输运性质

Saturday, March 11, 2023 5:30 PM

输运性质(transport properties)一般指材料的传质和传热相关的性质。包括粘度、导热系数和扩散系数。狭义上这些都指线性不可逆热力学下的概念，分别对应于：Navier-Stokes方程、热方程和扩散方程。NS方程描述动量输运，扩散方程描述质量输运，热方程描述热输运。

此外，还有关于电荷的输运性质，或称电输运性质。包括电导率，介电常数，磁导率。

Conduction and Diffusion in Percolating Systems, Table 1 Mathematically equivalent potential theory problems

Transport coefficient	Flux law	Potential–field relation
Electrical conductivity σ	$\mathbf{J}=\sigma\mathbf{E}$	$\mathbf{E}=-\nabla V$ from Maxwell's $\nabla\times\mathbf{E}=0$
Dielectric permittivity ϵ	$\mathbf{D}=\epsilon\mathbf{E}$	$\mathbf{E}=-\nabla V$ from Maxwell's $\nabla\times\mathbf{E}=0$
Magnetic permeability μ	$\mathbf{B}=\mu\mathbf{H}$	$\mathbf{H}=-\nabla V$ from Maxwell's $\nabla\times\mathbf{H}=0$
Transport coefficient	Flux–potential relation	
Thermal conductivity κ	Fourier's Law (temperature T)	$\mathbf{Q}=-\kappa\nabla T$
Diffusivity D	Fick's Law (concentration c)	$\mathbf{j}=-D\nabla c$
Permeability k	Darcy's Law (pressure P, viscosity η)	$\mathbf{q}=-(k/\eta)\nabla P$

输运性质在空间中的非均质性及其逾渗与材料结构的逾渗是相对独立的问题。因为动力学性质与结构(静态性质)之间没有普适的确定关系。

仅在输运性质的逾渗层面上讨论，以导体/绝缘体复合材料为例，我们观察的是材料整体的电导率(表观的)随导体比例的变化规律。取决于导电区的形貌和尺寸分布规定，材料的表观电导率在某一导体组成比例 p_c 下发生突变。在 p_c 附近，$\sigma_{eff}(p)\sim const\times(p-p_c)^t$，$t$ 是电导率的临界指数。

如果我们进一步对输运性质的临界指数与静态性质的临界指数之间的关系感兴趣，那就无法回避动力学性质与静态性质的关系问题。

已知导体在绝缘体中分布的结构信息(密度涨落、团簇尺寸分布…)如何推算材料的总体电导率？这本身就是材料科学中的经典难题。连续介质的几种建模方法，已在Hughe的章节中总结了。这里不详细介绍。

B. Hughes (2021), in: M. Sahimi and A. Hunt eds., Complex Media and Percolation Theory, Springer

Meester and Roy (1996) Continuum Percolation, Cambridge University Press

Ex. Poisson-centered conducting spheres of constant radius

$\phi_c \approx 0.2895 \pm 0.0005$ J. Phys. A 30: L585 (1997)

Swiss cheese model

$\phi_c \simeq 0.03$ J. Appl. Phys. 71: 2727 (1992)

对于格子(离散)模型，一个canonical example就是random resistor network。专著：

B. Hughes (1996) Random walks and random environments (vol. 1&2), Clarendon.

一般的随机电阻网络模型仍是复杂的。若电阻网络的键满足独立同分布 $f(g)$

$$f(g)=(1-p)\delta_+(g)+p\,h(g),\quad 0<p<1$$

$h(g)$ 是电导的某条件分布，$\delta_+(g)$ 是 δ 函数的右半边，则为general percolation conduction problem.
若

$$f(g)=(1-p)\delta_+(g)+p\,\delta(g-g_0),\quad 0<p<1$$

（即当 $h(g)\equiv\delta(g-g_0)$），则为 standard percolation conduction problem. 这时模型才比较易于进行直接的数学处理。但仍需指明网络的网格结构。工作只能给出逾渗的上下界。

电导率在临界点附近的标度律假设：

$$\sigma_{eff}(p) \approx \mu S\left([p-p_c]\lambda^{-1},\ a\mu^{-1}\lambda^{-A},\ \mu b^{-1}\lambda^{-B}\right)$$ Straley (1976) J. Phys. C 9:783

$S(x,y,z)$ 是一个函数，x,y,z 均小于 1，$S(x,y,z)\to\infty$ 当 x 或 y，或 $z\to 0$

在 $p=p_c$ 时再令 $\lambda^{t+s}=a/b$，$\mu=b\lambda^{t}$，则

$$\sigma_{eff}(p) \approx a^{u} b^{1-u} S(0,1,1),\quad u=t/(s+t)$$

Conduction and Diffusion in Percolating Systems, Table 2 Estimates of the conductivity (t) and superconductivity (s) exponents in two dimensions. Estimates from physical experiments and from numerical simulations are displayed separately. Where values of both t/v and t, or both s/v and s are given, these values of t/v or s/v were obtained first by finite-size scaling or related ideas, and the values of t or s were subsequently deduced. In two dimensions, it is known that $v=\frac{4}{3}$ exactly (asterisked entries use this value to compute t or s from t/v or s/v), and also that $s=t$ exactly, but no such results are available for $d=3$. For the molecular trajectory algorithm (Cen et al. 2012a), the first way analyses motion on all clusters at $p=p_c$, while the second analyses motion on the incipient infinite cluster at $p=p_c$

t/v	t	Experiment type and source
0.95 ± 0.05	≈ 1.26*	Photolithography on metal films (Palevski and Deutscher 1984)
	1.32 ± 0.25	Nanoscale bismuth clusters (Dunbar et al. 2003)
t/v	t	Numerical technique and source
0.95 ± 0.01	1.28 ± 0.03	Transfer matrix (Derrida and Vannimenus 1982)
0.968 ± 0.005	≈ 1.291*	Transfer matrix (bond) (Zabolitzky 1984)
	1.291 ± 0.024	Random walk simulation ($p > p_c$) (Poole and Salt 1996)
0.970 ± 0.009	≈ 1.293*	Enumerate random walks on backbone (Hong et al. 1984)
0.971 ± 0.005		Molecular trajectory first way (Cen et al. 2012a)
≈ 0.972	≈ 1.296*	Random walk simulation (Rammal et al. 1984)
$0.973^{+0.005}_{-0.003}$	$1.297^{+0.007}_{-0.004}$	Finite-size scaling (Lobb and Frank 1984)
0.975 ± 0.005	≈ 1.300*	Transfer matrix (site) (Zabolitzky 1984)
0.977 ± 0.008		Molecular trajectory second way (Cen et al. 2012a)
0.979 ± 0.006	≈ 1.305*	Finite-size scaling (Rammal et al. 1985)
	1.31 ± 0.04	Monte Carlo (Fogelholm 1980)
0.9826 ± 0.0008	1.3100 ± 0.0011*	Finite-size scaling (bond and site) (Grassberger 1999)
s/v	s	Numerical technique and source
0.9745 ± 0.0015	1.299 ± 0.002	Special purpose computer (Normand et al. 1988)
0.977 ± 0.010	≈ 1.303*	Transfer matrix (Herrmann et al. 1984)

Conduction and Diffusion in Percolating Systems, Table 3 Estimates of the conductivity (t) and superconductivity (s) exponents in three dimensions. Several estimates of t obtained before 1984 that are very low compared to more modern estimates are not shown. Where values of t/ν or s/ν are given, these values were obtained first by finite-size scaling or related ideas, and the values of t or s were subsequently deduced. Neither ν nor p_c are known exactly and estimates are sensitive to choices made by the cited authors. All estimates are for the simple cubic lattice bond problem, except for (i) the random walk estimate (Roman 1990) for the simple cubic lattice site problem; (ii) the molecular trajectory algorithm (Cen et al. 2012b); and (iii) three studies considering both site and bond problems – the special purpose computer transfer matrix calculation (Normand and Herrmann 1995); the Monte Carlo study (Kozlov and Lagues 2010) in which t and t/ν were obtained independently by studying lattices of size L at occupancy p in the cases $p = p_c$, L variable and L fixed, p variable, respectively, and used to deduce that $\nu = 0.876 \pm 0.006$; and the separate finite-size scaling analyses of the site and bond problems (Li and Chou 2009)

t/ν	ν used	t	Source
2.095 ± 0.016	0.89 ± 0.01	1.867 ± 0.035	Finite-size scaling (Sahimi et al. 1983b)
2.21 ± 0.03			Lattice random walks with $p > p_c$ (Cen et al. 2012b)
2.26 ± 0.02			Molecular trajectory algorithm (Cen et al. 2012b)
2.26 ± 0.04			Special purpose computer (Normand and Herrmann 1995)
2.276 ± 0.012	0.88 ± 0.02	2.003 ± 0.047	Finite-size scaling (Gingold and Lobb 1990)
2.282 ± 005			Current distribution moments (Batrouni et al. 1996)
2.283 ± 0.003		2.00 ± 0.01	Two finite-size scaling methods (Kozlov and Laguës 2010)
2.288 & 2.302			Finite size scaling (Li and Chou 2009)
2.305 ± 0.015	≈ 0.88	≈ 2.0	Finite-size scaling (Clerc et al. 2000)
		2.02 ± 0.02	Monte Carlo as $p \to p_c$ (Clerc et al. 2000)
≈ 2.315			Generalized transfer matrix (Byshkin and Turkin 2005)
2.32 ± 0.02			Lattice random walks at p_c (Cen et al. 2012b)
2.48 ± 0.07			Lattice random walks (Roman 1990)
s/ν	ν used	s	Source
0.782 ± 0.019			Finite-size scaling (Sahimi 1984)
0.85 ± 0.04	≈ 0.88	≈ 0.75	Transfer matrix (Herrmann et al. 1984)
0.835 ± 0.005			Special purpose computer (Normand and Herrmann 1990)

对于扩散系数/导热系数（以扩散为例）

需要考虑的是溶质在非均质环境中的扩散问题。或更明确地说，要考虑溶质在材料中的扩散系数的空间涨落及其渝渗问题。

这涉及了分形上的随机行走的大量理论工作。也在 Hughes (2021) 章节中总结了。其中比较为人所知的问题是 Ant in the Labyrinth 模型/问题，主要关注的是均方回转半径/位移 ∝ 聚合度/步长$^{\square}$ 的指数 d_w.

但 $\langle S_n \rangle$ 如何联系到扩散系数，以至于扩散系数空间分布的渝渗转变如何，Hughes (2021) 未有涉及。也许对于非均质体系，$\langle S_n \rangle \neq 2Dn$。($d_w \neq 2$) 故只能以 $\langle S_n \rangle \propto n^{d_w}$ 来说。

d_w 的具体分析 Hughes (2021) 和我总结的 Cates 工作。包括 fracton dimension 概念