Fig. 6 for the particular case of water at the spinodal, $T = 600$ K. Inertia of the liquid surrounding the bubble results in the pressure at the bubble surface increasing with increasing bubble velocity. As shown, the pressure increases *almost* (see inset) to the saturation pressure at the maximum velocity point B. For this example, the maximum bubble radial velocity is 150 m/s. For a special upstream state just below state B in Fig. 6, the downstream state for the bubble solution is the CJ point on the corresponding adiabat.

In order to compare the model predictions with experiment, a choice of bubble growth velocity must be made. As mentioned earlier, experimental evidence suggests that nature selects the velocity which yields the CJ state. No rigorous theoretical justification of this choice is available and it must be considered a plausible but speculative hypothesis at this time.

Experiments with butane droplets [1] yielded estimates of 7 m/s for the equivalent evaporation wave velocity and an estimated density of 200 kg/m^3 for the density of the liquid-vapor mixture inside the bubble. Computations [13] using the measured superheat limit as the ambient condition, yields a CJ evaporation wave velocity of 19 m/s and a bubble density of 140 kg/m^3. The corresponding bubble radial velocity is predicted to be 56 m/s, much higher than the measured radial velocity of about 15 m/s. However, in the experiments only a fraction of the bubble surface was evaporating and it makes more sense to compare equivalent evaporation wave velocities rather than bubble radial velocities.

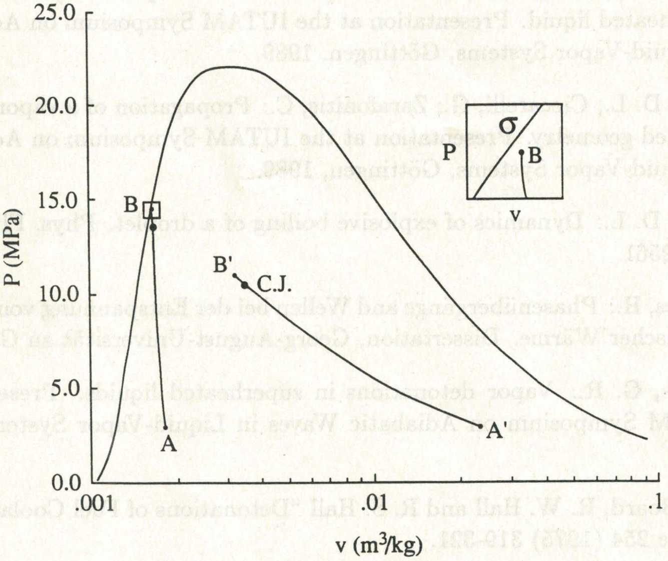

Figure 6. Solution of bubble growth model for water superheated to 600 K at 2.89 MPa (on spinodal). Curve AB is the locus of liquid states just upstream of the bubble (evaporation wave). Curve A′B′ is the locus of states for the liquid-vapor mixture within the bubble. CJ indicates the Chapman-Jouguet point. The inset shows the distinction between the maximum velocity point B and the saturation curve σ.

This comparison, while not definitive, is certainly encouraging and suggests further exploration of the CJ hypothesis for bubble growth is worthwhile. Our hypothesis is an alternative to the ad hoc assumption of Nguyen *et al.* [16], who postulate a relationship between interfacial liquid velocity and the degree of superheat. Their assumption results in the prediction of downstream states and wave velocities that are significantly different from the present analysis. Application of the present model to other types of evaporation waves, such as the Hill and Sturtevant experiment [3], is in progress.

Acknowledgement

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