

Package ‘serrsBayes’

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Type Package

Title Bayesian Modelling of Raman Spectroscopy

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Description Sequential Monte Carlo (SMC) algorithms for fitting a generalised additive mixed model (GAMM) to surface-enhanced resonance Raman spectroscopy (SERRS), using the method of Moores et al. (2016) <[doi:10.48550/arXiv.1604.07299](https://doi.org/10.48550/arXiv.1604.07299)>. Multivariate observations of SERRS are highly collinear and lend themselves to a reduced-rank representation. The GAMM separates the SERRS signal into three components: a sequence of Lorentzian, Gaussian, or pseudo-Voigt peaks; a smoothly-varying baseline; and additive white noise. The parameters of each component of the model are estimated iteratively using SMC. The posterior distributions of the parameters given the observed spectra are represented as a population of weighted particles.

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URL <https://github.com/mooresm/serrsBayes>,
<https://mooresm.github.io/serrsBayes/>

BugReports <https://github.com/mooresm/serrsBayes/issues>

Depends R (>= 3.5.0), Matrix, truncnorm, splines

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computeLogLikelihood *Compute the log-likelihood.*

Description

This is an internal function that is only exposed on the public API for unit testing purposes. It computes the log-likelihood of the spline and the noise, once the spectral signature has been subtracted from the observed data. Thus, it can be used with either Lorentzian, Gaussian, or pseudo-Voigt broadening functions.

Usage

```
computeLogLikelihood(  
  obsi,  
  lambda,  
  prErrNu,  
  prErrSS,  
  basisMx,  
  eigVal,  
  precMx,  
  xTx,  
  aMx,  
  ruMx  
)
```

Arguments

| | |
|---------|---|
| obsi | Vector of residuals after the spectral signature has been subtracted. |
| lambda | smoothing parameter of the penalised B-spline. |
| prErrNu | hyperparameter of the additive noise |
| prErrSS | hyperparameter of the additive noise |
| basisMx | Matrix of B-spline basis functions |
| eigVal | eigenvalues of the Demmler-Reinsch factorisation |
| precMx | precision matrix for the spline |
| xTx | sparse matrix cross-product |
| aMx | orthogonal matrix A from the Demmler-Reinsch factorisation |
| ruMx | product of Ru from the Demmler-Reinsch factorisation |

Value

The logarithm of the likelihood.

copyLogProposals *Initialise the vector of Metropolis-Hastings proposals.*

Description

This is an internal function that is only exposed on the public API for unit testing purposes.

Usage

```
copyLogProposals(nPK, T_Prop_Theta)
```

Arguments

nPK number of Raman peaks in the spectral signature
 T_Prop_Theta Vector of logarithms of the MH proposals

Value

Vector of proposals

effectiveSampleSize *Compute the effective sample size (ESS) of the particles.*

Description

The ESS is a "rule of thumb" for assessing the degeneracy of the importance distribution:

$$ESS = \frac{(\sum_{q=1}^Q w_q)^2}{\sum_{q=1}^Q w_q^2}$$

Usage

```
effectiveSampleSize(log_weights)
```

Arguments

log_weights logarithms of the importance weights of each particle.

Value

the effective sample size, a scalar between 0 and Q

References

Liu, JS (2001) "Monte Carlo Strategies in Scientific Computing." Springer, NY, pp. 34–36.

Examples

```
x <- runif(100)
effectiveSampleSize(log(x))
```

| | |
|----------------|--|
| fitSpectraMCMC | <i>Fit the model using Markov chain Monte Carlo.</i> |
|----------------|--|

Description

Fit the model using Markov chain Monte Carlo.

Usage

```
fitSpectraMCMC(wl, spc, peakWL, lPriors, sd_mh, niter = 10000, nchains = 4)
```

Arguments

| | |
|---------|--|
| wl | Vector of nw1 wavenumbers at which the spectra are observed. |
| spc | n_y * nw1 Matrix of observed Raman spectra. |
| peakWL | Vector of locations for each peak (cm ⁻¹) |
| lPriors | List of hyperparameters for the prior distributions. |
| sd_mh | Vector of 2 * npeaks bandwidths for the random walk proposals. |
| niter | number of MCMC iterations per chain. |
| nchains | number of concurrent MCMC chains. |

Value

a List containing MCMC samples for the model parameters:

amplitude niter * nchains * npeaks Array of amplitudes.

scale niter * nchains * npeaks Array of scale parameters.

sigma niter * nchains Matrix of standard deviations.

n_acc The number of RWMH proposals that were accepted.

See Also

[marginalMetropolisUpdate](#)

Examples

```
wavenumbers <- seq(200,600,by=10)
spectra <- matrix(nrow=1, ncol=length(wavenumbers))
peakLocations <- c(300,500)
peakAmplitude <- c(10000,4000)
peakScale <- c(10, 15)
signature <- weightedLorentzian(peakLocations, peakScale, peakAmplitude, wavenumbers)
baseline <- 1000*cos(wavenumbers/200) + 2*wavenumbers
spectra[1,] <- signature + baseline + rnorm(length(wavenumbers),0,200)
lPriors <- list(scale.mu=log(11.6) - (0.4^2)/2, scale.sd=0.4, bl.smooth=10^11, bl.knots=20,
               amp.mu=5000, amp.sd=5000, noise.sd=200, noise.nu=4)
rw_bw <- c(100, 100, 2, 2)
result <- fitSpectraMCMC(wavenumbers, spectra, peakLocations, lPriors, rw_bw, 500)
result$n_acc
```

fitSpectraSMC

Fit the model using Sequential Monte Carlo (SMC).

Description

Fit the model using Sequential Monte Carlo (SMC).

Usage

```
fitSpectraSMC(
  wl,
  spc,
  peakWL,
  lPriors,
  conc = rep(1, nrow(spc)),
  npart = 10000,
  rate = 0.9,
  minESS = npart/2,
  destDir = NA
)
```

Arguments

| | |
|---------|--|
| wl | Vector of nwl wavenumbers at which the spectra are observed. |
| spc | n_y * nwl Matrix of observed Raman spectra. |
| peakWL | Vector of locations for each peak (cm ⁻¹) |
| lPriors | List of hyperparameters for the prior distributions. |
| conc | Vector of n_y nanomolar (nM) dye concentrations for each observation. |
| npart | number of SMC particles to use for the importance sampling distribution. |
| rate | the target rate of reduction in the effective sample size (ESS). |
| minESS | minimum effective sample size, below which the particles are resampled. |
| destDir | destination directory to save intermediate results (for long-running computations) |

Value

a List containing weighted parameter values, known as particles:

weights Vector of importance weights for each particle.

beta npart * npeaks Matrix of regression coefficients for the amplitudes.

scale npart * npeaks Matrix of scale parameters.

sigma Vector of npart standard deviations.

alpha bl.knots * n_y * npart Array of spline coefficients for the baseline.

basis A dense nwl * bl.knots Matrix containing the values of the basis functions.

expFn npart * nwl Matrix containing the spectral signature.

ess Vector containing the effective sample size (ESS) at each SMC iteration.

logEvidence Vector containing the logarithm of the model evidence (marginal likelihood).

accept Vector containing the Metropolis-Hastings acceptance rate at each SMC iteration.

sd.mh niter * 2npeaks Matrix of random walk MH bandwidths at each SMC iteration..

References

Chopin (2002) "A Sequential Particle Filter Method for Static Models," *Biometrika* 89(3): 539–551, doi: [10.1093/biomet/89.3.539](https://doi.org/10.1093/biomet/89.3.539)

Examples

```
wavenumbers <- seq(200,600,by=10)
spectra <- matrix(nrow=1, ncol=length(wavenumbers))
peakLocations <- c(300,500)
peakAmplitude <- c(10000,4000)
peakScale <- c(10, 15)
signature <- weightedLorentzian(peakLocations, peakScale, peakAmplitude, wavenumbers)
baseline <- 1000*cos(wavenumbers/200) + 2*wavenumbers
spectra[1,] <- signature + baseline + rnorm(length(wavenumbers),0,200)
lPriors <- list(scale.mu=log(11.6) - (0.4^2)/2, scale.sd=0.4, bl.smooth=10^11, bl.knots=20,
              beta.mu=5000, beta.sd=5000, noise.sd=200, noise.nu=4)

## Not run:
result <- fitSpectraSMC(wavenumbers, spectra, peakLocations, lPriors, npart=500)

## End(Not run)
```

fitVoigtIBIS

Fit the model with Voigt peaks using iterated batch importance sampling (IBIS).

Description

Fit the model with Voigt peaks using iterated batch importance sampling (IBIS).

Usage

```

fitVoigtIBIS(
  w1,
  spc,
  n,
  lResult,
  conc = rep(1, nrow(spc)),
  batch = rep(1, nrow(spc)),
  npart = 10000,
  rate = 0.9,
  mcAR = 0.234,
  mcSteps = 20,
  minESS = npart/2,
  minPart = npart,
  destDir = NA
)

```

Arguments

| | |
|---------|--|
| w1 | Vector of nwl wavenumbers at which the spectra are observed. |
| spc | n_y * nwl Matrix of observed Raman spectra. |
| n | index of the new observation |
| lResult | List of results from the previous call to “fitVoigtPeaksSMC” or “fitVoigtIBIS” |
| conc | Vector of n_y nanomolar (nM) dye concentrations for each observation. |
| batch | identifies to which batch each observation belongs |
| npart | number of SMC particles to use for the importance sampling distribution. |
| rate | the target rate of reduction in the effective sample size (ESS). |
| mcAR | target acceptance rate for the MCMC kernel |
| mcSteps | number of iterations of the MCMC kernel |
| minESS | minimum effective sample size, below which the particles are resampled. |
| minPart | target number of unique particles for the MCMC iterations |
| destDir | destination directory to save intermediate results (for long-running computations) |

References

Chopin (2002) "A Sequential Particle Filter Method for Static Models," *Biometrika* 89(3): 539–551, doi: [10.1093/biomet/89.3.539](https://doi.org/10.1093/biomet/89.3.539)

fitVoigtPeaksSMC *Fit the model with Voigt peaks using Sequential Monte Carlo (SMC).*

Description

Fit the model with Voigt peaks using Sequential Monte Carlo (SMC).

Usage

```
fitVoigtPeaksSMC(
  wl,
  spc,
  lPriors,
  conc = rep(1, nrow(spc)),
  npart = 10000,
  rate = 0.9,
  mcAR = 0.234,
  mcSteps = 20,
  minESS = npart/2,
  destDir = NA,
  minPart = npart
)
```

Arguments

| | |
|---------|--|
| wl | Vector of nwl wavenumbers at which the spectra are observed. |
| spc | n_y * nwl Matrix of observed Raman spectra. |
| lPriors | List of hyperparameters for the prior distributions. |
| conc | Vector of n_y nanomolar (nM) dye concentrations for each observation. |
| npart | number of SMC particles to use for the importance sampling distribution. |
| rate | the target rate of reduction in the effective sample size (ESS). |
| mcAR | target acceptance rate for the MCMC kernel |
| mcSteps | number of iterations of the MCMC kernel |
| minESS | minimum effective sample size, below which the particles are resampled. |
| destDir | destination directory to save intermediate results (for long-running computations) |
| minPart | target number of unique particles for the MCMC iterations |

Examples

```
wavenumbers <- seq(200,600,by=10)
spectra <- matrix(nrow=1, ncol=length(wavenumbers))
peakLocations <- c(300,500)
peakAmplitude <- c(10000,4000)
```

```

peakScale <- c(10, 15)
signature <- weightedLorentzian(peakLocations, peakScale, peakAmplitude, wavenumbers)
baseline <- 1000*cos(wavenumbers/200) + 2*wavenumbers
spectra[1,] <- signature + baseline + rnorm(length(wavenumbers),0,200)
lPriors <- list(scaG.mu=log(11.6) - (0.4^2)/2, scaG.sd=0.4, scaL.mu=log(11.6) - (0.4^2)/2,
  scaL.sd=0.4, bl.smooth=5, bl.knots=20, loc.mu=peakLocations, loc.sd=c(5,5),
  beta.mu=c(5000,5000), beta.sd=c(5000,5000), noise.sd=200, noise.nu=4)
## Not run:
result <- fitVoigtPeaksSMC(wavenumbers, spectra, lPriors, npart=50, mcSteps=1)

## End(Not run)

```

getBsplineBasis *Compute cubic B-spline basis functions for the given wavenumbers.*

Description

This function computes penalised cubic B-splines using the method proposed by Eilers & Marx (1996). The spline coefficients can be computed efficiently using sparse matrix algebra, as described in Sect. 2.3.3 of Green & Silverman (1994) and Appendix B of Ruppert, Wand & Carroll (2003).

Usage

```
getBsplineBasis(V, n.b, pen, prec = 1e-08)
```

Arguments

| | |
|------|--|
| V | a vector of wavenumbers, $\Delta\tilde{\nu}$. |
| n.b | the number of basis functions to use. |
| pen | the smoothing penalty hyperparameter. |
| prec | a constant scale factor. |

Value

a list containing:

basis A dense nwl by $n.b$ matrix containing the values of the basis functions.
precision A sparse $n.b$ by $n.b$ `dsCMatrix`, the inverse of the prior covariance.
distance The distance between each knot (cm^{-1}).
knots The knot locations.

References

Eilers, PHC & Marx, BD (1996) "Flexible smoothing with B-splines and penalties," *Statist. Sci.* 11(2): 89–121, doi: [10.1214/ss/1038425655](https://doi.org/10.1214/ss/1038425655)

Green, PJ & Silverman, BW (1994) "Nonparametric Regression and Generalized Linear Models: a roughness penalty approach" Chapman & Hall, Boca Raton, FL, pp. 11–21.

Ruppert, D; Wand, MP & Carroll, RJ (2003) "Semiparametric Regression" CUP, Cambridge, UK, pp. 336–340.

See Also[sparseMatrix](#)

`getVoigtParam`*Compute the pseudo-Voigt mixing ratio for each peak.*

Description

Calculates the mixing parameter η_j from the scales of the Gaussian/Lorentzian components.

Usage

```
getVoigtParam(scale_G, scale_L)
```

Arguments

| | |
|----------------------|--|
| <code>scale_G</code> | Vector of standard deviations σ_j of the Gaussian components. |
| <code>scale_L</code> | Vector of scale parameters ϕ_j of the Lorentzian components. |

Details

First, calculate a polynomial average of the scale parameters according to the approximation of Thompson et al. (1987):

$$f_{G,L} = (\sigma_j^5 + 2.69\sigma_j^4\phi_j + 2.42\sigma_j^3\phi_j^2 + 4.47\sigma_j^2\phi_j^3 + 0.07\sigma_j\phi_j^4 + \phi_j^5)^{1/5}$$

Then the Voigt mixing parameter η_j is defined as:

$$\eta_j = 1.36 \frac{\phi_j}{f_{G,L}} - 0.47 \left(\frac{\phi_j}{f_{G,L}} \right)^2 + 0.11 \left(\frac{\phi_j}{f_{G,L}} \right)^3$$

Value

The Voigt mixing weights for each peak, between 0 (Gaussian) and 1 (Lorentzian).

References

Thompson, Cox & Hastings (1987) "Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al_2O_3 ," J. Appl. Crystallogr. 20(2): 79–83, doi: [10.1107/S0021889887087090](https://doi.org/10.1107/S0021889887087090)

| | |
|---------|--|
| 1sTamra | <i>Surface-enhanced Raman spectrum of tetramethylrhodamine+DNA (T20)</i> |
|---------|--|

Description

Surface-enhanced Raman spectrum of tetramethylrhodamine+DNA (T20)

Usage

1sTamra

Format

A list containing 2 variables:

wavenumbers a numeric Vector of 2401 wavenumbers (cm⁻¹)

wavenumbers a 1 * 2401 Matrix of intensity values (a.u.)

marginalMetropolisUpdate

Update all of the parameters using a single Metropolis-Hastings step.

Description

Updates all of the parameters using a single Metropolis-Hastings step, such that the baseline cancels out in the MH ratio, using the marginalisation identity of Chib (1995). If `npart > 1`, then multiple MCMC chains will be executed independently in parallel using OpenMP. This means that all functions used for the proposal distributions and to evaluate the MH ratio need to be thread-safe. Specifically, no calls to `R::rnorm`, `R::dnorm`, nor their `Rcpp` equivalents, can be made from within the parallel portion of the code.

Usage

```
marginalMetropolisUpdate(
  spectra,
  n,
  conc,
  wavelengths,
  peakWL,
  betaMx,
  scaleMx,
  sigma,
  expMx,
  baselines,
  sd_mh,
  priors
)
```

Arguments

| | |
|-------------|--|
| spectra | $n_y * nwl$ Matrix of observed Raman spectra. |
| n | number of observations to use in calculating the likelihood |
| conc | Vector of n nanomolar (nM) dye concentrations |
| wavelengths | Vector of nwl wavenumbers at which the spectra are observed. |
| peakWL | Vector of locations for each peak (cm^{-1}) |
| betaMx | $npeaks * npart$ Matrix of regression coefficients to update. |
| scaleMx | $npeaks * npart$ Matrix of scale parameters to update. |
| sigma | Vector of npart standard deviations to update. |
| expMx | $nwl * npart$ Matrix of expectations of the Lorentzian or Gaussian function. |
| baselines | $nKnots * n_y * npart$ Array of smoothing splines. |
| sd_mh | Vector of $2 * npeaks$ bandwidths for the random walk proposals. |
| priors | List of hyperparameters for the prior distributions. |

Value

The number of RWMH proposals that were accepted.

References

- Chib (1995) "Marginal Likelihood from the Gibbs Output," JASA 90(432): 1313–1321, doi: [10.1080/01621459.1995.10476635](https://doi.org/10.1080/01621459.1995.10476635)
- Rosenthal (2000) "Parallel computing and Monte Carlo algorithms" Far East J. Theor. Stat. 4(2): 207–236, URL: <https://www.pphmj.com/abstract/1961.htm>

 methanol

Raman spectrum of methanol (CH₃OH)

Description

Raman spectrum of methanol (CH₃OH)

Usage

methanol

Format

A list containing 2 variables:

wavenumbers a numeric Vector of 331 wavenumbers (cm^{-1})

wavenumbers a $1 * 331$ Matrix of intensity values (a.u.)

| | |
|---------------|---|
| mhUpdateVoigt | <i>Update the parameters of the Voigt peaks using marginal Metropolis-Hastings.</i> |
|---------------|---|

Description

Updates all of the parameters (location, amplitude, std. dev., and scale) using a single Metropolis-Hastings step, such that the baseline cancels out in the MH ratio, using the marginalisation identity of Chib (1995). Note: if `npart > 1`, then multiple MCMC chains will be executed independently in parallel using OpenMP. This means that all functions used for the proposal distributions and to evaluate the MH ratio need to be thread-safe. Specifically, no calls to `R::rnorm`, `R::dnorm`, nor their `Rcpp` equivalents, can be made from within the parallel portion of the code.

Usage

```
mhUpdateVoigt(
  spectra,
  n,
  kappa,
  conc,
  wavenum,
  thetaMx,
  logThetaMx,
  mhChol,
  priors
)
```

Arguments

| | |
|-------------------------|---|
| <code>spectra</code> | <code>n_y * nwl</code> Matrix of observed Raman spectra. |
| <code>n</code> | number of observations to use in calculating the likelihood. |
| <code>kappa</code> | likelihood tempering parameter. |
| <code>conc</code> | Vector of <code>n_y</code> nanomolar (nM) dye concentrations |
| <code>wavenum</code> | Vector of <code>nwl</code> wavenumbers at which the spectra are observed. |
| <code>thetaMx</code> | $(4+npeaks*4) \times npart$ Matrix of parameter values for each peak. |
| <code>logThetaMx</code> | $(4+npeaks*4) \times npart$ Matrix of logarithms of the parameters. |
| <code>mhChol</code> | lower-triangular Cholesky factorisation of the covariance matrix for the random walk proposals. |
| <code>priors</code> | List of hyperparameters for the prior distributions. |

Value

The number of RWMH proposals that were accepted.

References

Chib (1995) "Marginal Likelihood from the Gibbs Output," JASA 90(432): 1313–1321, doi: [10.1080/01621459.1995.10476635](https://doi.org/10.1080/01621459.1995.10476635)

Rosenthal (2000) "Parallel computing and Monte Carlo algorithms" Far East J. Theor. Stat. 4(2): 207–236, URL: <https://www.pphmj.com/abstract/1961.htm>

mixedVoigt

Compute the spectral signature using Voigt peaks.

Description

Calculates the value of the pseudo-Voigt broadening function at the given wavenumbers, given the parameters of the peaks. This function is thread-safe.

Usage

```
mixedVoigt(location, scale_G, scale_L, amplitude, wavenum)
```

Arguments

| | |
|-----------|--|
| location | Vector of location parameters of the peaks (cm^{-1}) |
| scale_G | Vector of standard deviations σ_j of the Gaussian components. |
| scale_L | Vector of scale parameters ϕ_j of the Lorentzian components. |
| amplitude | Vector of amplitudes of the peaks (a.u.) |
| wavenum | Vector of wavenumbers at which to compute the function. |

Value

The value of the pseudo-Voigt function at the given wavenumbers.

References

Thompson, Cox & Hastings (1987) "Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al_2O_3 ," J. Appl. Crystallogr. 20(2): 79–83, DOI: doi: [10.1107/S0021889887087090](https://doi.org/10.1107/S0021889887087090)

Examples

```
Cal_V <- seq(300, 400, by=5)
loc <- c(320, 350, 375)
scG <- c(10, 5, 1)
scL <- c(3, 20, 7)
amp <- c(100, 500, 200)
mixedVoigt(loc, scG, scL, amp, Cal_V)
```

| | |
|-------------------|---|
| resampleParticles | <i>Resample in place to avoid expensive copying of data structures, using a permutation of the ancestry vector.</i> |
|-------------------|---|

Description

Resample in place to avoid expensive copying of data structures, using a permutation of the ancestry vector.

Usage

```
resampleParticles(log_weights, ampMx, scaleMx, peaks, baselines, n_y, nwl)
```

Arguments

| | |
|-------------|--|
| log_weights | logarithms of the importance weights of each particle |
| ampMx | npeaks x npart Matrix of amplitudes for each particle. |
| scaleMx | npeaks x npart Matrix of scale parameters for each particle. |
| peaks | nwl x npart Matrix containing the expectation of the Lorentzian mixture. |
| baselines | nwl x n_y x npart Array of smoothing splines. |
| n_y | number of observations |
| nwl | number of wavenumbers |

Value

Vector of indices to the parents of the resampled particles.

References

Murray, L.M., Lee, A. & Jacob, P.E. (2015) "Parallel resampling in the particle filter" [arXiv:1301.4019v3](#)

See Also

[residualResampling](#)

| | |
|--------------------|---|
| residualResampling | <i>Compute an ancestry vector for residual resampling of the SMC particles.</i> |
|--------------------|---|

Description

Compute an ancestry vector for residual resampling of the SMC particles.

Usage

```
residualResampling(log_wt)
```

Arguments

log_wt logarithms of the importance weights of each particle.

Value

Vector of indices to the particles that will be propagated forward to the next generation (i.e. the parents)

References

Liu & Chen (1998) "Sequential Monte Carlo methods for dynamic systems," JASA 93(443): 1032-1044, doi: [10.1080/01621459.1998.10473765](https://doi.org/10.1080/01621459.1998.10473765)

Douc, Cappe & Moulines (2005) "Comparison of resampling schemes for particle filtering" In Proc. 4th IEEE Int. Symp. ISPA, pp. 64-69, doi: [10.1109/ISPA.2005.195385](https://doi.org/10.1109/ISPA.2005.195385)

| | |
|--------|--|
| result | <i>SMC particles for TAMRA+DNA (T20)</i> |
|--------|--|

Description

Posterior distribution for pseudo-Voigt parameters, obtained by running 'fitVoigtPeaksSMC' on a spectrum from Gracie et al. (Anal. Chem., 2016). 1000 SMC particles with 32 peaks. For details, see the vignette.

Usage

```
result
```

Format

A list containing 15 variables:

weights normalised importance weights for each particle

location location parameters of 32 peaks

beta amplitudes of 32 peaks

scale_G scale of the Gaussian (RBF) broadening

scale_L scale of the Lorentzian (Cauchy) broadening

sigma standard deviation of the additive white noise

lambda smoothing parameter of the cubic B-splines

priors List of informative priors

ess history of the effective sample size

kappa history of the likelihood tempering

accept history of Metropolis-Hastings acceptance rates

mhSteps history of Metropolis-Hastings steps

times history of times for each SMC iteration

time computation time taken by the SMC algorithm

result2

SMC particles for methanol (CH₃OH)

Description

Posterior distribution for pseudo-Voigt parameters, obtained by running ‘fitVoigtPeaksSMC’ on a Raman spectrum of methanol with 4 peaks. For details, refer to the vignette.

Usage

result2

Format

A list containing 15 variables.

reWeightParticles *Update the importance weights of each particle.*

Description

Update the importance weights of each particle.

Usage

```
reWeightParticles(
  spectra,
  peaks,
  baselines,
  i,
  start,
  sigma,
  old_weights,
  alpha,
  idx
)
```

Arguments

| | |
|-------------|--|
| spectra | $n_y * nwl$ Matrix of observed Raman spectra. |
| peaks | $nwl * npart$ Matrix containing the spectral signatures for each observation. |
| baselines | $nwl * npart$ Matrix containing the current values of the baselines. |
| i | index of the current observation to use in calculating the likelihood |
| start | index of the next wavelength to use in calculating the likelihood, permuted by idx |
| sigma | Vector of $npart$ standard deviations for each particle. |
| old_weights | logarithms of the importance weights of each particle. |
| alpha | the target learning rate for the reduction in effective sample size (ESS). |
| idx | permutation of the indices of the wavelengths. |

Value

a List containing:

ess The effective sample size, after reweighting.

weights Vector of updated importance weights.

index index of the last wavelength used.

evidence SMC estimate of the logarithm of the model evidence.

References

- Pitt, dos Santos Silva, Giordani & Kohn (2012) "On some properties of Markov chain Monte Carlo simulation methods based on the particle filter" *J. Econometrics* 171(2): 134–151, DOI: doi: [10.1016/j.jeconom.2012.06.004](https://doi.org/10.1016/j.jeconom.2012.06.004)
- Zhou, Johansen & Aston (2015) "Towards Automatic Model Comparison: An Adaptive Sequential Monte Carlo Approach" [arXiv:1303.3123](https://arxiv.org/abs/1303.3123) [stat.ME]

serrsBayes

Bayesian modelling and quantification of Raman spectroscopy

Description

This R package implements sequential Monte Carlo (SMC) algorithms for fitting a generalised additive mixed model (GAMM) to Raman spectra. These multivariate observations are highly collinear and lend themselves to a reduced-rank representation. The GAMM separates the hyperspectral signal into three components: a sequence of Lorentzian or Gaussian peaks; a smoothly-varying baseline; and zero-mean, additive white noise. The parameters of each component of the model are estimated iteratively using SMC. The posterior distributions of the parameters given the observed spectra are represented as a population of weighted particles.

Details

Raman spectroscopy can be used to identify molecules by the characteristic scattering of light from a laser. The pattern of peaks in a Raman spectrum corresponds to the vibrational modes of the molecule. The shift in wavenumber of the photons is proportional to the change in energy state, which is reflected in the locations of the peaks. Surface-enhanced Raman scattering (SERS) is a technique that amplifies the Raman signal using metallic substrates, such as nanoparticles. The laser can also be tuned to the resonant frequency of the molecule, which is known as surface-enhanced resonance Raman scattering (SERRS). Under controlled experimental conditions, the amplitudes of the peaks are linearly related to the concentration of the molecule, from the limit of detection (LOD) up to monolayer coverage of the nanoparticle surface.

The GAMM represents the peaks and baseline as continuous functions. The background fluorescence is modelled using a penalised cubic spline, while the peaks are an additive mixture of squared exponential (Gaussian) or Lorentzian (Cauchy) kernels:

$$Y = \sum_{m=1}^M \alpha_{i,m} B_m(\nu_j) + \sum_{p=1}^P s(\nu_j | l_p, A_p, \phi_p) + \epsilon_{i,j}$$

where Y is a matrix of hyperspectral observations $y_{i,j}$ that have been discretised at wavenumbers ν_j ; B_m are the M spline basis functions with coefficients $\alpha_{i,m}$; $s(\nu_j | l_p, A_p, \phi_p)$ are the radial basis functions for each peak, with location l_p , amplitude A_p , and scale ϕ_p parameters. $\epsilon_{i,j}$ is assumed to be zero mean, additive white noise with constant variance σ^2 .

This model-based approach accounts for differences in resolution and experimental conditions, enabling comparison and alignment of heterogeneous spectra. The relationship between concentration and peak intensity can be quantified by fitting a Bayesian functional regression:

$$A_p = c_i \beta_p$$

where c_i is the nanomolar (nM) concentration of the molecule in the i th spectrum, $c_{LOD} < c_i \leq c_{MLC}$. The regression model produces highest posterior density (HPD) intervals for the limit of detection of each peak. A consistent, unbiased estimate of the model evidence (also known as the marginal likelihood) is also computed. This can be used to evaluate whether Gaussian or Lorentzian peaks are a better fit to the data.

Author(s)

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References

Moores, Gracie, Carson, Faulds, Graham & Girolami "Bayesian modelling and quantification of Raman spectroscopy," [arXiv preprint](#)

Examples

```
# simulate some data with known parameter values
wavenumbers <- seq(700,1400,by=2)
spectra <- matrix(nrow=1, ncol=length(wavenumbers))
peakLocations <- c(840, 960, 1140, 1220, 1290)
peakAmplitude <- c(11500, 2500, 4000, 3000, 2500)
peakScale <- c(10, 15, 20, 10, 12)
signature <- weightedLorentzian(peakLocations, peakScale, peakAmplitude, wavenumbers)
baseline <- 1000*cos(wavenumbers/200) + 2*wavenumbers
spectra[1,] <- signature + baseline + rnorm(length(wavenumbers),0,200)
plot(wavenumbers, spectra[1,], type='l', xlab="Raman offset", ylab="intensity")
lines(wavenumbers, baseline, col=2, lty=4)
lines(wavenumbers, baseline + signature, col=4, lty=2)

# fit the model using SMC
lPriors <- list(scale.mu=log(11.6) - (0.4^2)/2, scale.sd=0.4, bl.smooth=10^11, bl.knots=50,
               beta.mu=5000, beta.sd=5000, noise.sd=200, noise.nu=4)

## Not run:
## takes approx. 1 minute for 100 SMC iterations with 10,000 particles
result <- fitSpectraSMC(wavenumbers, spectra, peakLocations, lPriors)
plot.ts(result$ess, xlab="SMC iterations", ylab="ESS")

# sample 200 particles from the posterior distribution
samp.idx <- sample.int(length(result$weights), 200, prob=result$weights)
plot(wavenumbers, spectra[1,], type='l', xlab="Raman offset", ylab="intensity")
for (pt in samp.idx) {
  bl.est <- result$basis %*% result$alpha[,1,pt]
  lines(wavenumbers, bl.est, col="#C300009")
  lines(wavenumbers, bl.est + result$expFn[pt,], col="#0000C309")
}

## End(Not run)
```

| | |
|---------|---|
| sumDexp | <i>Sum log-likelihoods of i.i.d. exponential.</i> |
|---------|---|

Description

This is an internal function that is only exposed on the public API for unit testing purposes.

Usage

```
sumDexp(x, rate)
```

Arguments

| | |
|------|---|
| x | Vector of i.i.d. exponential random variables |
| rate | parameter of the exponential distribution |

Details

The sum of the log-likelihoods (log of the product of the likelihoods) for independent, identically-distributed, exponential random variables. Note: this Rcpp function is thread-safe, unlike the equivalent alternatives.

Value

log-likelihood of x

See Also

```
sum(dexp(x, rate, log=TRUE))
```

| | |
|-------------|---|
| sumDlogNorm | <i>Sum log-likelihoods of i.i.d. lognormal.</i> |
|-------------|---|

Description

This is an internal function that is only exposed on the public API for unit testing purposes.

Usage

```
sumDlogNorm(x, meanlog, sdlog)
```

Arguments

| | |
|---------|---|
| x | Vector of i.i.d. lognormal random variables |
| meanlog | mean of the distribution on the log scale |
| sdlog | standard deviation on the log scale |

Details

The sum of the log-likelihoods (log of the product of the likelihoods) for independent, identically-distributed, lognormal random variables. Note: this Rcpp function is thread-safe, unlike the equivalent alternatives.

Value

log-likelihood of x

See Also

`sum(dlnorm(x, meanlog, sdlog, log=TRUE))`

Examples

```
x <- rlnorm(100)
sumDlogNorm(x, 0, 1)
```

sumDnorm

Sum log-likelihoods of Gaussian.

Description

This is an internal function that is only exposed on the public API for unit testing purposes.

Usage

```
sumDnorm(x, mean, sd)
```

Arguments

| | |
|------|--|
| x | Vector of i.i.d. Gaussian random variables |
| mean | Vector of means |
| sd | Vector of standard deviations |

Details

The sum of the log-likelihoods (log of the product of the likelihoods) for independent, identically-distributed, Gaussian random variables. Note: this Rcpp function is thread-safe, unlike the equivalent alternatives.

Value

log-likelihood of x

See Also

`sum(dnorm(x, mean, sd, log=TRUE))`

Examples

```
x <- rnorm(100)
mu <- rep(0,length(x))
sd <- rep(1,length(x))
sumDnorm(x,mu,sd)
```

| | |
|------------------|---|
| weightedGaussian | <i>Compute the spectral signature using Gaussian peaks.</i> |
|------------------|---|

Description

Calculates the value of the squared exponential radial basis function at the given wavelengths, given the parameters of the peaks. This function is thread-safe.

Usage

```
weightedGaussian(location, scale, amplitude, wavelengths)
```

Arguments

| | |
|-------------|---|
| location | Vector of location parameters of the peaks (mean). |
| scale | Vector of scale parameters of the peaks (standard deviation). |
| amplitude | Vector of amplitudes of the peaks. |
| wavelengths | Vector of wavenumbers at which to compute the function. |

Value

The value of the Gaussian function at the given wavelengths.

Examples

```
Cal_V <- seq(300,400,by=5)
loc <- c(320,350,375)
sca <- c(10,5,18)
amp <- c(1000,5000,2000)
weightedGaussian(loc,sca,amp,Cal_V)
```

weightedLorentzian *Compute the spectral signature using Lorentzian peaks.*

Description

Calculates the value of the Lorentzian function at the given wavelengths, given the parameters of the peaks. This function is thread-safe.

Usage

```
weightedLorentzian(location, scale, amplitude, wavelengths)
```

Arguments

| | |
|-------------|---|
| location | Vector of location parameters of the peaks. |
| scale | Vector of scale parameters of the peaks. |
| amplitude | Vector of amplitudes of the peaks. |
| wavelengths | Vector of wavenumbers at which to compute the function. |

Value

The value of the Lorentian function at the given wavelengths.

Examples

```
Cal_V <- seq(300,400,by=5)
loc <- c(320,350,375)
sca <- c(10,5,18)
amp <- c(1000,5000,2000)
weightedLorentzian(loc,sca,amp,Cal_V)
```

weightedMean *Compute the weighted arithmetic means of the particles.*

Description

This SMC estimate of the means can be used to centre independent Metropolis-Hastings proposals.

Usage

```
weightedMean(particles, log_weights)
```

Arguments

| | |
|-------------|--|
| particles | npeaks * npart Matrix of parameter values for each particle. |
| log_weights | logarithms of the importance weights of each particle. |

Value

A vector of means, one for each row.

See Also

[weighted.mean](#)

| | |
|------------------|--|
| weightedVariance | <i>Compute the weighted variance of the particles.</i> |
|------------------|--|

Description

This SMC estimate of the variance can be used to scale the bandwidth of adaptive, Gaussian random walk Metropolis-Hastings proposals.

Usage

```
weightedVariance(particles, log_weights, mean)
```

Arguments

| | |
|-------------|--|
| particles | npeaks * npart Matrix of parameter values for each particle. |
| log_weights | logarithms of the importance weights of each particle. |
| mean | Vector of weighted means of each particle. |

Value

A vector of variances, one for each row.

See Also

[wtd.var](#)

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