Molecular flow venting of a volume with an outgassing or desorbing source

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Introduction

- **During design, development, and ground testing of NASA GSFC spaceflight hardware, project personnel wonder how such items will fare under high vacuum conditions, whether in space or in thermal vacuum (TV) chambers during integration and test activities**
  - Effects of transient overpressures or volatile condensable material (VCM) contaminants due to outgassing or desorption within certain cavities or TV chambers
- **Generally, enclosure venting or chamber evacuation is characterized by fixed pumping speeds under free molecular (FM) flow conditions**
- **On the other hand**
  - Classical diffusion-limited outgassing varies with an inverse square root relationship with time
  - Surface desorption of water vapor often follows inverse time characteristics
  - Often, outgassing or offgassing follows a more general power law decay
- **Analytical descriptions of these systems produce integrals where both numerator and denominator become unbounded, and often no solution has been identified**

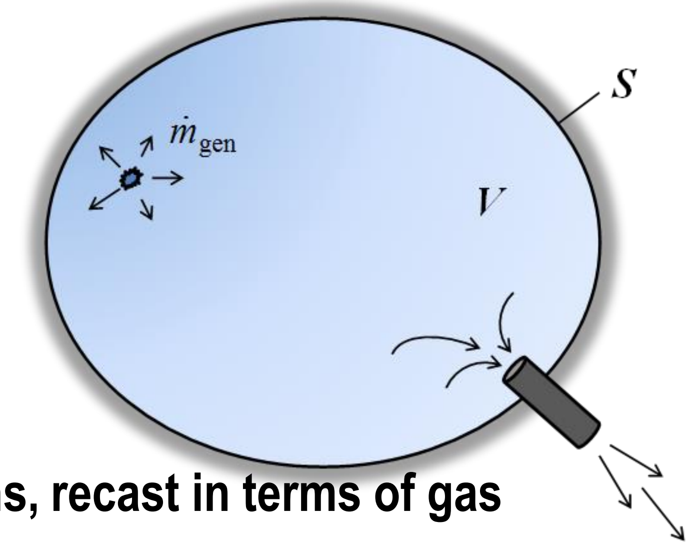
Objective

- The purpose of this presentation is to present full solutions for high vacuum environments with generalized outgassing in the presence of venting or pumping by taking advantage of a mathematical function generator technique that produces solutions for these problematic integrals

Mass Conservation Statement

- **General mass accumulation rate**
  - Mass generation rate within volume rigid *V*
  - Net rate vented across bounding surface *S*

$$\frac{d}{dt}\iiint_V \rho \, dV = \dot{m}_{\text{gen}} - \oiint_S \rho \mathbf{u} \cdot \mathbf{dS}$$



- **For ideal gas behavior under isothermal conditions, recast in terms of gas load throughput for pressure *p***

$$V\frac{dp}{dt} = \dot{m}_{\text{gen}} RT - \oiint_S p\mathbf{u} \cdot \mathbf{dS}$$

Mass Conservation—Sink Term

- **The surface integral represents gas load for venting or pumping**
  - May be expressed as a product of conductance C and pressure differential across the bounding surface $p - p_\infty$; where $p_\infty = 0$, C may also represent pumping speed
- **Rewriting,**

$$\frac{d\tilde{p}}{dt} = \frac{\dot{m}_{\mathrm{gen}} RT}{V} - \frac{\tilde{p}}{\tau}, \quad \text{where} \quad \tilde{p} \equiv p - p_\infty \quad \text{and} \quad \tau \equiv \frac{V}{C}$$

- **The next step deals with different descriptions for the mass generation term, which is instantaneously exposed to the chamber at elapsed time $t = 0$**

Mass Generation—Classical Diffusion

- **Based on Fick's Second Law of Diffusion for one-dimensional flow of a trace species with initial uniform concentration c_0 and diffusivity v in a material having surface area A and thickness L, issuing into a background environment with concentration c_∞**

$$\dot{m}_{\text{gen}} = \Delta c_0 A \sqrt{\frac{\nu}{\pi t}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \left(\exp\left[-\frac{n^2 L^2}{\nu t} \right] \right) \right]$$

  - The first term in square brackets represents diffusion from an infinitely thick material

- **Substitution into the throughput equation yields**

$$\frac{d\tilde{p}}{dt} = \Delta c_0 RT \frac{A}{V} \sqrt{\frac{\nu}{\pi t}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \left(\exp\left[-\frac{n^2 L^2}{\nu t} \right] \right) \right] - \frac{\tilde{p}}{\tau}$$

Classical Diffusion (cont.)

- **Regrouping,**

$$\frac{d\tilde{p}}{dt}+\frac{\tilde{p}}{t}=\frac{a}{\sqrt{t}}+\frac{2a}{\sqrt{t}}\left[\sum_{n=1}^{\infty}(-1)^n e^{-\frac{t_n}{t}}\right];\quad \text{where}\quad \tau_n\equiv\frac{n^2L^2}{\nu}\quad \text{and}\quad a\equiv\Delta c_0 RT\frac{A}{V}\sqrt{\frac{\nu}{\pi}}$$

- **After some rearrangement, letting $s \equiv t/\tau$, $\Delta s \equiv s_2 - s_1$, and $\beta = \beta_n \equiv \tau_n/\tau$, the general solution over time interval $t_2 - t_1$ becomes**

$$\tilde{p}_2=\tilde{p}(t_2)=\tilde{p}_1 e^{-\Delta s}+a\sqrt{\tau}e^{-s_2}\int_{s_1}^{s_2}\frac{e^s}{\sqrt{s}}ds+2a\sqrt{\tau}\sum_{n=1}^{\infty}(-1)^n e^{-s_2}\int_{s_1}^{s_2}\frac{e^{s-\frac{\beta}{s}}}{\sqrt{s}}ds$$

- **One more variable substitution will remove those pesky denominators: $s \equiv x^2$**

$$\boxed{\tilde{p}_2=\tilde{p}_1 e^{-\Delta s}+2a\sqrt{\tau}e^{-x_2^2}\int_{x_1}^{x_2}e^{x^2}dx+4a\sqrt{\tau}\sum_{n=1}^{\infty}(-1)^n e^{-x_2^2}\int_{x_1}^{x_2}e^{x^2-\frac{\beta}{x^2}}dx}$$

Classical Diffusion—Infinitely Thick Soln.

- **The solution to the first integral corresponds to the chamber response for outgassing from a material thick enough that the trace volatile concentration remains essentially unperturbed at depth *L* over the period under consideration**
  - Its solution involves the Dawson function or Dawson's Integral $D(x)$

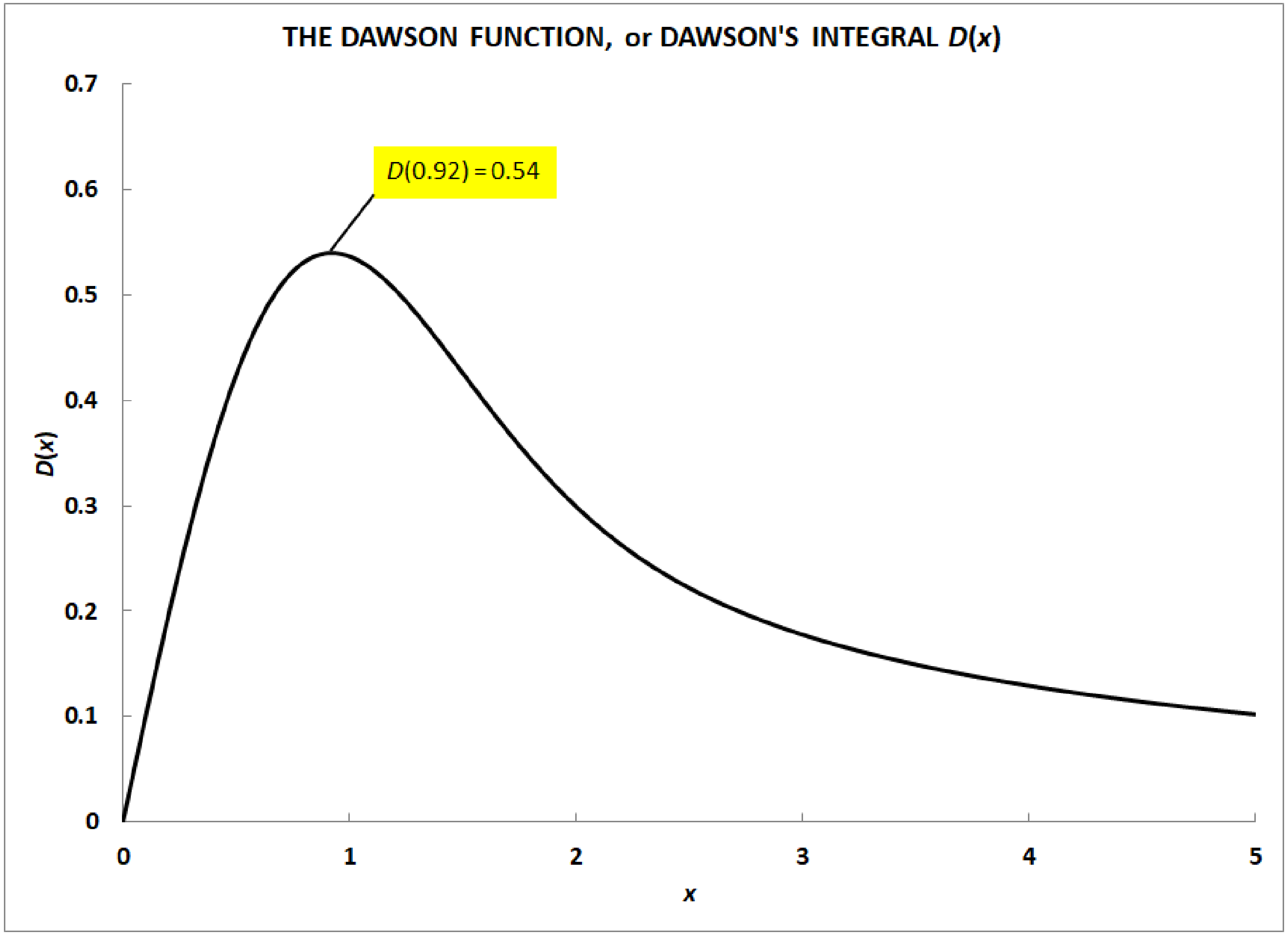
$$D(x) \equiv e^{-x^2} \int_0^x e^{x^2}\, dx$$

- **The vessel pressure response to this form of outgassing is**

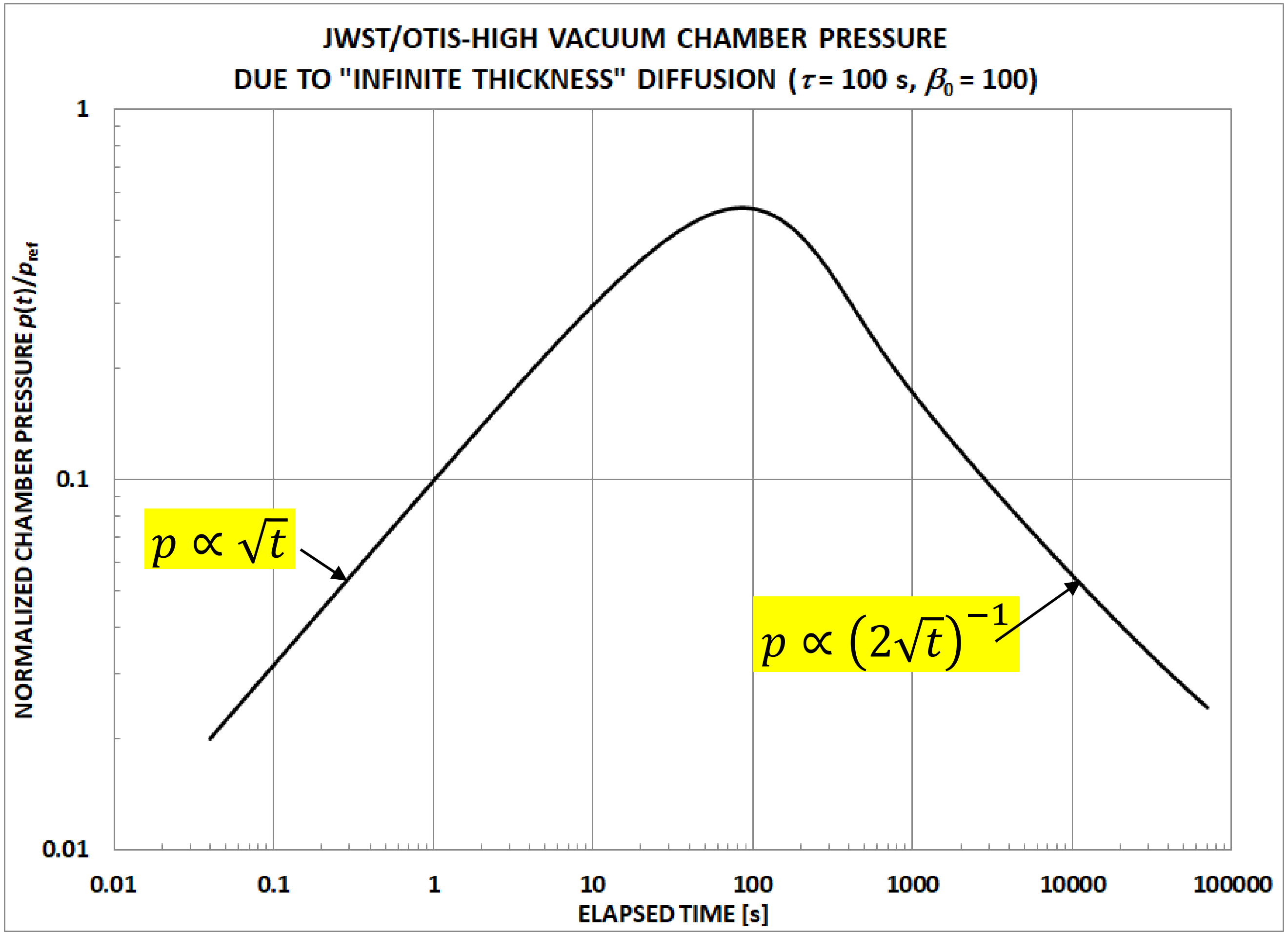
$$\tilde{p}(t_2) = \tilde{p}_1 e^{-\Delta s} + 2\Delta c_0 RT \frac{A}{V}\sqrt{\frac{\nu\tau}{\pi}}\left[D(x_2) - e^{-\Delta s} D(x_1)\right], \quad \text{where} \quad x = \sqrt{s} = \sqrt{\frac{t}{\tau}}$$

- **Note that the source influence on a chamber's pressure rises linearly from $x = 0$ even though the mass loss rate at $t = 0$ is infinite!**
- **Plot for baseline example case:**
  - $p_1 = p_\infty = 0$; $\tau = 100$ s, and $\beta_0 = 100$; $p(t) = p_{ref} D\left(\sqrt{t/\tau}\right)$

Dawson’s Integral



Classical Diffusion—Infinitely Thick Soln., Example



Classical Diffusion—Infinitely Thick Soln.

- **Plotted on log-log scale, the pressure solution is nearly symmetric about $t = \tau$**
  - For small t (small x), $D(x) \approx x$
  - For large t (large x), $D(x) \approx {}^{1}/_{2x}$
- **Limiting case, large t, physical variables reproduce the quasistatic limit $\frac{dp}{dt} = 0$**
  - which also becomes independent of volume

$$\tilde{p}(t) \to \frac{\dot{m}_{\text{gen}}(t) RT}{C}$$

Function Generator Technique—Intro

- **That last variable substitution *s* = *x*² introduced a few slides back is the first step of a novel approach defining mathematical functions that solve integrals if a general form…**

$$\int_0^y f(u)e^u du$$

- **…may be transformed to something proportional to the following by an appropriate variable substitution**

$$I(x) = \int e^{g(x)} dx$$

- **The integral may be scaled with a pre-exponential factor to produce**

$$F(x) \equiv I(x)e^{-g(x)} = e^{-g(x)} \int e^{g(x)} dx$$

  – The product of *F*(*x*) and the integrand produces the solution to the integral!

- **Function *F*(*x*) will satisfy its own differential equation:** $\boxed{\frac{dF}{dx} + F\frac{dg}{dx} = 1}$

Function Generator Technique

- **Produced series of NASA Contractor Reports describing general properties of *F*(*x*), including**
  - Asymptotic expansion for large transformed argument x
  - Maclaurin series for small values of x
  - Numerical integration scheme using 2^{nd} order Adams-Moulton implicit method
- **Validation efforts include application to existing functions**
  - Dawson's Integral
  - Modified Bessel function of the first kind
  - Error function
  - Incomplete lower gamma function
  - Exponential Integral
  - Variety of simple functions
- **Used to discover over half a dozen new functions to date**

Classical Diffusion—Finite Thickness Soln.

- **Return to the general solution:**

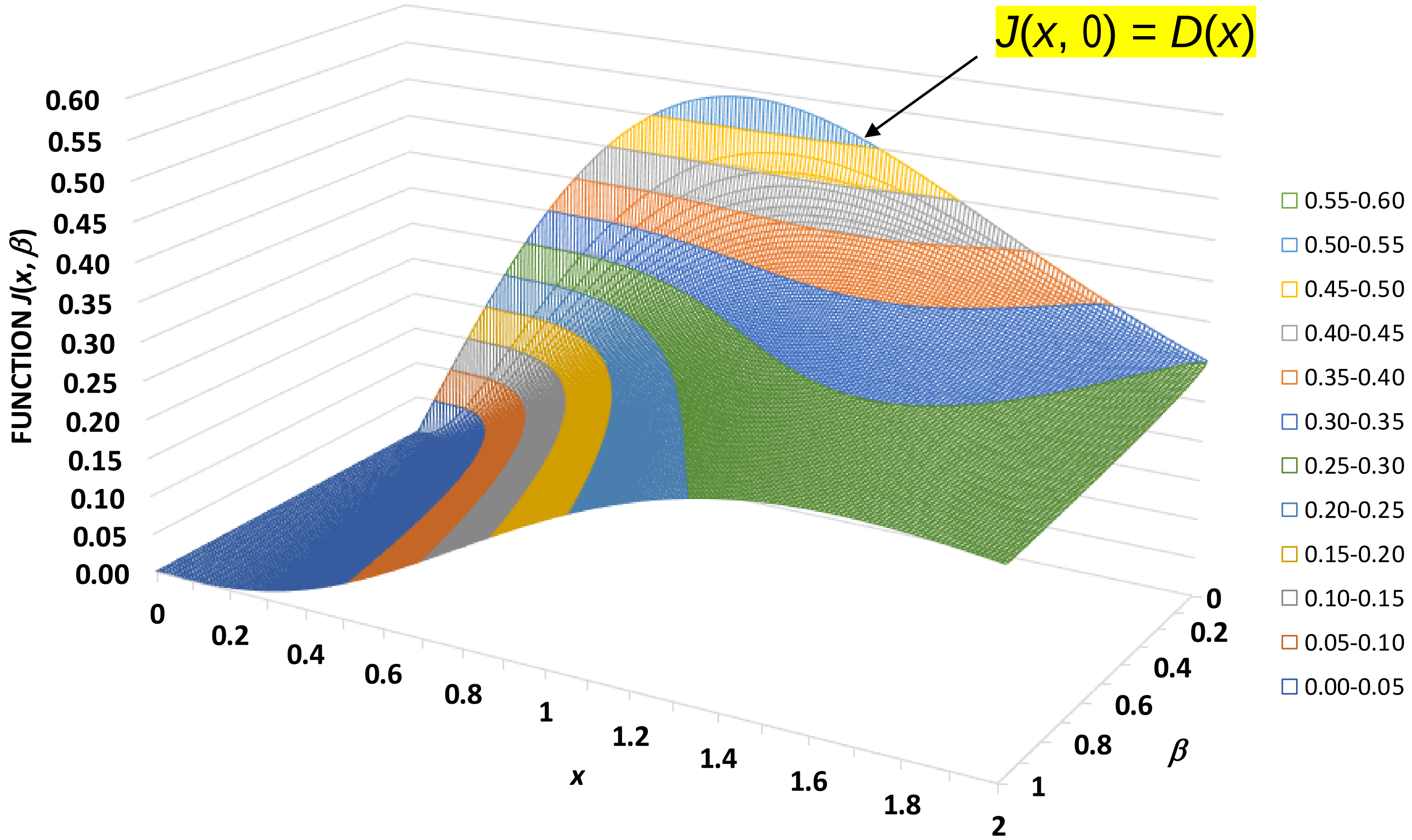
$$\boxed{\tilde{p}_2 = \tilde{p}_1 e^{-\Delta s} + 2a\sqrt{\tau} e^{-x_2^2} \int_{x_1}^{x_2} e^{x^2} dx + 4a\sqrt{\tau} \sum_{n=1}^{\infty} (-1)^n e^{-x_2^2} \int_{x_1}^{x_2} e^{x^2 - \frac{\beta}{x^2}} dx}$$

- **The first integral is solved by the Dawson function**
  - What about the second one?
- **Modify integration factor to define *J*(*x*, *β*) in the form of *F*(*x*)**

$$J(x,\beta) \equiv I_n(x) \exp\left(\frac{\beta}{x^2}\right) \equiv e^{-x^2 + \frac{\beta}{x^2}} \int_0^x e^{x^2 - \frac{\beta}{x^2}} dx$$

$$\frac{dJ}{dx} + 2x\left(1 + \frac{\beta}{x^4}\right) J = 1$$

Contour Map for $J(x, \beta)$



Classical Diffusion—Thickness Parameter

- **Recall that $\beta = \beta_n$ is actually a factor in an infinite series**
  - Let $\beta_n = n^2\beta_0$, where

$$\beta_0 \equiv \frac{L^2}{\nu\tau}$$

- **This parameter is like a baseline ratio of time constants (diffusivity/venting)**
  - If the diffusivity time constant is large relative to the venting time constant, b_0 is small, terms in the infinite series will follow $D(x)$ closely, and vessel pressure will quickly reflect the influence of a rapidly depleting source

Classical Diffusion—Finite Thickness Gen. Soln.

- **Transient pressure within vessel due to a thin-layer source governed by diffusion-limited outgassing as described by Fick's Second Law is**

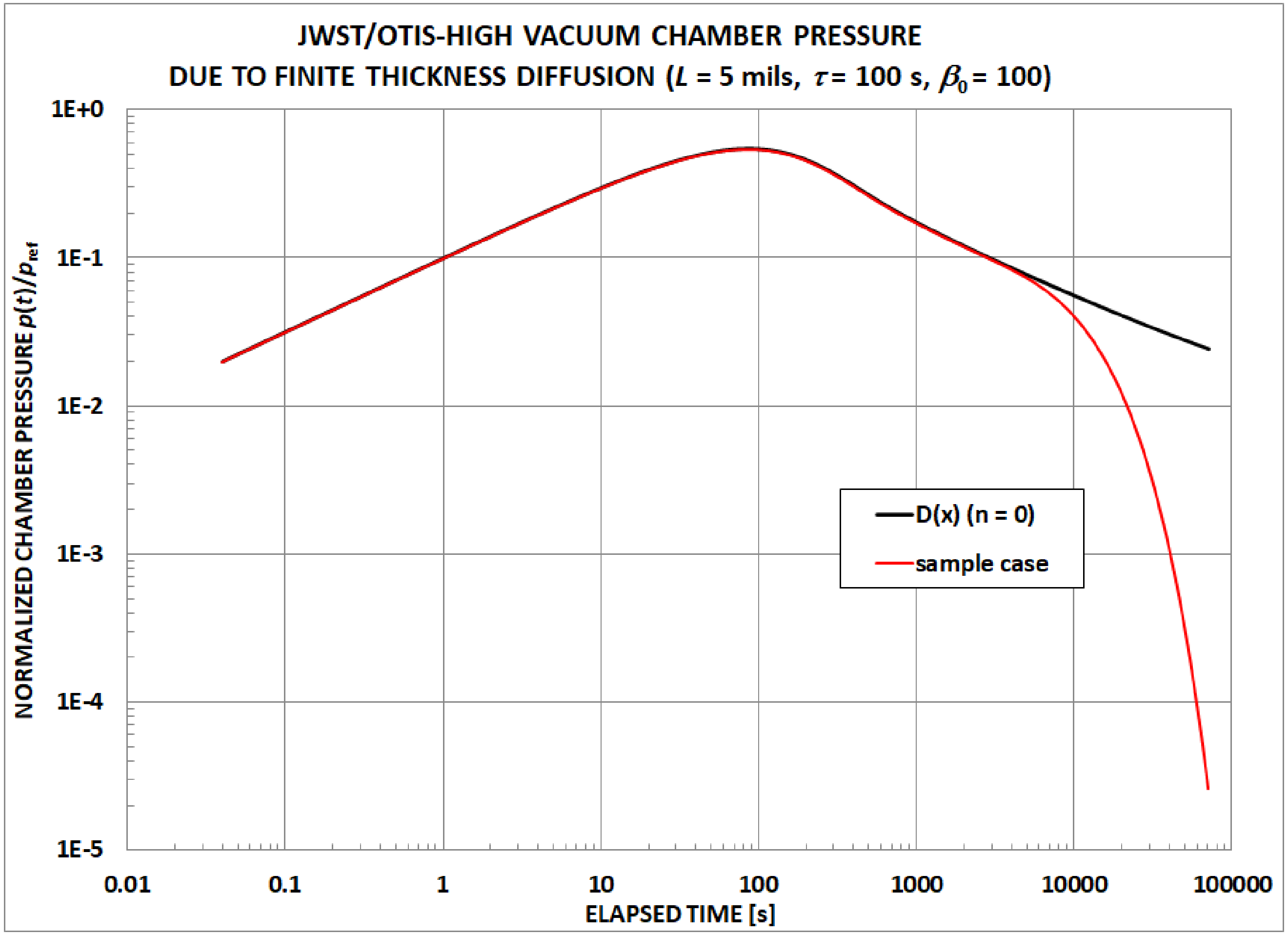
$$\tilde{p}(t_2) = \tilde{p}_1 e^{-\Delta s} + 2c_0 RT \frac{A}{V}\sqrt{\frac{\nu\tau}{\pi}} \times$$

$$\left\{ D(x_2) - e^{-\Delta s} D(x_1) + 2\sum_{n=1}^{\infty}(-1)^n \left[J\left(x_2, n^2\beta_0\right) e^{\frac{-n^2\beta_0}{x_2^2}} - J\left(x_1, n^2\beta_0\right) e^{-\Delta s} e^{\frac{-n^2\beta_0}{x_1^2}} \right] \right\}.$$

- **For $t_2 \gg t$ and $p_1 = 0$ at $t_1 = 0$,**

$$\tilde{p}(t_2) \rightarrow 2c_0 RT \frac{A}{V}\sqrt{\frac{\nu\tau}{\pi}} \left\{ \frac{1}{2x} + 2\sum_{n=1}^{\infty}(-1)^n \left[\frac{1}{2x} e^{\frac{-n^2\beta_0}{x_2^2}} \right] \right\} = \frac{\dot{m}_{gen}(t_2)RT}{C}$$

Classical Diffusion—Finite Thickness Case



Power-Law Decay Sources

- **Material outgassing rates almost always follow power-law decay behavior, although sometimes not in the analytically classical sense**
  - When this is so, it usually decays quicker than inverse square root time
  - Surface desorption also has this behavior, often follows 1/*t*

$$\dot{m}_{gen} = \frac{kA}{t^{\eta}}$$

- **Differential equation for gas load throughput becomes**

$$\frac{d}{ds}\left(\tilde{p}e^{s}\right) = K\frac{e^{s}}{s^{\eta}}; \quad \text{where} \quad K \equiv \frac{kART\tau^{1-\eta}}{V}$$

- **General soln.:**

$$\boxed{\tilde{p}(t) = \tilde{p}_1 e^{-\Delta s} + K\left[\left(e^{-s}\int_0^s \frac{e^{s}}{s^{\eta}}ds\right) - e^{-\Delta s}\left(e^{-s_1}\int_0^{s_1} \frac{e^{s}}{s^{\eta}}ds\right)\right]}$$

Solution Approach

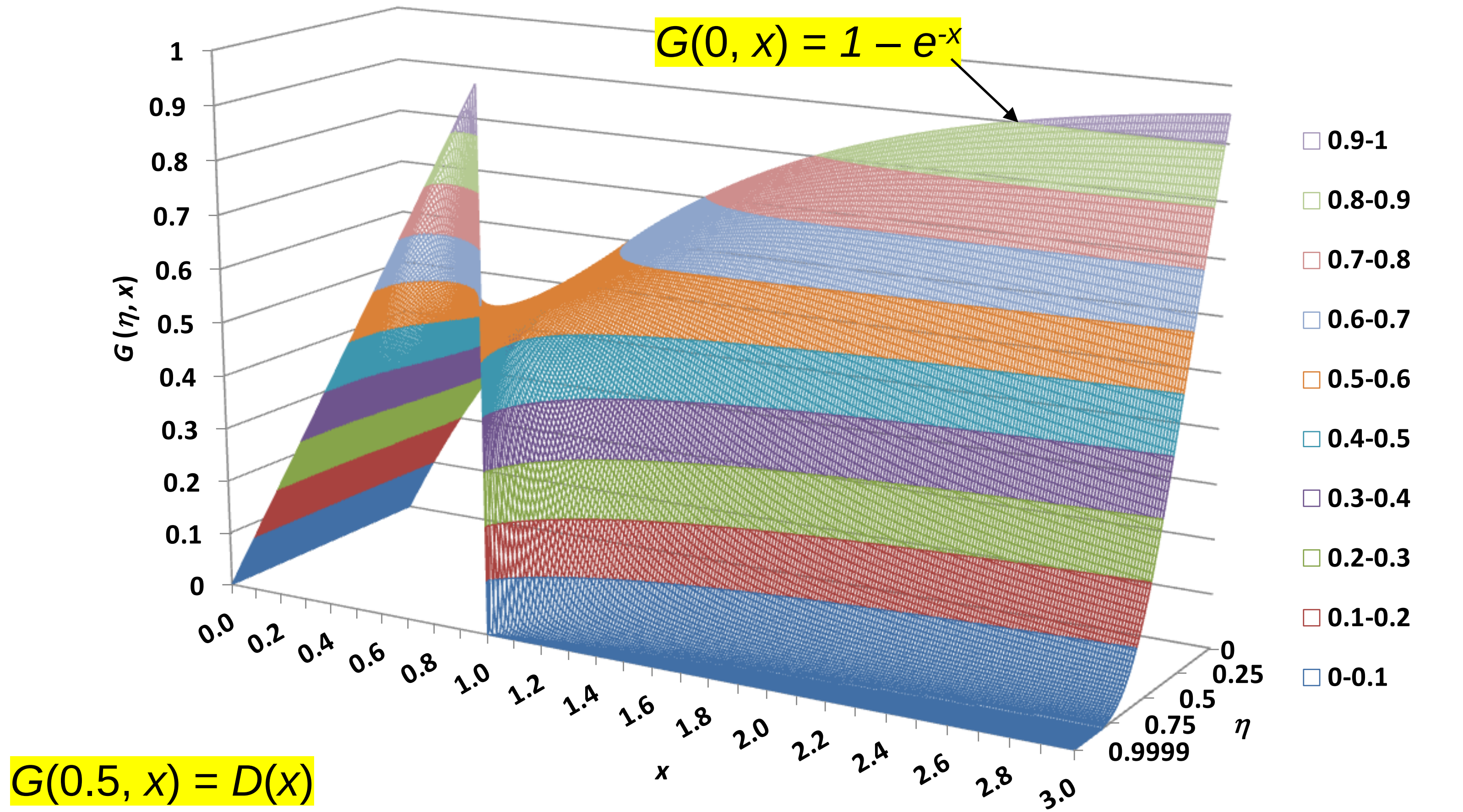
- **As for classical diffusion, the procedure for direct numerical solution appears problematic**
  - Integrand has a singularity at $s = 0$
  - Numerator and denominator both increase without bounds
- **Apply function generator approach**
  - When $0 \leq \eta < 1$, let

$$e^{-s}\int_0^s \frac{e^s}{s^\eta}\,ds = be^{-x^b}\int_0^x e^{x^b}\,dx \equiv bG(\eta,x);\quad \text{where}\quad x \equiv \sqrt[b]{s}\quad \text{and}\quad b \equiv 1/(1-\eta)$$

- **The function $G(\eta, x)$ satisfies**

$$\frac{dG}{dx} + bx^{b-1}G = 1$$

Contour Map for $G(\eta, x)$



Power Law Decay Solution

- **For η < 1, the general solution becomes**

$$\tilde{p}(t) = \tilde{p}_1 e^{-\Delta s} + \frac{K}{1-\eta}\left[G(\eta, x_2) - e^{-\Delta s} G(\eta, x_1)\right]$$

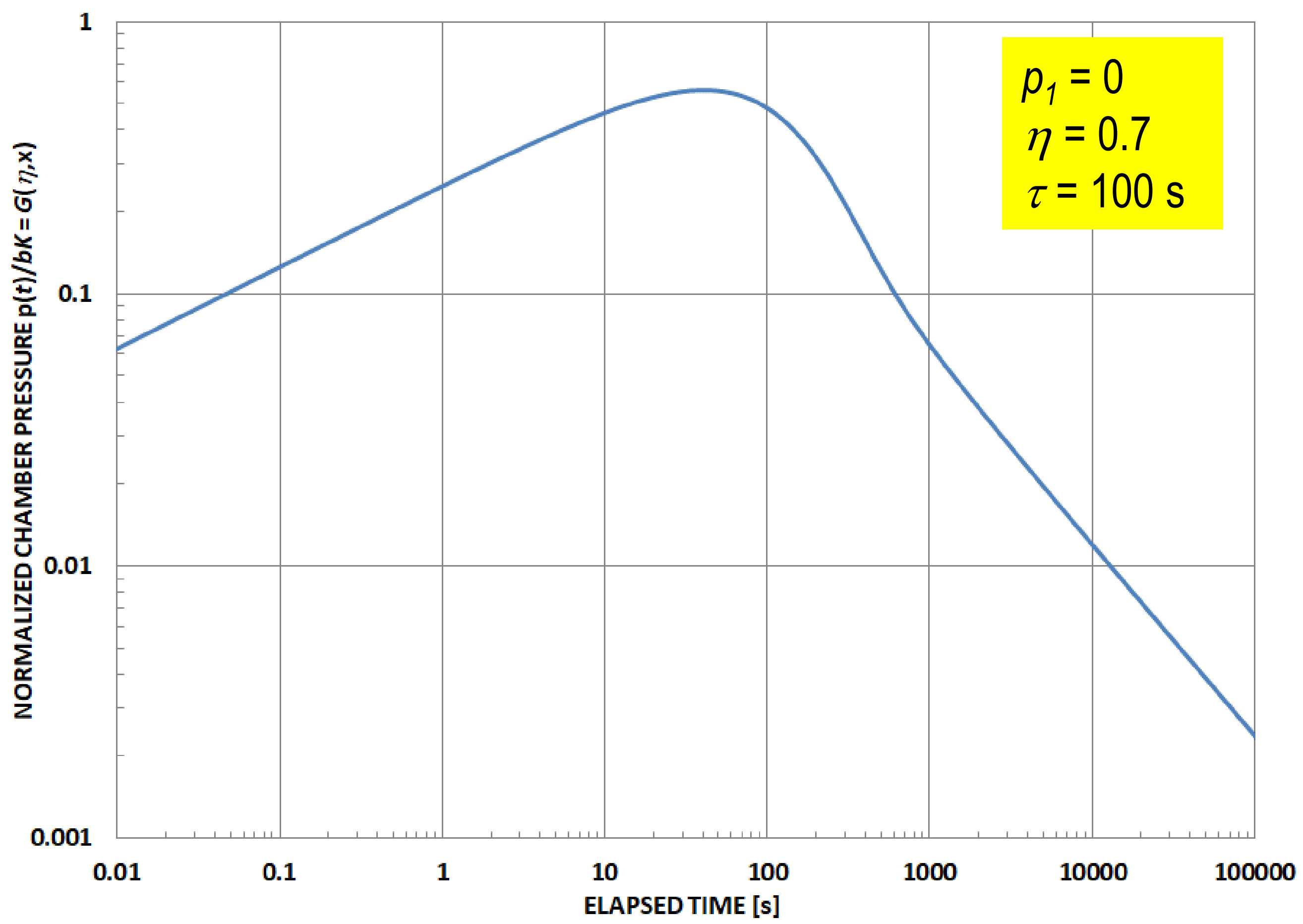
- **For large *x***

$$G(\eta, x \to \infty) \to \frac{1}{b x^{b-1}}$$

  – In physical units,

$$\tilde{p}(t) \to \frac{K}{s^{\eta}} = \frac{\dot{m}_{gen}(t) R T}{C}$$

Power Law Decay, Example Case



Power Law Desorption Soln., $\eta = 1$

- **When $\eta = 1$, a different variable substitution should be used**
  - Let $y = \ln s$; then

$$e^{-s}\int_0^s \frac{e^s}{s}\,ds = e^{-e^y}\int_{-\infty}^{y} e^{e^y}\,dy \equiv F(y)$$

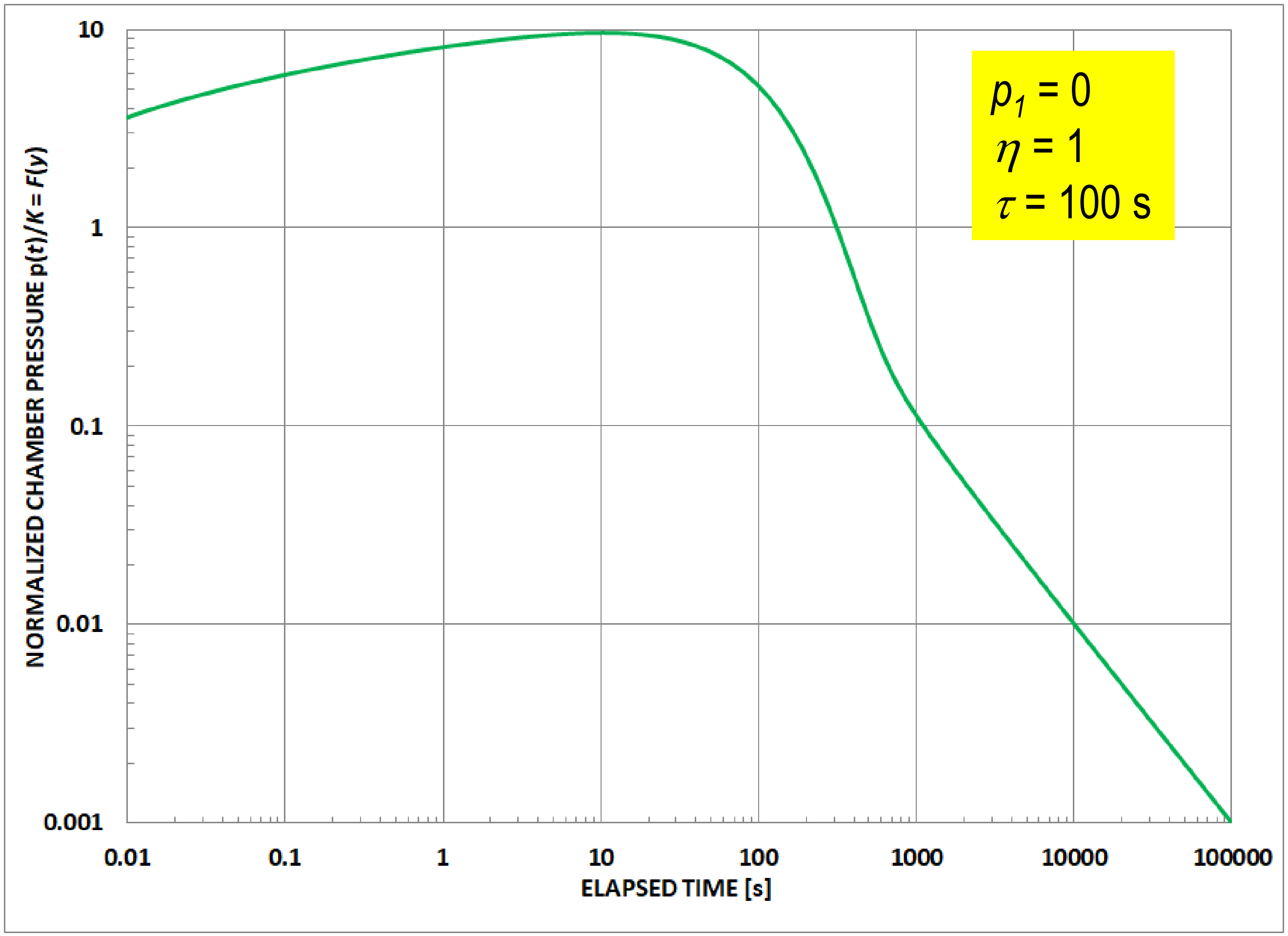
- **This integral is solved by the negative branch of the exponential integral function Ei(ξ)**
  - When $\xi = -s = -e^y$
  - The relationship between these two functions is

$$F(y) \equiv e^{-e^y}\int_{-\infty}^{y} e^{e^y}\,dy = -e^{-e^y}\,\mathrm{Ei}\left(-e^y\right)$$

- **For large *y*,**

$$F(y \to \infty) \to e^{-y} = \frac{\tau}{t}; \quad \text{and} \quad \tilde{p}(t) \to \frac{\dot{m}_{gen}(t)RT}{C}$$

Surface Desorption Example Case



Concluding Remarks

- A number of solutions have been found that describe the evolution of vacuum chamber pressure in high vacuum due to pumping against the presence of a source exhibiting classical diffusion, desorption, or more general power-law decay behavior
- For classical diffusion, the full solution associated with one-dimensional outgassing from a source having finite-thickness has been presented for all elapsed time
- Model source fluxes exhibiting power-law decay are initially infinite, and results describing vessel pressure from the non-linear ODEs characterizing these environments also produce integrals where numerators and denominators become unbounded, making direct numerical integration difficult
- Recent discovery of a mathematical function generator technique overcomes these difficulties and provides analytical solutions for these integrals and provides certain physical insights
- This technique has shown much promise, producing novel analytical results for other physical problems like transient column density for an evaporating droplet, and has been useful in exploring the behavior of existing mathematical functions to help understand the approach to limiting descriptions

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