

Photophoretic levitation of engineered aerosols for geoengineering

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Aerosols could be injected into the upper atmosphere to engineer the climate by scattering incident sunlight so as to produce a cooling tendency that may mitigate the risks posed by the accumulation of greenhouse gases. Analysis of climate engineering has focused on sulfate aerosols. Here I examine the possibility that engineered nanoparticles could exploit photophoretic forces, enabling more control over particle distribution and lifetime than is possible with sulfates, perhaps allowing climate engineering to be accomplished with fewer side effects. The use of electrostatic or magnetic materials enables a class of photophoretic forces not found in nature. Photophoretic levitation could loft particles above the stratosphere, reducing their capacity to interfere with ozone chemistry; and, by increasing particle lifetimes, it would reduce the need for continual replenishment of the aerosol. Moreover, particles might be engineered to drift poleward enabling albedo modification to be tailored to counter polar warming while minimizing the impact on equatorial climates.

atmospheric physics | solar radiation management | climate change

The possibility of increasing the earth's albedo to offset CO₂-driven warming has been a subject of speculation for decades (1). Over the last few years, more systematic research and debate on the topic has emerged spurred by Crutzen's (2) call for systematic analysis of geoengineering in response to the continued acceleration of anthropogenic CO₂ emissions (3) and the threat of abrupt climate change. Most research has focused on the possibility of injecting sulfur into the stratosphere (2, 4–8), although more elaborately engineered aerosols (9) and space-based solar scattering systems have also been proposed (9, 10). Here I examine the possibility that particles might be engineered to exploit photophoretic forces (11–16), enabling the manipulation of particle distribution and radiative forcing in ways that could not be achieved with sulfate aerosol.

Limitations of Sulfate Aerosols

The salient advantage of sulfate aerosols as a means to modify the earth's albedo is that nature has already performed relevant experiments in the form of volcanic injections of sulfur, such as the 1991 eruption of Mount Pinatubo, which deposited ~9 Mt sulfur in the stratosphere creating sulfate aerosols that cooled the earth by ~0.5 C within a year (17).

As a tool for climate engineering, sulfates are, however, a blunt instrument. Disadvantages of sulfates include the following: First, it is difficult to produce sulfate aerosol with an appropriate size distribution. The mass-specific scattering efficiency of a sulfate aerosol (or similar dielectric sphere) is strongly dependent on its radius. The scattering efficiency peaks at ~0.3 μm diameter and decreases rapidly for larger or smaller droplets, yet when aerosols are generated by continuous injection of SO₂ the resulting size distribution tends to be substantially larger than optimal because most of the added sulfur is deposited on existing particles. This substantially limits the radiative forcing produced by large sulfur injections and can make it difficult to produce a radiative forcing sufficient to offset the radiative effect of a CO₂ doubling (4). The problem is compounded if sulfate aerosols reach the warmer temperatures in the upper stratosphere where

the vapor pressure of H₂SO₄ is sufficiently high to enable vapor-phase transfer of mass from smaller to larger particles, compounding the difficulty of maintaining a suitable aerosol size distribution.

Second, a significant fraction of the light scattered by sulfate aerosols is scattered in the forward direction, increasing the ratio of diffuse-to-direct insolation at the surface. The Pinatubo eruption, for example, increased the amount of clear sky diffuse sunlight reaching near surface by more than a factor of 2 (18). The increase in diffuse radiation will in turn tend to whiten the visual appearance of the daytime sky and produce side effects ranging from alteration of ecosystem productivity (19) to the reduction in the output from concentrating solar power systems (20).

Finally, sulfates in the lower stratosphere provide reactive surfaces that can accelerate the catalytic removal of ozone by accelerating the conversion of chlorine from reservoir species to ClO. This effect may be more serious if water vapor concentrations in the lower stratosphere increase with increasing global temperatures (21).

The problems of particle size control, forward scattering, and interference with ozone chemistry would apply, in varying degrees, to other nonsulfate aqueous aerosols in the lower stratosphere (22).

Given the disadvantages of sulfate aerosols as a tool for climate engineering, it is worthwhile to explore the possibility of designing scatters that might enable perturbations in radiative forcing to be more precisely tailored or to be achieved with less severe side effects.

Photophoretic Forces on Aerosols

Photophoretic forces arise when radiation produces a temperature difference between an aerosol particle and the surrounding gas (11–13). The forces are most significant when the mean free path of the gas molecules is large compared to the particle's size. Two kinds of photophoretic force have been described. The thermal gradient (ΔT) force arises from a radiatively driven temperature inhomogeneity: Gas molecules leave the warm surface with, on average, higher energy than molecules leaving the cool surface, thus generating an average force away from the hotter side of the particle (Fig. 1A). The accommodation coefficient ($\Delta\alpha$) force arises from variation of the thermal accommodation coefficient across the particle, where the accommodation coefficient, α , is the probability that a impinging molecule of gas will thermally equilibrate with the surface (Fig. 1B). Accommodation coefficients in air vary widely with reported values ranging, for example, from ~0.95 for Al to 0.55 for Pt for temperatures near 315 K (23). The $\Delta\alpha$ force is body-fixed and can act on isothermal particles as long as there is a temperature difference between the particle and the gas.

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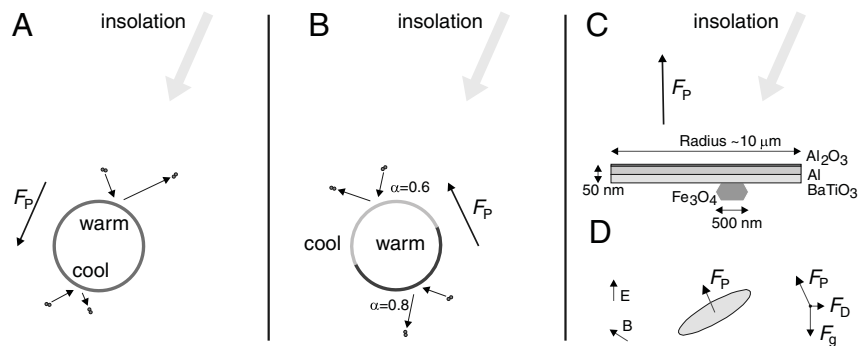


Fig. 1. Schematic illustration of photophoretic forces. *A* and *B* show, respectively, thermal gradient (ΔT) and accommodation coefficient ($\Delta\alpha$) forces acting on idealized spherical particles. Note that for ΔT , the photophoretic force (F_P) is aligned with the asymmetry in the radiation field that drives the thermal gradient, in this case the incident solar radiation (insolation); whereas for $\Delta\alpha$, the vector is oriented along the asymmetry in the accommodation coefficients and rotates with the particle. *C* illustrates design of the disk described in the text, whereas *D* illustrates the fields and forces acting on the disk as described in *SI Text*.

The $\Delta\alpha$ force can produce a net upward (levitating) force when a particle is aligned by gravitational torques. The resulting time-average force is called gravito-photophoretic (13). Such forces may alter the dynamics of natural aerosols in the upper atmosphere contributing to the formation of thin layers of aerosol observed in the mesosphere (12, 15, 16) and perhaps loft soot from the stratosphere to the mesosphere (14, 16).

Brownian motion randomizes a particle's orientation as the orienting torque becomes small compared to the particle's thermal energy. Particles with radii above $1\ \mu\text{m}$ are readily aligned by gravitational torques, but because the photophoretic force is proportional to surface area the upward force per unit mass declines as r^{-1} . For smaller particles, the gravitational torque and hence the time-average upward force is proportional to r^4 , so the net gravito-photophoretic force per unit mass declines as r^3 (*SI Text*). The upshot is that for approximately spherical particles, the gravito-photophoretic $\Delta\alpha$ force can only levitate particles with sizes around $1\ \mu\text{m}$ —far larger than the optimum for mass-efficient scattering—and even then the levitation is only effective above about 10 km, the height at which the mean free path of air molecules approaches the particle size.

Model and Results

A particle with a permanent electric or magnetic dipole moment would experience an orienting torque in the terrestrial electric or magnetic field that would, as with gravito-photophoresis, produce a time-averaged force parallel to the orienting field. One might, by analogy, call the resulting forces electro- or magnetophotophoretic.

Magnetic or electrostatic torques can greatly exceed gravitational torques for small aerosols allowing particles that were engineered to exploit electro- or magnetophotophoresis to exhibit dynamical properties not found in natural aerosols. For example, electro- or magnetophotophoresis could be used to enable a particle to levitate in the lower atmosphere and could be used to levitate particles smaller than $0.1\ \mu\text{m}$.

Engineered particles need not be spherical. The most mass-efficient geometry for a scattering is a thin disk with radius larger than the wavelength of light. Such a design would produce minimal forward scattering when the disk's radius is substantially larger than the wavelength of light, eliminating the diffuse radiation problem encountered with sulfate aerosols. The use of electric or magnetic materials allows disks to be oriented horizontally, and the use of material with contrasting accommodation coefficients allows for levitation.

An Idealized Example. As a specific example, consider a thin disk with radius $\sim 5\ \mu\text{m}$ and thickness 50 nm composed of three layers: 5 nm aluminum oxide, 30 nm of metallic aluminum, and finally

15 nm of barium titanate (Fig. 1C). The thickness of the Al layer is chosen so that it has high solar-band reflectivity and is nearly transparent to outgoing thermal infrared so as to produce a large mass-specific negative radiative forcing (cooling) (9). The Al_2O_3 layer serves to protect the Al layer from oxidation. The thickness of the BaTiO_3 is chosen so that the electrostatic torque from the atmospheric electric field is sufficient to orient the disk horizontally against torques arising from reasonable asymmetries in thickness or α across the disk (24). Assuming a relatively small, and therefore conservative, 15% difference in α between the two materials (23), the photophoretic force on the disk would exceed 2 times its weight under diurnally averaged illumination at altitudes in the middle stratosphere or mesosphere assuming it absorbed only 10% of the solar flux (Fig. 2 and *SI Text*).

The $\Delta\alpha$ force is proportional to the temperature differential between particle and ambient air which, in turn, depends on the difference between the particle's radiative equilibrium temperature and the ambient temperature. The resulting force is therefore strongly dependent on the particle's optical properties. In a particle with a large ϵ_S/ϵ_T , the ratio of solar-spectrum to thermal-spectrum emissivity will be warmer than middle atmosphere air and will be lofted to the mesopause, whereas a particle

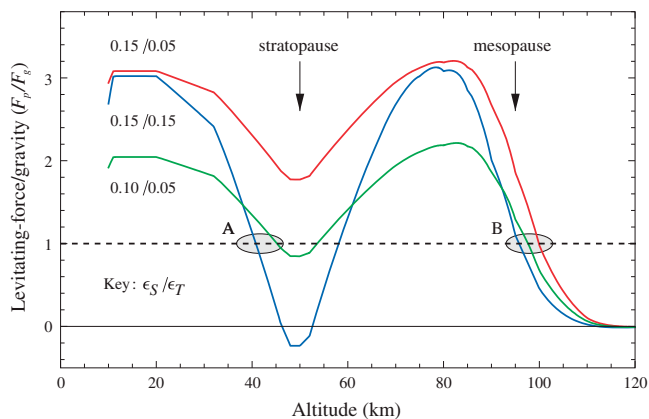


Fig. 2. Photophoretic force versus altitude. The upward photophoretic force, F_P , is normalized by the downward gravitational force, F_G , so that a particle is stably levitated at $F_P/F_G = 1$ (dashed line). Downward forces ($F_P/F_G < 0$) can occur near the stratopause when the particle's radiative equilibrium temperature is less than ambient; forces decline to zero above the mesopause as particle temperatures become radiatively controlled. Particles may be trapped below the stratopause at "A" or below the mesopause at "B." Forces are computed for three combinations of solar and thermal band emissivity by solving the energy balance equation shown in *SI Text*, assuming a disk with $h = 50\ \text{nm}$, $\rho = 3,000\ \text{kg m}^{-3}$, $\bar{\alpha} = 0.7$, and $\delta\alpha = 0.15$. Calculations assume the 1976 Standard Atmosphere (30) and $T_E = 255\ \text{K}$.

with a smaller ϵ_S/ϵ_T that has a radiative temperature below that of the stratopause will be confined below about 45 km (Fig. 2).

It might be possible to tailor particle properties so that levitated particles are trapped either below the stratopause or below the mesopause as shown by points “A” or “B” in Fig. 2. In either case, such particles might avoid two of the disadvantages of stratospheric sulfates: the increase in diffuse radiation and the increase in reactive surface area in the lower stratosphere, which can accelerate ozone depletion (2). Photophoretic levitation would enable longer atmospheric lifetimes, and by lofting aerosols out of the stratosphere it would reduce the most significant impact on ozone chemistry.

Controlling the Latitudinal Distribution of Radiative Forcing. Photophoretic forces might be used to control the latitudinal distribution of particles. Most simply, particles confined near the stratopause (point “A” in Fig. 2) would be transported poleward by the Brewer–Dobson circulation.

Alternatively, the addition of a weak magnetic dipole will break the rotational symmetry of a particle that is levitated by gravito- or electrophotopheresis, partially orienting it along the terrestrial magnetic field and so inducing a magnetophotophoretic effect that could be used to make the particle drift toward one of the magnetic poles while being stably levitated near the stratopause or mesopause. For example, the addition of a weak magnetic moment perpendicular to the plane of the disk described above would tilt the disk toward one of the terrestrial magnetic poles producing a meridional component of the $\Delta\alpha$ force (Fig. 1D). A single $\sim 0.5\ \mu\text{m}$ magnetite nanoparticle adhering to the disk would provide sufficient torque. The resulting poleward velocities are of order $10^2\ \text{m/s}$ for particles confined beneath the stratopause, whereas for particles confined near the mesopause, velocities can exceed $10\ \text{m/s}$ (*SI Text*).

At the stratopause, the meridional velocities achievable with the tilted disk design appear to be slower than the average transport velocities in the Brewer–Dobson circulation (25), but the meridional drift velocity might still allow some additional control of zonal radiative forcing. Velocities may well be large enough at the mesopause, but it is difficult to estimate mean velocity because particle altitude, velocity, and mesospheric winds all have strong diurnal cycles, and the time-average transport will likely depend on the relative phase of the three cycles.

More complex particle designs could achieve substantially higher meridional velocities. Many alternative combinations of forces and orienting torques might be exploited to produce a net poleward force; indeed, poleward migration might be accomplished without electrostatic or magnetic forces (*SI Text*).

Poleward migration of scattering particles might allow the reduction in solar radiative forcing to be concentrated near the poles perhaps counteracting the ice-albedo feedback that amplifies CO_2 -driven polar warming while minimizing the impact on mid-latitude and tropical climates (26). Such an ability might be relevant in the event that warming triggers rapid deglaciation (27).

Discussion

The use of particles engineered to exploit photophoretic forces may enable more selective geoengineering with fewer adverse effects than would the use of sulfate aerosol. Further, the ability to orient particles and to achieve long atmospheric lifetimes might enable deployment of more spectrally selective scattering systems such as patterned gratings or multilayer coatings (9).

Disadvantages and Uncertainties. Long particle lifetimes may be a disadvantage as it makes geoengineering less easily reversible than is the case with short-lived particles. This risk could be mitigated by choosing particle designs with shorter lifetimes for testing and initial deployment. Given the presence of hard-UV flux and reac-

tive atomic oxygen found in the mesosphere, it should be easy to design short-lived particles; design and fabrication of long-lived particles will likely be the engineering challenge.

Unresolved issues include (i) the ability to fabricate and deploy such particles at reasonable cost, (ii) the ability to predict the distribution of particles given the complex interplay of photophoretic motion, gravitational settling and advection by the winds of the middle atmosphere, and, of course, (iii) predicting the effectiveness and risks of climate engineering however the alteration in radiative forcing is achieved.

Finally, although use of engineered particles may offer substantial advantages over sulfate aerosols as a means to manipulate radiative forcing of climate, there is a corresponding disadvantage: We lack the direct natural analog provided by volcanic injection of SO_2 . This lack of analog means that we should be more concerned about unexpected side effects, unknown unknowns, and consider how a careful progression from testing to monitored subscale deployment could constrain the risks.

The Cost of Engineered Particles. Is it possible to fabricate such particles at sufficiently low cost? Any definitive answer would, of course, require a sustained broad-based research effort. The following argument serves only to suggest that one cannot discount the possibility: Approximately $10^9\ \text{kg}$ of engineered particles similar to the example described above would need to be deployed to offset the radiative effect of CO_2 doubling. Assuming a lifetime of 10 years, the particles must be supplied at a rate of $10^8\ \text{kg/yr}$. A plausible upper bound on the acceptable cost of manufacture can be gained by noting that the monetized cost of climate impacts and similarly the cost of substantial reductions in greenhouse gas (GHG) emissions are both of order 1% of global gross domestic product (GDP) (28). Suppose one demanded that the annualized cost of particle manufacture be less than 1% of the cost of abating emissions, that is 10^{-4} of the $\sim 60 \times 10^{12}$ global GDP. Under these assumptions, the allowable manufacturing cost is 60/kg. Many nanoscale particles are currently manufactured at costs significantly less than this threshold. Silica-alumina ceramic hollow microspheres with diameters of $1\ \mu\text{m}$ (e.g., 3M Zeeospheres) can be purchased in bulk at costs less than 0.3/kg. Moreover, bulk vapor-phase deposition methods exist to produce monolayer coatings on fine particles, and there are rapid advances in self-assembly of nanostructures that might be applicable to bulk production of engineered aerosols.

These scaling calculations certainly do not prove that nanoscale particles for climate engineering could be successfully manufactured and deployed. They do suggest that the possibility of doing this over the coming decades cannot be dismissed.

Any climate engineering scheme will only partially and imperfectly compensate for the climatic impacts of GHGs, and it will likely impose significant risks of its own. Given common estimates of the monetized cost of climate damages, the value of reducing climate change by geoengineering could exceed 1% of GDP. It is, therefore, plausible that the costs of geoengineering will be all but irrelevant to decisions about deployment, which will focus on the risk-to-risk trade-off between the risk of geoengineering and the risk of climate damages; assuming, of course, that the direct costs of geoengineering are limited to a small fraction, say 0.1%, of GDP. Thus it might be that the cost of engineered particles could approach 1,000/kg before the costs of manufacture played a significant role in deployment decisions.

Implications for Research on Solar Radiation Management The possibility that engineered aerosols may offer capabilities and risks beyond those arising from injection of sulfate suggest that a balanced research effort on climate modification using stratospheric scatterers should not be limited to exploring the effects of sulfate aerosols—the focus of essentially all current research—but should explore a wider range of technological options for altering

the atmospheric radiation budget. Research on understanding the environmental risks and benefits of such geoengineering must be coupled with a more systematic exploration of the technical options that might be employed to alter the radiative forcing of climate.

Limitations of Solar Radiation Management. Whether or not the ideas proposed here prove to be fruitful, it seems likely that some method will eventually allow humanity to manipulate the solar forcing of climate at low cost and with few side effects arising directly from the system used scatter solar radiation. Such an ability would provide a powerful tool to reduce the risks of climate change, but it cannot possibly solve all the problems arising from the growing burden of anthropogenic CO₂ (8). Although a reduction in insolation can compensate for the effect of increased CO₂ on the global-average surface temperature, it will necessarily

reduce radiant energy fluxes at the surface and this will, in turn, reduce the export of latent heat resulting in a climate with less precipitation and less evaporation than the preindustrial climate. Moreover, the mere knowledge of such methods might itself be problematic if it weakened the commitment to curb emissions (1). Despite this, the continued acceleration of anthropogenic emissions (3) coupled with growing concern about the possibility of dangerous nonlinear responses to climate forcing (27) argue for more systematic exploration of the feasibility and risks of geoengineering (2, 29).

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1. Keith DW (2000) Geoengineering the climate: History and prospect. *Annu Rev Energy Env* 25:245–284.
2. Crutzen PJ (2006) Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma? *Climatic Change* 77:211–219.
3. Canadell JG, et al. (2007) Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proc Natl Acad Sci USA* 104:18866–18870.
4. Heckendorn P, et al. (2009) The impact of geoengineering aerosols on stratospheric temperature and ozone. *Environ Res Lett* 4:045108.
5. Wigley TML (2006) A combined mitigation/geoengineering approach to climate stabilization. *Science* 314:452–454.
6. Rasch PJ, Crutzen PJ, Coleman DB (2008) Exploring the geoengineering of climate using stratospheric sulfate aerosols: The role of particle size. *Geophys Res Lett* 35:L02809.
7. Trenberth KE, Dai A (2007) Effects of Mount Pinatubo volcanic eruption on the hydrological cycle as an analog of geoengineering. *Geophys Res Lett* 34:L15702.
8. Tilmes S, Müller R, Salawitch R (2008) The sensitivity of polar ozone depletion to proposed geoengineering schemes. *Science* 320:1201–1204.
9. Teller E, Wood L, Hyde R (1997) *Global Warming and Ice Ages: I. Prospects for Physics Based Modulation of Global Change* (Lawrence Livermore Natl Laboratory, Livermore, CA) p 20.
10. Angel R (2006) Feasibility of cooling the Earth with a cloud of small spacecraft near the inner Lagrange point (L1). *Proc Natl Acad Sci USA* 103:17184–17189.
11. Ehrenhaft F (1918) Die photophoresis. *Ann Phys Berlin* 361:81–132.
12. Orr C, Jr, Keng EYH (1964) Photophoretic effects in the stratosphere. *J Atmos Sci* 21:475–478.
13. Rohatschek H (1996) Levitation of stratospheric and mesospheric aerosols by gravitophotophoresis. *J Aerosol Sci* 27:467–475.
14. Pueschel RF, et al. (2000) Vertical transport of anthropogenic soot aerosol into the middle atmosphere. *J Geophys Res Atmos* 105:3727–3736.
15. Cheremisin AA, Vassilyev YV, Horvath H (2005) Gravitophotophoresis and aerosol stratification in the atmosphere. *J Aerosol Sci* 36:1277–1299.
16. Wurm G, Krauss O (2008) Experiments on negative photophoresis and application to the atmosphere. *Atmos Environ* 42:2682–2690.
17. Soden BJ, Wetherald RT, Stenchikov GL, Robock A (1992) Global cooling after the eruption of Mount Pinatubo: A test of climate feedback by water vapor. *Science* 296:727–730.
18. Olmo FJ, Tovar J, Alados-Arboledas L, Okulov O, Ohvril HO (1999) A comparison of ground level solar radiative effects of recent volcanic eruptions. *Atmos Environ* 33:4589–4596.
19. Gu L, et al. (2003) Response of a deciduous forest to the Mount Pinatubo eruption: Enhanced photosynthesis. *Science* 299:2035–2038.
20. Murphy DM (2009) Effect of stratospheric aerosols on direct sunlight and implications for concentrating solar power. *Environ Sci Technol* 43:2784–2786.
21. Kirk-Davidoff DB, Hints E, Anderson JG, Keith DW (1999) The effect of climate change on ozone depletion through changes in stratospheric water vapour. *Nature* 402:399–401.
22. Blackstock JJ, et al. (2009) *Climate Engineering Responses to Climate Emergencies* (Novim, Santa Barbara, CA).
23. Ho CY (1989) *Thermal Accommodation and Adsorption Coefficients of Gases* (Hemisphere Publishing Corp, Washington, DC).
24. Fong DD, et al. (2004) Ferroelectricity in ultrathin perovskite films. *Science* 304:1650–1653.
25. Jones DBA, Andrews AE, Schneider HR, McElroy MB (2001) Constraints on meridional transport in the stratosphere imposed by the mean age of air in the lower stratosphere. *J Geophys Res Atmos* 106:10243–10256.
26. MacCracken MC (2009) On the possible use of geoengineering to moderate specific climate change impacts. *Environ Res Lett* 4:045107.
27. Bambara JL, Alley RB, Joughin I (2007) Rapid response of modern day ice sheets to external forcing. *Earth Planet Sci Lett* 257:1–13.
28. Metz B, Davidson O, Swart R, Pan J, eds. (2001) *Climate Change 2001: Mitigation: Contribution of Working Group III to the Third Assessment Report of the IPCC* (Cambridge Univ Press, Cambridge, UK).
29. Keith DW, Parson E, Morgan MG (2010) Research on global sun block needed now. *Nature* 463:426–427.
30. Anonymous (1976) *U.S. Standard Atmosphere* (U.S. Government Printing Office, Washington, DC).