Vanessa Robins, University of Colorado at Boulder
"Computational Topology with Applications to Fractal Geometry"

Karen L. Shuman, Dartmouth College
"Signal Processing with the Jacobi Group"

Masha Sosonkina, University of Minnesota–Duluth
"Preconditioning Strategies for Linear Systems Arising in Tire Design"

Jenny Switkes, Claremont Graduate University
"Models of Coevolutionary Interaction"

Lesley Ward, Harvey Mudd College
"Brownian Motion and the Shape of a Region's Boundary"

Julia M. Wilson, University of Wisconsin-Milwaukee
"Non-uniqueness of Boundaries of CAT(0) Groups"

Golbon Zakeri, Argonne National Laboratory and the University of Wisconsin–Milwaukee
"You Too Can Optimize Using a Metacomputer"

A Mathematician at NIST Today

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Introduction

In these highlights of the work of a mathematician in a government laboratory, I will tell you about the similarities to as well as the differences from a mathematician working in academia. The National Institute of Standards and Technology (NIST) is the oldest government laboratory in the United States. It was founded in 1901 as the National Bureau of Standards; it now employs some 2000 scientists and engineers engaged in basic and applied research on the chemical, physical, and electrical properties of materials that are important to U.S. industry and commercial

competitiveness. Much of this research is used to develop standards and measurement techniques that are used by industry to certify and maintain the quality of industrial products and processes. Mathematicians have been a part of NIST from its earliest days, providing mathematical expertise and collaborating with scientists and engineers on NIST projects. In addition, mathematicians in the past conducted pioneering work on various aspects of mathematical and computational science; these included numerical linear algebra and Monte Carlo methods. Research on these topics continues today, and newer topics such as parallel computation and mathematical modeling have become important areas of work as well. The project I am about to describe arose from a collaboration with scientists working at NIST who were interested in the problem of gloss loss in paint. I started out working as a mathematician developing a model of paint weathering and used some basic results from the theory of point processes—a topic that if not new to paint technologists is certainly not widely known. The project took an unusual direction as a result of a conversation with a computer scientist (I will describe later), and my role has evolved so that now I am coordinating a computer graphic rendering effort to develop photorealistic images based on light scattering measurement of surfaces. Paint modeling is not an obvious topic of research for most mathematicians—certainly not one with my training. I started working on this topic because one of my "hobbies" is random numbers. Shortly after I arrived at NIST, I attended a talk on clustering in random number sequences. It was one of the best presentations on randomness that I've ever seen. It combined simple, but vivid visual demonstrations (including a big jar of colored jelly beans and a Bingo card cutout of a random number table) of facts about recurrent events that are not well known outside the mathematical community. What made the presentation so surprising was that the speaker was a paint scientist—Lou Floyd of the Glidden Paint Company of Ohio. I realized then and there, this was a potential application area to watch. A few years later, I did get the opportunity to work with the NIST host for that talk, Jon Martin. As removed from the world of mathematics as might be, the paint industry is of great industrial importance. Its revenues include a significant share of the U.S. GDP, and its importance to the automobile industry, for example, comes from the fact that painting a car is the most expensive part of the automobile manufacturing process. There is a long list of other industries for which the issue of paint or coating appearance is critical—textiles, paper, housing, and traffic safety to name a few.

In the beginning, the purpose of our collaboration was to investigate the role of initial paint coating characteristics on subsequent gloss loss of a painted surface that erodes during weathering and exposure to ultraviolet light, as might take place when a car coating loses its gloss and intensity of color over the years due to exposure to sunlight.

1. *Modeling and Simulation*

The work reported here was done jointly with Jonathan Martin and Michael Galler of the Building and Fire Research Laboratory at NIST [4]. It is probably useful to first define what we mean by paint. We will take it to be a composite material consisting of a polymeric matrix (not the mathematical kind) called a binder and spherical pigment particles. In the gloss loss study, the spherically shaped pigments were assumed to be titanium dioxide with diameters ranging from 0.1 to 0.3 microns. We assumed that gloss loss was caused by surface roughening due to the fact that paint binder erodes under exposure to ultraviolet light. An experimental approach to this problem would involve determining the surface structure of the paint film, measuring the degree of gloss, and then systematically varying the surface structure by changing the paint composition in order to identify the relationship between surface structure, paint composition, and gloss loss over time. This would be an expensive and time-consuming process that could be facillitated by modeling. By examining a simplified caricature of the weathering process, we hoped to identify relationships between a limited number of coating characteristics and gloss (as measured by surface roughness). By quantifying these relationships, we hoped to organize some of the relevant coating variables that would need to be a part of any experimental effort. This would aid, and possibly shorten, the experimental design process and help to distinguish the important variables from the less important. It's important to note that we simulated changes in surface morphology and the layers of coating that are exposed during weathering, not the chemistry of the weathering process. We followed the changes in a two-dimensional 900 × 400 array of pixels representing a two-dimensional cross section of a paint film. For our purposes, the important parameters of this coating were:

- PVC = pigment volume concentration
  = volume of pigment particles / total volume
- size distribution of pigment particles
- clustering of pigment particles (degree of flocculation)

What Is Gloss? The mirrorlike appearance of a new car that is popularly known as gloss is called "distinctness of image" (DOI) by paint technologists. Human beings are good at detecting this attribute (until recently, they were better than the best glossometers), and gloss plays a strong (sometimes determining) role in the decision to purchase an automobile. Specular intensity, or mean reflectance, will be used as a quantitative measure of the DOI even though the correlation between the two is not perfect.

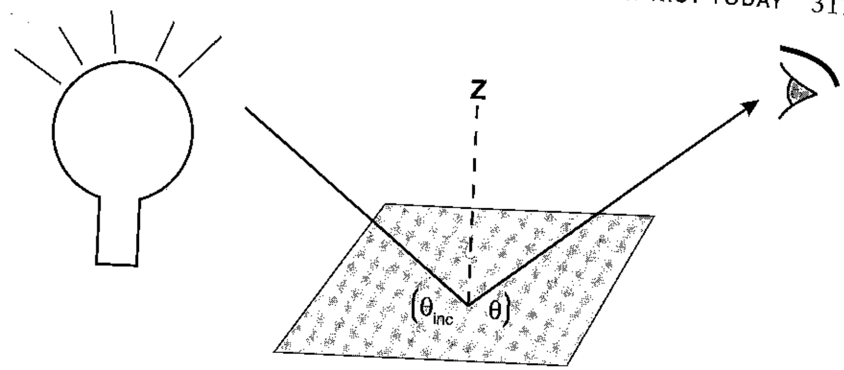

Figure 4. GLOSS. What is it? Specular gloss. $R(\upsilon)$ = ratio of field incident in direction υ to field incident in direction υ_{inc}—the incident direction. R is called the *reflectance*.

Better characterization of DOI is a complex problem involving human psychophysics and is beyond the scope of our discussion. However, we are working on rendering images of surfaces based on good physical models of light reflectance. This should be useful in dealing with some of these difficulties. The reflectance $R(\theta)$ can be described (see figure 4) as the ratio of the light field scattered from the surface in the direction θ to the field incident to the surface with direction θ_{inc} where the angles are measured as depicted in figure 4. To get an expression for the mean reflectance, our version of gloss, we will use physical optics theory as summarized by Beckmann and Spizzichino [1] that, in principle, predicts the angular distribution of light flux reflected off a rough surface as a function of the angle and wavelength of the incident light. After the weathering process has proceeded for a period of time, the top of the two-dimensional cross section is indeed rough in appearance. Weathering is an inherently random process, so the resulting roughened surface may be considered to be random. The theory we use assumes that for each fixed time T, the surface heights $\{z(x, y, \omega, T)\} - \infty \leq x, y, \leq \infty$ are the realization or sample of a Gaussian random process. We simplify the representation of heights even further by assuming they are independent of y, in view of the fact we simulated a two-dimensional cross section. The range of integration is therefore over a single horizontal coordinate. The mean reflectance is:

$$\mu = \lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} \zeta(x, \omega, T)dx \qquad (1)$$

where $z(x, y, \omega, T) = \zeta(x, \omega, T)$ is now the height. The variance of the height is then

$$\sigma^2 = \lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} [\zeta(x,\omega,T)]^2 \, dx - \mu^2 \tag{2}$$

The parameters μ and σ are limiting values that are independent of x and ω. The existence of these limits is a consequence of the fact that the random process $\{\zeta(x, \omega, T)\}_{x\in(-\infty,\infty)}$ is ergodic and has first and second moments [3].

Figures 5 and 6 show a numerical test of the Gaussian hypothesis (i.e., normally distributed in a single dimension x). For a fixed value of x, a normal probability plot was created by plotting values whose first coordinates were 100 heights at position x created from 100 different runs of the simulation. The second coordinate of these points came from a hundred normally distributed values with mean $\hat{\mu} = \left\langle \sum_{i=1}^{N} z_i/N \right\rangle$ and variance $\hat{\sigma}^2 = \left\langle \sum_{i=1}^{N} (z_i - \mu)^2/N \right\rangle$ where $\{z_i\}_{i=1}^{N}$ are heights $z_i = \zeta(x_i, \omega, T)$,

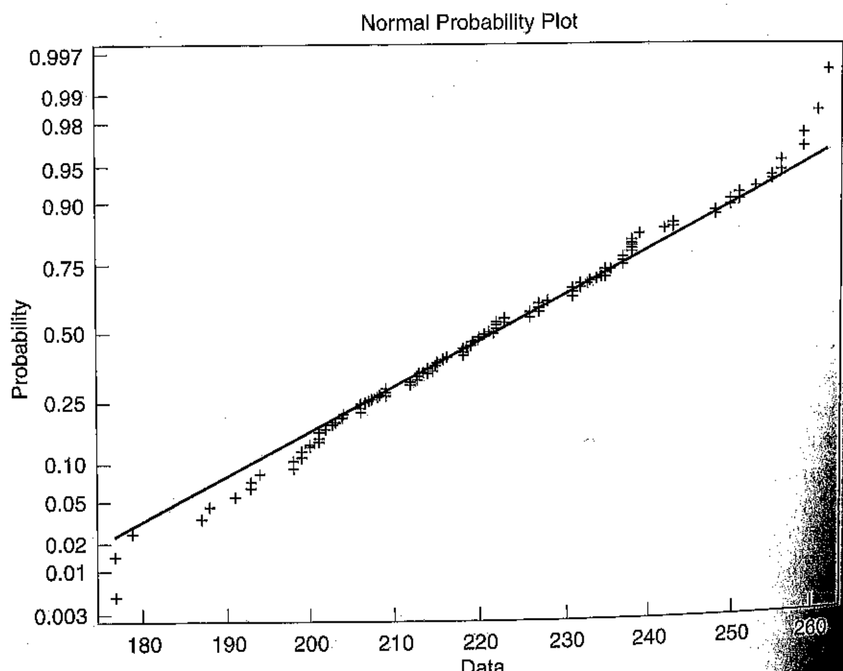

Figure 5. Position $x = 350$; data are heights of profile

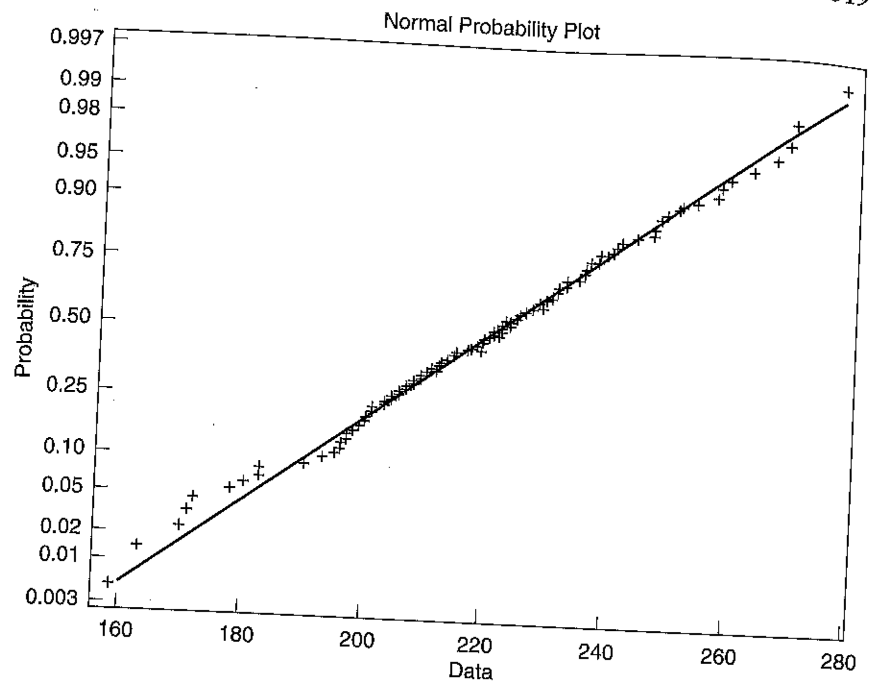

Figure 6. Position $x = 100$; data are heights of profile

$-L \le x_i \le L$ and $\langle r(\omega) \rangle$ is the average value of the random variable $r(\omega)$ over the 100 different runs. In the estimates $\hat{\mu}$ and $\hat{\sigma}$, limiting integrals have been replaced by finite sums. The number of points, N, was chosen so that the fluctuation in the values of the sums was relatively small from run to run, thus averaging over 100 runs was not strictly necessary. The horizontal and vertical coordinates were ordered in increasing value and then plotted. If the heights are normally distributed, the points should lie along the 45 degree line. The results of a calculation with $x = 100, 350$, $T = 1200$ time steps or about 50% of the weathering cycle, and $N = 800$ are shown. We see that agreement with the line is good and therefore consistent with the assumption of normality.

Gloss and Mean Reflectance. Surface roughness as defined by σ is connected with gloss because of the following equation for the mean reflectance:

$$\langle R(\theta) \rangle = \exp\left[-\frac{1}{2} \left(\frac{4\pi\sigma\cos(\theta)}{\lambda} \right)^2 \right] \tag{3}$$

when $\theta = \theta_{inc}$, the incident angle. $\langle R(\theta) \rangle$ is the expected value or average over all sample paths of the process. Note that the reflectance of a ray of light scattered off a randomly rough surface is random, thus we focus on the mean reflectance.

From equation 3 we can see that small roughness is associated with high gloss and vice versa. The derivation uses the assumptions about surface statistics just discussed [1].

Description of Simulation. To simulate photolytic degradation, a collimated uniform "beam" of UV light is projected onto the surface of the paint film, penetrating the binder matrx with a strength that decreases exponentially with depth. As the beam proceeds downward, it damages the binder directly by absorption by binder or indirectly as light is reflected off pigment particles and goes to the binder, where it is absorbed. It is assumed that the damage from the reflected light is uniform over the entire surface and includes binder located in areas that are shielded from direct radiation. Initially, pigment particles shield the binder below them. This eventually leads to the formation of "pedestals" that support single pigment particles as seen in the micrographs of Kampf et al. [5]. Eventually indirect and reflected radiation erodes the pedestals and the now loosened pigment particles are removed from the simulation. More details concerning the simulation can be found in [4].

2. *Results of Simulation*

The results of the simulations support the contention that paint films, composed of large numbers of small, well-dispersed pigment particles, retain gloss over the long term of the weathering cycle. During the early part of the weathering cycle, however, the opposite conclusions can be drawn.

Effect of PVC on Gloss. Several simulations with PVC values of 15%, 25%, and 35% were performed, each lasting 1500 time steps. Figure 7 shows that after an initial transient, the coatings with the largest PVC had the smallest σ (highest gloss) over the entire course of simulation. Thus, higher PVC leads to higher gloss. It is interesting to note that at the beginning of the simulation, coatings with the lowest PVC have the highest gloss (see figure 8).

Effect of Pigment Size Distribution on Gloss. The simulation used pigment particle of two sizes representing small and large particles, respectively, with the diameter of the large particle (43 pixels) being about three times that of the smaller (15 pixels). With S denoting the percent in the coating of small pigment particles, figure 9 shows the σ values of a set of

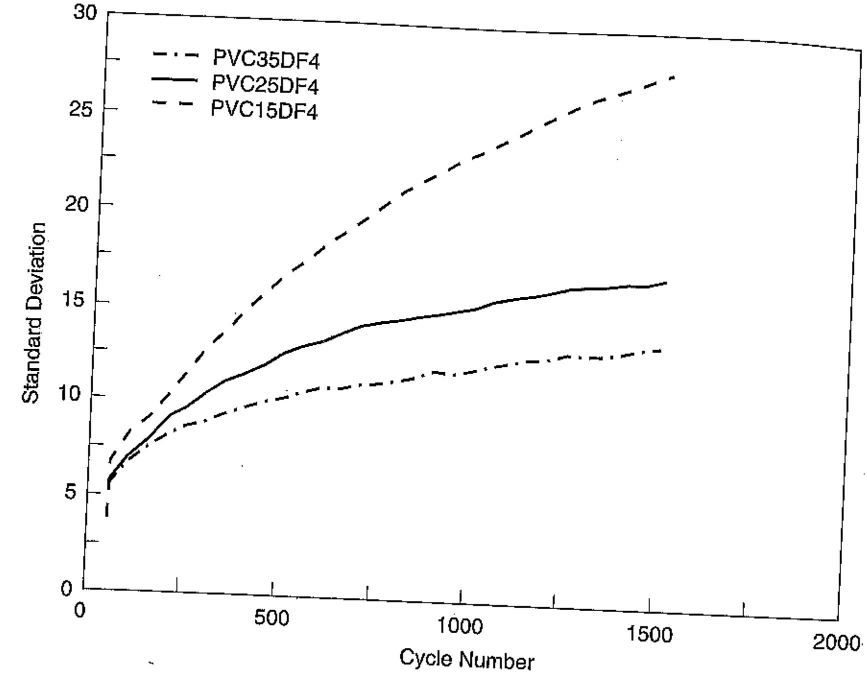

Figure 7. Roughness versus time for DF 4, PVC 15, 25, 35

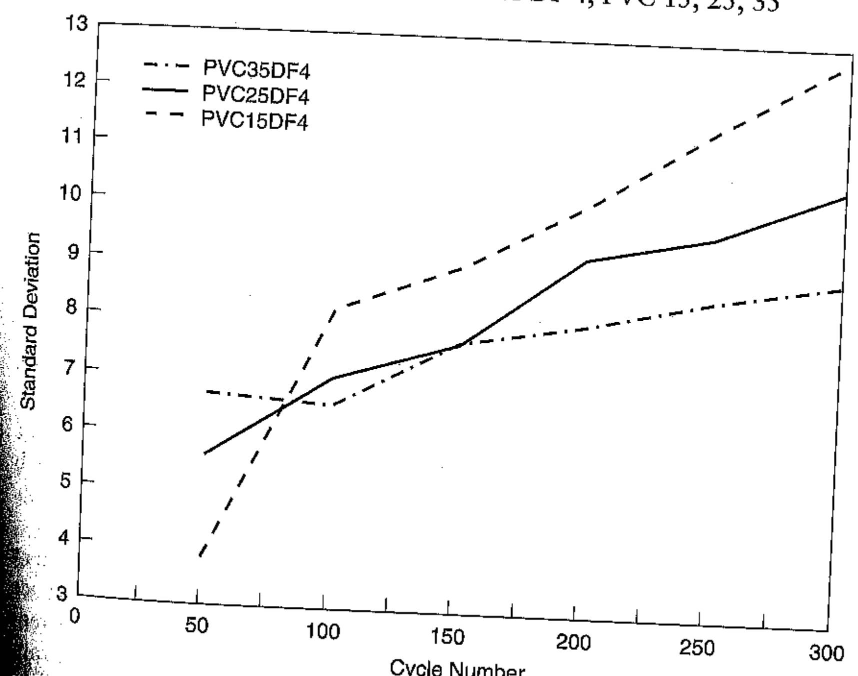

Figure 8. Roughness versus time for DF 4, PVC 15, 25, 35 (early in the simulation cycle)

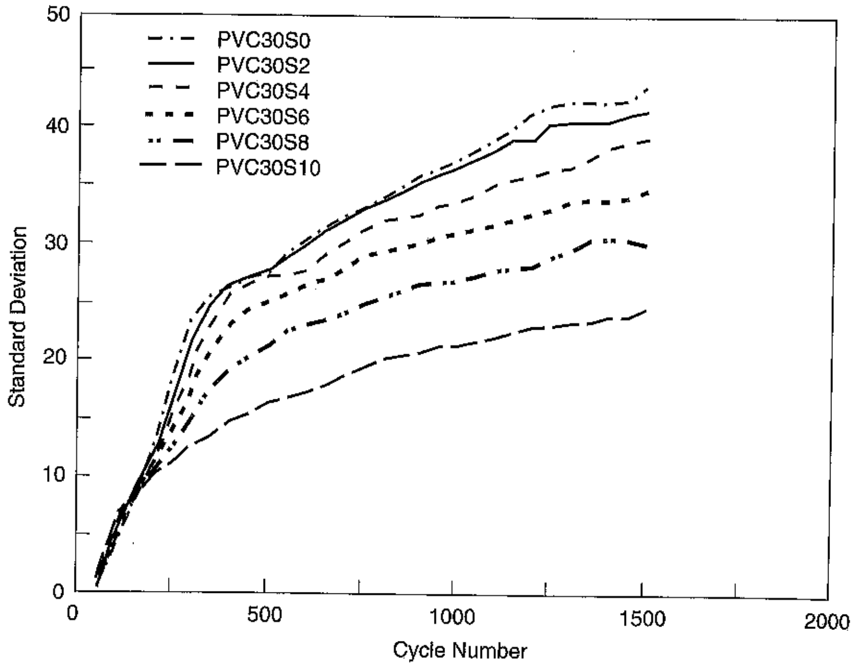

Figure 9. Roughness versus time PVC 30, S0, S2, S4, S6, S8, S10

simulations with varying initial values of $S = 0$, 20, 40, 60, 80, 100%. Except for an initial transient, the coatings with the larger percentage of small pigment particles retained a higher gloss throughout the weathering cycle. Early in the cycle, however (see figure 10), we see, as with PVC, a reversal where, for a period of time, coatings with the larger percentage of small pigment particles have the least gloss. These results suggest that if a manufacturer is interested in coatings that retain their gloss over the long run, then the coatings must contain a high percentage of small pigment particles. However, the kind of gloss that interests consumers is lost well into a weathering cycle [2], so there may be some advantage to using a coating with fewer small pigment particles, since such a coating is (e.g., in the case of titanium dioxide particles) much cheaper.

Effect of Pigment Dispersion on Gloss. At first, we modeled pigment particle dispersion by varying the minimum nearest neighbor distance (dF) beween randomly placed pigment particles in a manner consistent with the PVC. By randomly placed, we mean an approximation of a random close packing. When $dF = 0$, the pigment particles are allowed to touch each other. If dF is larger, the degree of pigment particle dispersion

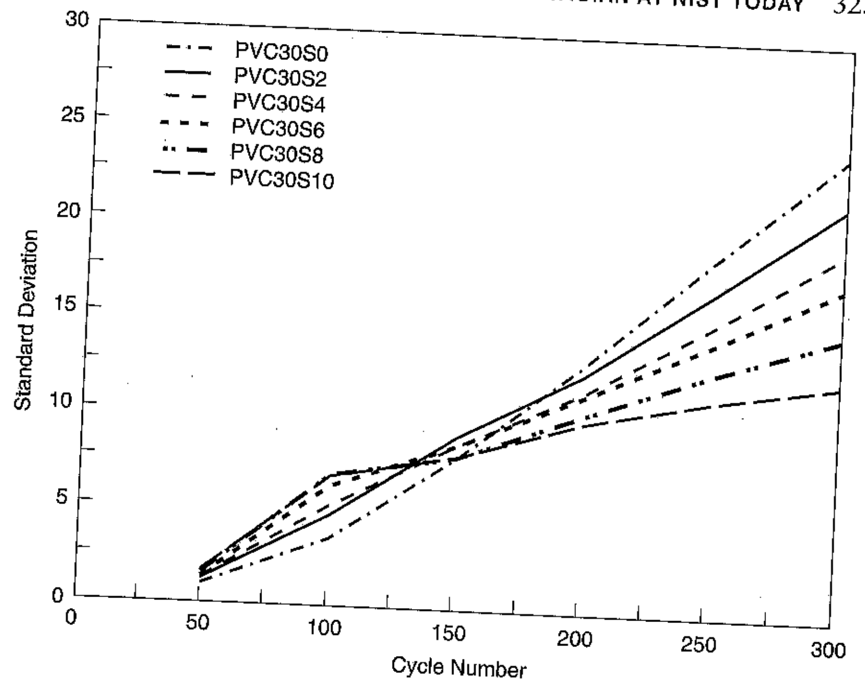

Figure 10. Roughness versus time PVC 30, S0, S2, S4, S6, S8, S10 (early in the simulation cycle)

is larger. In simulations using a number of coatings with several dF values, we found that gloss increases with increase in dF (i.e., better dispersion). This is visually illustrated in figures 11 and 12 showing the cross sections of two simulations at 1200 time steps.

Poisson Point Process. In an effort to derive an analytically tractable way to describe pigment particle dispersion or its opposite (flocculation), we introduced a model of pigment placement based on sampling from the Neyman-Scott point process. To model clustering or flocculation, N uniformly distributed points, (x_i, y_i), $i = 1 \cdots N$, are selected to be the centers of N flocculates or clusters of pigment particles. "Uniform" here means uniformly distributed in the rectangular cross section. However, all these steps can be easily carried out in a three-dimensional setting. Within the ith cluster, we select M_i points uniformly distributed in a circle with center (x_i, y_i) and radius (R). The numbers N and M are discrete Poisson random variables with mean μ and ν, respectively. Thus the parameters of this pigment placement scheme are μ, ν, and R. It is convenient to introduce the variable $\lambda = \frac{\mu}{A}$, the number of clusters per unit area, where A is the area of the cross section. A rough approximation of the pigment volume

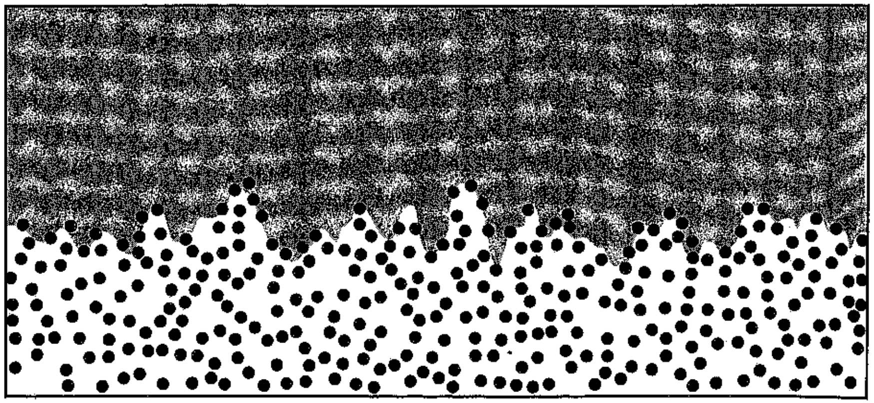

Figure 11. PVC = 35%; $dF = 0$

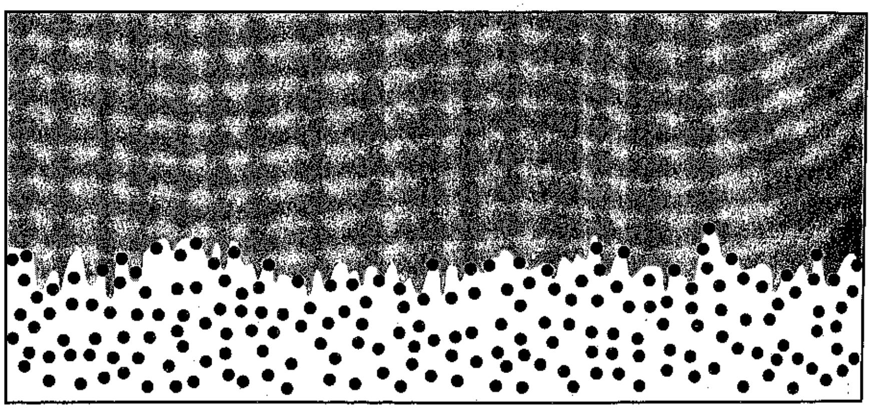

Figure 12. PVC = 35%; $dF = 4$

concentration, the theoretical PVC or TPVC, can be expressed in terms of the model parameters. In the two dimensional setting this is

$$TPVC = \frac{\mu \nu S}{A} = \lambda \nu S \qquad (4)$$

where S is the area of a single pigment particle. In three dimensions, areas are replaced by volumes. Suppose Ω is a region of area, $A(\Omega)$. If $n(\Omega)$ is the number of pigment particles in Ω, then we define the degree of flocculation to be the amount of fluctuation in the number of pigment particles as one samples different regions Ω. We express this in terms of the variance of $n(\Omega)$ [6]

$$var[n(\Omega)] = 2\pi p^2 G_1 + p\nu G_2 + pA(\Omega) - (pA(\Omega))^2 \qquad (5)$$

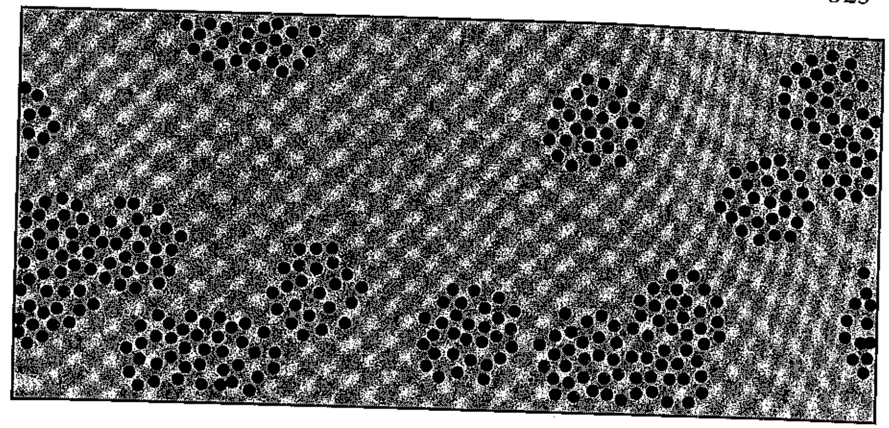

Figure 13.

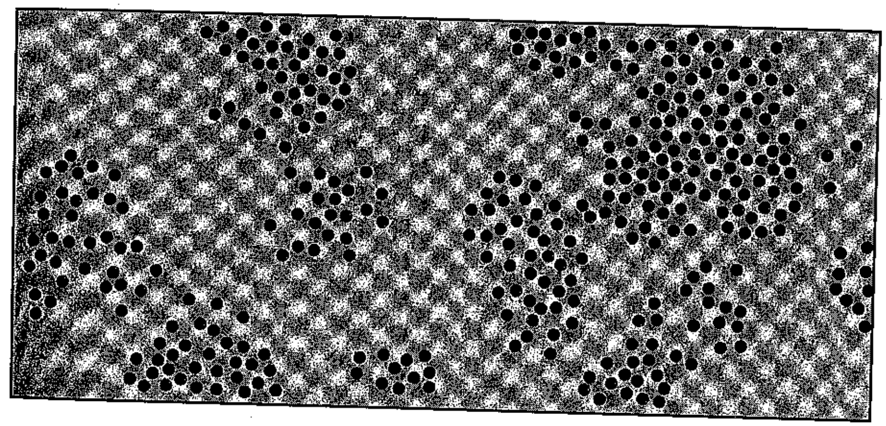

Figure 14.

where $p = \lambda\nu$, G_1 is a geometric constant depending on the area and shape of Ω and G_2 is another geometric constant that depends only on R which is fixed. The constant G_1 is known for simple geometric shapes Ω. Equation 5 shows that the variability of $n(\Omega)$ can be increased keeping the TPVC fixed by increasing the mean cluster size ν but keeping p fixed. Indeed, by equation 4, $TPVC = pS$. We therefore have a way of describing various degrees of dispersion. We illustrate this with figures 13 and 14 that show two realizations of the Neyman-Scott process. The first figure has $\mu = 10$, $\nu = 30$, and the second has $\mu = 30$, $\nu = 10$. The TPVC is the same; both figures were chosen so that the actual PVC (in planar terms) differs from the $TPVC$ by no more than 0.1%. However, the pigments in figure 14 appear to be better dispersed than those in figure 13. The figures illustrate a situation that might arise when a surfactant is added to a flocculated paint, because that addition changes the paint dispersion without changing the PVC.

3. *Computer Graphic Rendering of Surface Appearance*

Members of the more mathematically oriented divisions at NIST often get together for lunch. One day, a year or so before I began to work on the paint project, Holly Rushmeier, a computer scientist in a neighboring division, joined our table. Talk turned to her work. Holly had made fundamental contributions to computer rendering: a new, but very rapidly developing area of computer graphics that used models of light scattering and light source characteristics to develop photorealistic images. This technology had the potential to enable product designers to visualize the appearance of a surface based on information about its light-scattering properties even if the surface didn't exist. Realizing this potential depended first of all on being able to get this information. Optical properties of a surface composed of a given material are summarized in a function known as the BRDF—short for the bidirectional distribution function. Although there is some discussion as to how much, it is clear that the accuracy of a rendered image depends a great deal on how well the BRDF is represented either by data from direct optical measurements, or by mathematical models, or by a combination of the two. Unfortunately, the BRDF is a complicated function, so trade-offs between accuracy and computational efficiency must be made. As Holly, Jon, and I worked to develop ideas for a follow-on project, one of its goals became clear. Since BRDF approximations for rendering programs for computer graphics applications were developed in isolation from the BRDF measurement and modeling community, we would have to build a software interface using the high-precision measurements and modeling done at NIST into formats suitable for input into a rendering program. Just as this new project began, Holly left NIST to take a position at IBM Watson Laboratory. I took over management of this part of the project. Much of what I do involves coordinating the work of optical physicists, material scientists, and computer scientists. The interface work is now completed, and work is proceeding on creating and evaluating images of selected materials. The final figure (figure 15) shows two coated black glass samples with surface roughnesses, 201nm and 805nm, respectively, as measured by the standard deviation we previously discussed. The figures illustrate the decrease in gloss associated with the increased roughness. These images were created by Gary Meyer and Harold Westlund of the University of Oregon from NIST measurements of two coated black glass samples. The samples were 2000 miles away from the

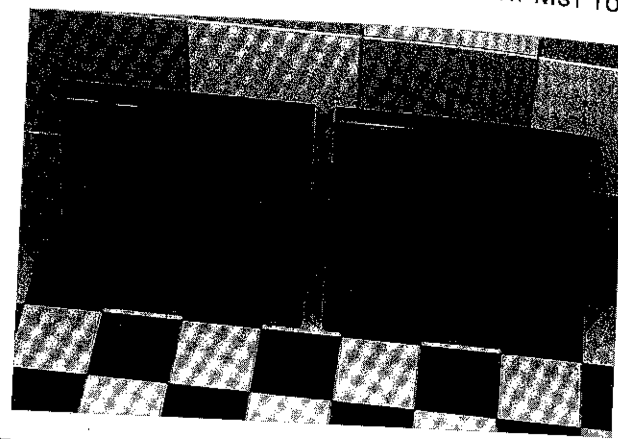

Figure 15. Decrease in gloss associated with increased surface roughness

renderers. A few months later, I flew to Oregon and brought the samples along for visual comparison. Holding up one of them, Meyer said this was the second highlight of his career. It was also a highlight for me—playing a role as part of an interdiscplinary team, using my skills as a mathematician (not in proving theorems but in being able to see the "big" picture), and in communicating and coordinating the work toward its completion.

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