Residual attractive force between superparamagnetic nanoparticles

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Abstract

A superparamagnetic nanoparticle (SPN) is a nanometre-sized piece of a material that would, in bulk, be a permanent magnet. In the SPN the individual atomic spins are aligned via Pauli effects into a single giant moment that has easy orientations set by shape or magnetocrystalline anisotropy. Above a size-dependent blocking temperature $T_b(V, \tau_{obs})$, thermal fluctuations destroy the average moment by flipping the giant spin between easy orientations at a rate that is rapid on the scale of the observation time $\tau_{obs}$. We show that, despite the vanishing of the average moment, two SPNs experience a net attractive force of magnetic origin, analogous to the van der Waals force between molecules that lack a permanent electric dipole. This could be relevant for ferrofluids, for the clumping of SPNs used for drug delivery, and for ultra-dense magnetic recording media.

1 Introduction

In many areas of physics, forces are effectively suppressed in the interaction between separated fragments of matter, because of the neutrality of each fragment with respect to the appropriate charge quantity. Nevertheless "residual" forces still occur between these fragments, typically with a decay (as a function of the spatial separation $D$ between the fragments) that is different from that of the "bare" interaction.
For example, ordinary matter consisting of atoms and molecules is typically neutral with respect to electrical charge, but two well-separated charge-neutral fragments always experience at least the van der Waals or dispersion interaction. This is a residual force that arises because the zero-point motions of the electrons on the two fragments are correlated via the Coulomb interaction, leading to a non-zero time-averaged force of Coulombic origin, despite overall charge neutrality of each fragment. For neutral molecules distant $D$, this leads to an interaction energy varying as $-D^{-6}$. This is to be compared with the bare Coulomb interaction proportional to $Q_1 Q_2 D^{-1}$ that acts between between fragments with nonzero electric charges $Q_1$, $Q_2$. ($D^{-6}$ is replaced by $D^{-7}$ when $D$ is large enough that retardation of the electromagnetic interaction needs to be considered [1, 2]).

Similarly the nuclear force between two nucleons has sometimes been regarded as a residual color interaction between color-neutral objects.

Here we propose a similar residual force, of magnetic dipolar origin, acting between two "superparamagnetic nanoparticles (SPNs)". By this we mean that each nanometre-sized particle is composed of a material that is ferromagnetic in its bulk state [3, 4]. Typically at the temperatures of interest, the elementary electron spins inside an individual nanoparticle remain locked together by the microscopic exchange interaction, yielding effectively a single giant spin with a magnetic dipole moment $d_0$. If the directions of the giant moments remain steady over time, two such nanoparticles experience a conventional magnetic dipole-dipole energy proportional to $d_0^{(1)} d_0^{(2)} f(\theta_1, \phi_1; \theta_2, \phi_2)/R^3$. Here $R$ is the spatial separation of the nanoparticles, and $f$ is a dimensionless function of the angles between each fixed moment and the vector $\vec{R}$ joining the spatial locations of the nanoparticles. However each particle has one or more "easy axes" in directions determined by magnetocrystalline or, more typically, shape anisotropy. The latter effect arises in the strong angular dependence of the magnetostatic self-energy of a non-spherical magnetised particle. We will consider the simplest case, in which the particle is sufficiently elongated that it has a single easy axis, i.e. dominant uniaxial shape anisotropy. Then the energy of a single nanoparticle is lowest when its giant spin (dipole moment, $\vec{d}$) lies parallel or antiparallel to this easy axis. Because the energy barrier $E_0$ for rotation of $\vec{d}$ between easy orientations (not mechanical rotation of the particle) derives from the magnetic self-energy of the nanoparticle, it decreases with decreasing volume of the nanoparticle. For very small particles, therefore, the projection of $\vec{d}$ on
a measurement axis averages to zero over time, because of repeated thermal flipping of the giant spin \([3]\), caused by thermal agitation from the heat bath (e.g. a fluid or solid matrix) that surrounds the nanoparticle. Thus on time average the nanoparticle is "neutral" i.e. it has a zero magnetic moment.

When the thermal agitation of the giant spin is insufficient to flip it between easy orientations within the observation time, \(\tau_{\text{obs}}\), the nanoparticle is "blocked", i.e. apparently frozen as to its magnetism. This occurs below the blocking temperature of this nanoparticle, \(T_b\), which depends on \(E_0\) and therefore on the volume \(V\) of the nanoparticle. If the relaxation time of \(\vec{d}\) over the barrier \(E_0\) is \(\tau\), then \(T_b\) is defined by \(\tau(T_b) = \tau_{\text{obs}}\). Blocking is thus a purely dynamic phenomenon: extending the observation time, or lowering the frequency, lowers \(T_b\) and vice-versa \([3]\). For the present case of SPNs suspended in a fluid, the observation time \(\tau_{\text{obs}}\) will be a relevant time for mechanical motion of the SPN through the fluid. - e.g. a rotational or translational diffusion time. Note that the direct dipolar magnetic interaction between SPNs could in principle lead them to clump. However when \(T > T_b\) the motion of the SPNs through the fluid will not "see" the bare dipolar magnetic interaction between the SPNs, as it has been averaged away between attractive and repulsive values during the thermal flipping of the spins. It could lead to additional Brownian type of damping and diffusion of course, but we show here that there is also a net attractive force between SPNs even above the blocking temperature.

The destruction of the permanent magnetic moments by thermal fluctuations is highly undesirable in the case of a magnetic data recording medium, where very fine magnetic particles in the nanometer size range will be needed in order to pack the magnetically stored data as densely as possible for the next generation of devices. The thermal destruction of the permanent moments means that data cannot be stored over long times.

On the other hand, as will be discussed below, the same thermal flipping occuring for \(T > T_b\) is beneficial in the case of nanoparticles deliberately suspended in human blood as carriers for drug or thermal therapies, since now the clumping of the nanoparticles from magnetic dipole interaction is suppressed because each particle has effectively a zero magnetic moment. The strong clumping that would occur for fully ferromagnetic particles from their \(R^{-3}\) dipole-dipole interactions could be clinically dangerous, potentially causing blockage of blood vessels, difficulty of elimination etc. We will show below, however, that despite the vanishing of the average individual moments, there is a residual attractive interaction between two superparam-
agnetic nanoparticles separated by distance \( R \), that falls off as \((\text{const})/R^6\). It is the magnetic analog of the van der Waals or dispersion force that arises via the Coulomb interaction between fluctuating electric dipoles on two electrically neutral molecules \([5]\) lacking permanent dipole moments. This residual force could also lead to clumping of the nanoparticles, and so its analysis could be significant in modern magnetic-particle therapies \([4]\).

2 Simple preliminary model

The model described here is based on an argument frequently used to explain the attractive van der Waals energy proportional to \(-R^{-6}\) that arises between temporary electric dipoles occurring on a pair of electronically neutral atoms separated by distance \( R \) (see e.g. \([5]\)). It is not rigorous derivation, but may help to elucidate the more careful and general mathematical treatment to be provided in later Sections. Consider two superparamagnetic nanoparticles SPN1 and SPN2 as defined above. While averaging to zero over time as described above, the magnetic moment \( \vec{d}^{(1)} \) on SPN1 can exhibit a short-lived thermal (or quantal) fluctuation so that its value \( \vec{d}^{(1)}(t) \) is nonzero at some particular time \( t \). For simplicity we will assume that only magnetizations of SPN1 and SPN2 along one axis (say \( \hat{z} \)) are possible so that \( \vec{d}^{(1)}(t) = d^{(1)}(t)\hat{z} \), and we will consider the case that the spatial separation \( \vec{R} \) between SPN1 and SPN2 is parallel to \( \hat{x} \). Then the spontaneous moment \( \vec{d}_1(t) \) produces a dipolar magnetic induction (B-field)

\[
\vec{b}^{(2)}(t) = -\frac{\mu_0}{4\pi} R^{-3} d^{(1)}(t)\hat{z}
\]

at the position of SPN2. Responding to this field, SPN2 produces its own magnetic moment

\[
d^{(2)}(t) = \chi^{(2)}\vec{b}^{(2)}(t) = -\chi^{(2)}\frac{\mu_0}{4\pi} R^{-3} d^{(1)}(t)\hat{z}
\]

where \( \chi^{(2)} \) is the dynamic magnetic susceptibility of SPN2, assumed for now to represent an instantaneous response to the field. (Note that here \( \chi \) represents the response of the total magnetic moment of the SPN to a small applied magnetic induction \( \vec{b} \). By contrast, the symbol \( \chi \) is normally used for the response of the magnetic moment \emph{per unit volume} to a small applied magnetic field \( \vec{h} \). Thus for a single SPN of volume \( V \),

\[
d = \chi b; \quad \frac{d}{V} = \chi h; \quad \chi = \frac{\mu_0 \chi}{V}
\]
The dipole (1) in turn produces a dipolar magnetic induction back at the position of SPN1:

\[
\vec{b}^{(1)}(t) = -\frac{\mu_0}{4\pi} \frac{1}{R^3} \vec{d}^{(2)}(t) \hat{z} = \left(-\frac{\mu_0}{4\pi} R^{-3}\right) \left(-\chi^{(2)} \frac{\mu_0}{4\pi} R^{-3} d^{(1)}(t) \right) \hat{z} \\
= \left(\frac{\mu_0}{4\pi}\right)^2 R^{-6} \chi^{(2)} d^{(1)}(t) \hat{z}.
\]

The interaction energy of this back-field with the original moment \(d^{(1)}(t)\) is

\[
E = -\vec{b}^{(1)}(t) \cdot \vec{d}^{(1)}(t)
\]

and this energy has a time or thermal ensemble average

\[
\langle E \rangle = -\left(\frac{\mu_0}{4\pi}\right)^2 R^{-6} \chi^2 \langle (d^{(1)}(t))^2 \rangle
\]

which is non-zero because \(\langle (d^{(1)}(t))^2 \rangle \neq 0\) even though \(\langle d^{(1)}(t) \rangle = 0\).

This negative energy produces, upon differentiation with respect to \(R\), a net time-averaged attractive force between SPN1 and SPN2 that falls off as \(R^{-7}\).

The above simplified theory produces the basic physics and the \(R^{-7}\) force, but it glosses over a number of issues, such as the role of entropic effects at finite temperature, the tensor nature of the magnetic dipole-dipole interaction, the quantal aspects of the problem, and the retardation of the electromagnetic field. Also, the response \(\chi^2\) has been assumed to be instantaneous, whereas there can be a strong and important frequency dependence (time-delayed aspect) to the linear response of a SPN. All of these considerations are treated in detail in the theory given the next Section.

3 Detailed theory

The magnetic dipolar energy (hamiltonian) between two particles with magnetic dipoles \(\vec{d}^{(1)}\) and \(\vec{d}^{(2)}\), separated in space by a nonzero vector \(\vec{R} = \vec{R}_1 - \vec{R}_2\), is of form

\[
H^{(12)} = -R^{-3} \sum_{ij=1}^{3} d^{(1)}_i T_{ij}(\vec{R}) d^{(2)}_j
\]

where

\[
T_{ij} = \frac{\mu_0}{4\pi} \frac{3 R_i R_j - \delta_{ij} R^2}{R^2}.
\]
We assume that we are above the blocking temperature, $T > T_b$, i.e. that the temperature is high enough (compared with the anisotropy energy barrier), that each isolated giant magnetic dipole has zero thermal expectation taken over the time-scale of interest

$$< d^{(1)}_0 > = 0 = < d^{(2)}_0 > .$$

The theory to be developed here is meaningful provided that the thermal fluctuations of the moment occur on a time-scale $\tau$ that is short compared to the time $\tau_{obs} \equiv T_{mech}$ for the nanoparticle to change its spatial position (or physical angular orientation) appreciably, within its fluid medium. Under these conditions we will derive a residual attractive force between the two superparamagnetic nanoparticles, that could for example be used to study residual clumping effects in fluid suspension at temperatures above the blocking temperature.

The quantum-thermal expectation, denoted $< >$, of the interaction energy between the giant spins is

$$E^{(12)} \equiv < H^{(12)} > = -R^{-3} \sum_{ij=1}^{3} T_{ij}(\hat{R}) < d^{(1)}_i d^{(2)}_j >$$

However at finite temperature it is not this energy but the corresponding thermal Helmholtz free energy

$$A = < H^{(12)} > - T S$$

that must be considered, where $S$ is the entropy. We achieve an expression for $A$ via a Feynman-theorem argument in Appendix A for a classical treatment of the fluctuations, and in Appendix B for the fully quantal case. In either case the result is

$$A(\lambda = 1, T, R) - A(\lambda = 0, T, R) = \int_0^1 E^{(12)}_\lambda d\lambda$$

Here the subscript $\lambda$ means that the quantity is evaluated in the thermal ensemble with modified interaction

$$H^{(12)}_\lambda = \lambda H^{(12)} = -\lambda R^{-3} \sum_{ij=1}^{3} d^{(1)}_i T_{ij}(\hat{R}) d^{(2)}_j , \quad 0 \leq \lambda \leq 1$$

$$E^{(12)}_\lambda = < H^{(12)}_\lambda > .$$
Since the coupling will be zero (equivalent to $\lambda = 0$) at infinite separation $R \rightarrow \infty$, we can write Eq (4) as an expression for just the free energy of interaction between the two nanoparticles:

$$A(T, R) - A(T, R \rightarrow \infty) = \int_0^1 E^{(12)}_{\lambda} \frac{d\lambda}{\lambda}$$

$$= -R^{-3} \sum_{ij=1}^3 T_{ij}(\hat{R}) \int <d_i^{(1)} d_j^{(2)} >_\lambda d\lambda \quad (7)$$

The problem now reduces to the calculation of the equal-time cross-correlation function $<d_i^{(1)} d_j^{(2)} >_\lambda$ between the moments in a thermal ensemble with $\lambda$-reduced interaction.

The equal-time correlation function $<d_i^{(1)} d_j^{(2)} >_\lambda$ can be recovered from the time Fourier transform

$$g_\lambda(\omega) = \int_{-\infty}^{\infty} G_\lambda(t) \exp(-i\omega t) dt = \int_{-\infty}^{\infty} <d_i^{(1)}(0)d_j^{(2)}(t) >_\lambda \exp(-i\omega t) dt$$

of the time-displaced correlation function $G_\lambda$,

$$G_\lambda(t) \equiv <d_i^{(1)}(0)d_j^{(2)}(t) >_\lambda .$$

We can use the finite-temperature fluctuation-dissipation theorem (see e.g. [6]) to relate the fluctuation quantity $<d_i^{(1)} d_j^{(2)}>$ to the dipole-dipole response function $\bar{\chi}_{ij}^{(12)}$ of the combined interacting system, defined in Eq (10) below:

$$<d_i^{(1)} d_j^{(2)} >_{\lambda, \omega} + <d_j^{(2)} d_i^{(1)} >_{\lambda, \omega} = \frac{2\hbar}{1 - \exp(\beta \hbar \omega)} Im \left\{ \bar{\chi}_{ij,\lambda}^{(12)}(\omega + i0) + \bar{\chi}_{ji,\lambda}^{(21)}(\omega + i0) \right\}$$

where $\beta = \frac{1}{k_B T}$. Then

$$<d_i^{(1)} d_j^{(2)} >_{\lambda, equal time} = \frac{1}{2\pi} \int_{-\infty}^{\infty} g_\lambda(\omega) \exp(i\omega t)$$

$$= \int_{-\infty}^{\infty} \frac{\hbar}{\pi(1 - \exp(\beta \hbar \omega))} Im \left\{ \bar{\chi}_{ij,\lambda}^{(12)}(\omega + i0) + \bar{\chi}_{ji,\lambda}^{(21)}(\omega + i0) \right\} d\omega$$

This can also be expressed as a Matsubara sum by closing upwards in the complex $\omega$ plane, using Cauchy’s theorem to obtain a sum of residues at the poles $\omega_n = i\pi(2n)/(\beta \hbar)$, but we will not make explicit use of this here.
The interaction energy $E$ and Helmholtz free energy $A$ then become

$$E^{(12)}_{\lambda} = -\lambda R^{-3} \sum_{ij=1}^3 T_{ij}(\hat{R}) \int_{-\infty}^{\infty} \frac{\hbar}{\pi(1 - \exp(\beta \hbar \omega))} \text{Im} \left\{ \chi^{(12)}_{ij,\lambda}(\omega + i0) \right\} d\omega \quad (8)$$

$$A(R) - A(\infty) = \int_0^1 E^{(12)}_{\lambda} \frac{d\lambda}{\lambda} \quad (9)$$

We assume we know the dipole responses $\chi^{(1)}_{ij,\lambda}(\omega)$, $\chi^{(2)}_{ij,\lambda}(\omega)$ of each isolated giant dipole SPN1, SPN2 to an external B field $\vec{b}$ such that

$$d^{(1)}_i(\omega) \exp(-i\omega t) = \sum_j \chi^{(1)}_{ij}(\omega) b^{(1)}_j \exp(-i\omega t).$$

These individual responses must express the known superparamagnetic properties of individual systems. In general it should also describe any Brownian tumbling aspects of the response, in the case that the time scale of these tumbling motions overlaps that of the magnetic response behaviour of each SPN. For now we assume that the tumbling is slow so that only the magnetic response of a SPN oriented in a fixed spatial orientation is required to appear in $\chi$. (The interaction energy may of course depend on the details of this orientation, which will be manifested in the particular values of $\chi^{(12)}_{ij}$ in the chosen cartesian frame.) In Appendix C we discuss a simple model for the $\chi$ of a single isolated SPN. However, to calculate the interaction of two SPNs, Eq (8) requires knowledge of the cross-response function (cross-susceptibility) $\chi^{(12)}_{\lambda}$ for the interacting pair of SPNs. This is defined as the linear response of SPN1’s moment to an alternating B field that acts upon SPN2 only:

$$d^{(1)}_i(\omega) = \chi^{(12)}_{ij,\lambda}(\omega) b^{(2)}_j, \quad (10)$$

where the subscripts $i, j$ label cartesian components of the vectors. To calculate $\chi^{(12)}$ we now consider the slightly more general situation where independently-specified small external B fields $\vec{b}^{(1)} \exp(-i\omega t)$, $\vec{b}^{(2)} \exp(-i\omega t)$ are applied to the individual dipoles, in the presence of the dipolar coupling between the two systems.

In time-dependent mean-field theory (RPA), the equations of motion of the coupled systems are (all at arbitrary frequency $\omega$ and with Einstein summation convention for repeated indices):

$$d^{(1)}_\alpha = \chi^{(1)}_{\alpha \mu}(b^{(1)}_\mu + \lambda R^{-3} T_{\mu \beta} d^{(2)}_\beta) \quad (11)$$

$$d^{(2)}_\beta = \chi^{(2)}_{\beta \epsilon}(b^{(2)}_\epsilon + \lambda R^{-3} T_{\gamma \beta} d^{(1)}_\gamma) \quad (12)$$
These equations describe the evolution of each giant spin in an effective B field containing a time-dependent contribution due to the polarizaton of the other giant spin. Using \((\ref{12})\) to eliminate \(d_\beta^{(2)}\) in \((\ref{11})\), we get

\[
d_\alpha^{(1)} = \bar{\chi}_{\alpha\mu}^{(1)} (b_\mu^{(1)} + \lambda R^{-3} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} (b_\epsilon^{(2)} + \lambda R^{-3} T_{\epsilon\gamma} d_\gamma^{(1)}))
\]

\[
(\delta_{\alpha\gamma} - \lambda^2 \bar{\chi}_{\alpha\mu} R^{-3} T_{\mu\beta} \bar{\chi}_{\beta\epsilon} R^{-3} T_{\epsilon\gamma} d_\gamma^{(1)}) d_\gamma^{(1)} = \bar{\chi}_{\alpha\mu}^{(1)} b_\mu^{(1)} + \lambda \bar{\chi}_{\alpha\mu} R^{-3} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} h_\epsilon^{(2)}
\]

Then for \(b_\mu^{(1)} = 0\) (i.e. an external oscillating B field applied only to moment SPN2) we have

\[
d_\alpha^{(1)} = \chi_{\alpha\epsilon,\lambda}^{(12)} h_\epsilon^{(2)}
\]

where

\[
\chi_{\alpha\epsilon,\lambda}^{(12)} = (\varepsilon_{\lambda}^{-1})_{a\beta,\lambda} S_{\beta\epsilon}^{(12)}
\]

\[
S_{\beta\epsilon}^{(12)} = \chi_{\beta\mu}^{(1)} \lambda R^{-3} T_{\mu\nu} \bar{\chi}_{\nu\epsilon}^{(2)}
\]

\[
\varepsilon_{\lambda} = \begin{pmatrix}
1 - \lambda^2 R^{-6} \bar{\chi}_{1\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & -\lambda^2 R^{-6} \bar{\chi}_{1\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & -\lambda^2 R^{-6} \bar{\chi}_{1\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} \\
-\lambda^2 R^{-6} \bar{\chi}_{2\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & 1 - \lambda^2 R^{-6} \bar{\chi}_{2\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & -\lambda^2 R^{-6} \bar{\chi}_{2\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} \\
-\lambda^2 R^{-6} \bar{\chi}_{3\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & -\lambda^2 R^{-6} \bar{\chi}_{3\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma} & 1 - \lambda^2 R^{-6} \bar{\chi}_{3\epsilon}^{(1)} T_{\mu\beta} \bar{\chi}_{\beta\epsilon}^{(2)} T_{\epsilon\gamma}
\end{pmatrix}
\]

This becomes simpler if we have strictly uniaxial responses of the individual spins along (say) the x axis, i.e.

\[
\bar{\chi}_{\beta\mu}^{(1)} = \delta_{\beta1} \delta_{\mu1} \bar{\chi}^{(1)}
\]

and similarly for \(\bar{\chi}^{(2)}\). Then we can ignore the 2 and 3 components \(d_2^{(1)}, d_3^{(1)}\) and only need solve a scalar equation, giving

\[
\bar{\chi}^{(12)}_{\lambda} = \frac{\lambda \bar{\chi}^{(1)} R^{-3} T_{11} \bar{\chi}^{(2)}}{1 - \lambda^2 R^{-6} \bar{\chi}^{(1)} T_{11} \bar{\chi}^{(2)} T_{11}}
\]

and then from \((\ref{5})\)

\[
E_{\lambda}^{(12)} = -\lambda^2 R^{-6} T_{11}^2 \int_{-\infty}^{\infty} \frac{\hbar}{\pi (e^{(\beta h\omega)} - 1)} Im \frac{\bar{\chi}^{(1)} \bar{\chi}^{(2)}}{1 - \lambda^2 R^{-6} \bar{\chi}^{(1)} T_{11} \bar{\chi}^{(2)} T_{11}} d\omega
\]

From \((\ref{2})\), the corresponding free energy of the residual interaction is
\[ A(R) - A(\infty) = \int_{0}^{1} E^{(12)}(\lambda) \frac{d\lambda}{\lambda} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta\hbar\omega) - 1)} \text{Im} \left\{ \ln(1 - R^{-6} \tilde{\chi}^{(1)}(1) \tilde{\chi}^{(2)}(2) T_{11}^{2}) \right\} d\omega \]  

(15)

The corresponding force between SPN1 and SPN2 is

\[ F_{\mu} = -\frac{\partial A(\vec{R})}{\partial R_{\mu}} \]  

(16)

Eq (15) is valid for the uniaxial case but is readily generalized: there is in general a sum of logarithms of the eigenvalues of the matrix \( 1 - R^{-6} \tilde{\chi}^{(1)}(1) \tilde{\chi}^{(2)}(2) \).

Note that both \( \tilde{\chi}^{(1)} \) and \( \tilde{\chi}^{(2)} \) in (14, 15) are frequency-dependent. If the denominator of (14) vanishes for some frequency \( \omega_{0} \), then we have a finite oscillation of the magnetic moments for zero driving field - i.e. a free magnon collective oscillation mode of the coupled giant spins. Indeed the free energy (15) can be related to a sum of the thermal free energies of these magnons. Actually for the present model, namely \( \tilde{\chi}(\omega) = \tilde{\chi}_{0}/(1 - i\omega\tau) \) (see Appendix C) these frequencies will have a large imaginary part (damping), so there are really no magnons in the absence of an applied DC magnetic field. The exception is the case \( \omega \approx 0 \), where the damping vanishes. If one of the magnon frequencies vanishes, \( \omega_{0j} = 0 \), then we have an instability and the system will try to “freeze in” the magnon. This means that the denominator in (14) vanishes for zero frequency, which, as the coupling is increased, will happen first for \( \lambda = 1 \), i.e.

\[ 1 - R^{-6} \tilde{\chi}^{(1)}(0) \tilde{\chi}^{(2)}(0) T_{11}^{2} = 0. \]  

(17)

In time-dependent mean-field theories such as this, this behaviour is usually taken to indicate a transition to a broken-symmetry state - in this case the moments presumably freeze into a permanent ordering in the antiparallel configuration.

4 Energy in second order (weak coupling)

Note that if we only want the energy to second order in the interaction then from (8) we only need \( \tilde{\chi}^{(12)} \) to first order in \( T_{ij} \), so we can take \( \varepsilon_{\lambda} = I \) in
\[ \tilde{\chi}^{(12)}_{\alpha\epsilon\lambda} \approx \lambda \tilde{\chi}^{(1)}_{\beta\mu} R^{-3} T_{\mu\nu} \tilde{\chi}^{(2)}_{\nu\epsilon} . \]  

(18)

so that (8) becomes, since \( \int_0^1 \lambda^2 \frac{d\lambda}{\lambda} = \frac{1}{2} \),

\[ A^{\text{residual}} = A(R) - A(\infty) = \int_0^1 E^{(12)}_\lambda \lambda \frac{d\lambda}{\lambda} \]  

(19)

\[ = -\frac{1}{2} R^{-6} \sum_{i,j,\mu,\nu=1}^3 T_{ij} (\hat{R}) I_{ij\mu\nu} , \text{ where} \]

(20)

\[ I_{ij\mu\nu} = \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta \hbar \omega) - 1)} \text{Im} \left[ \tilde{\chi}^{(1)}_{i\mu} (\omega + i0) T_{\mu\nu} (\hat{R}) \tilde{\chi}^{(2)}_{\nu j} (\omega + i0) \right] d\omega . \]  

(21)

The \( R^{-6} \) dependence is apparent. In the case of uniaxial response

\[ A^{\text{residual}} = -\frac{1}{2} R^{-6} T_{11} (\hat{R}) T_{11} (\hat{R}) I , \text{ where} \]

(22)

\[ I = \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta \hbar \omega) - 1)} \text{Im} \left[ \tilde{\chi}^{(1)} (\omega + i0) T_{11} (\hat{R}) \tilde{\chi}^{(2)} (\omega + i0) \right] d\omega . \]  

(23)

From Appendix C, a simple model for a superparamagnetic susceptibility is \( \tilde{\chi}(\omega) = \tilde{\chi}_0 / (1 - i \omega \tau) \), and the frequency integral \( I \) in (22) can be estimated analytically in two limits depending on the thermal flipping time \( \tau \) of the giant spins (see Eqs (36) and (35) of Appendix C). This gives a residual free energy

\[ A^{\text{residual}} = -\frac{1}{2} R^{-6} T_{11}^2 \tilde{\chi}_0^2 \left\{ \begin{array}{ll} k_B T, & k_B T >> \hbar \tau^{-1} \\ \frac{1}{\pi} \frac{1}{\hbar \tau^{-1}}, & k_B T << \hbar \tau^{-1} \end{array} \right. \]  

(24)

and a residual van-der-Waals-like force

\[ F^{\text{residual}} = -\frac{\partial A^{\text{residual}}}{\partial \hat{R}} = 3 R^{-7} T_{11}^2 \tilde{\chi}_0 \left\{ \begin{array}{ll} k_B T, & k_B T >> \hbar \tau^{-1} \\ \frac{1}{\pi} \frac{1}{\hbar \tau^{-1}}, & k_B T << \hbar \tau^{-1} \end{array} \right. \]  

(25)

5 Orders of magnitude

5.1 SPNs below the blocking temperature

First consider the energy and force of interaction between two SPNs below their blocking temperature so that each has a permanent magnetic moment
of magnitude $d_0 = n\mu_B$. At separation $R$ the direct dipole-dipole energy is dependent on orientation but is of order

$$|E_{\text{direct}}| \approx \frac{\mu_0}{4\pi}d_0^2 R^{-3} = (10^{-7})(9 \times 10^{-24}n)^2(10^9)^3 \left[\frac{R}{10^{-9}}\right]^{-3}$$

$$= 8.1 \times 10^{-27} n^2 \left(\frac{10^{-9} m}{R}\right)^3 \text{ Joule} \quad (26)$$

For example if $n = 1000$ and $R = 1 \text{ nm}$, $E_{\text{direct}} \approx 10^{-20} \text{ J}$. At $T = 300K$ the thermal energy is $k_B T_{\text{room}} = 4 \times 10^{-21} \text{ J}$, so $E_{\text{direct}} \approx 2k_B T$. Thus if the two SPNs are not thermally suppressed at $T = 300K$ and are able to approach within a nanometer, they will not be prevented by thermal effects from rotating to the antiparallel configuration and binding (clumping).

The corresponding force $F_{\text{direct}}$ between the SPNs is highly orientation-dependent but is of order

$$|F_{\text{direct}}| \approx \frac{\mu_0}{4\pi} 3d_0^2 R^{-4} \approx 3 \times 8.1 \times 10^{-27}(10^{-9})^{-1}n^2 \left(\frac{10^{-9} m}{R}\right)^4 N$$

$$= 2 \times 10^{-17} n^2 \left(\frac{10^{-9} m}{R}\right)^4 N. \quad (27)$$

For $n = 1000$ and $R = 1 \text{ nm}$ this gives a force of order $20 \text{ pN}$, which is small but should be directly detectable via Atomic Force Microscopy (AFM) with single SPNs attached to substrate and tip.

### 5.1.1 SPNs above the blocking temperature

Now consider a similar system but with a blocking temperature below room temperature so that at $300K$ there are no permanent moments. Then the vdW-like theory derived above gives the free energy of interaction. For numerical estimates we assume uniaxial susceptibilities and work in the weak-coupling limit. We also assume that the giant spins have a zero-frequency susceptibility

$$\bar{\chi}_0 = \frac{(n\mu_B)^2}{k_B T} \quad (28)$$

corresponding to a giant moment of $n$ Bohr magnetons. Then (24) gives

$$A_{\text{residual}} \approx \begin{cases} 
-2 \times 10^{-7} \frac{n^4}{\tau^2} \left(\frac{10^{-9} m}{R}\right)^6 h\tau^{-1} \text{ Joule}, & h\tau^{-1} \gg k_B T \\
-2 \times 10^{-7} \frac{n^4}{\tau^2} \left(\frac{10^{-9} m}{R}\right)^6 k_B T \text{ Joule}, & h\tau^{-1} \ll k_B T 
\end{cases} \quad (29)$$
For example, let \( n = 1000, \ R = 1 \ \text{nm}, \ T = 300K, \) and \( \hbar \tau^{-1} << k_B T . \) Then \( A_{\text{residual}} \approx -2 \times 10^{-7} (1000)^4/(300)^2 k_B T = 2k_B T. \) This means that for the present case the residual energy predicted by the perturbative theory is about the same as the direct energy \([26]\), which is unphysical and simply means that the weak-coupling condition is not met and we need (at least) the full RPA theory here (Eq. \([13]\)). If we are in the limit \( \hbar \tau^{-1} >> k_B T \) the residual interaction will be even larger. In this case the system of two SPNs, despite the thermal averaging of an individual SPN, is most probably near to a transition to a spin-locked configuration. In the RPA theory the onset of this condition would correspond to a zero denominator in \([14]\). This would occur for 

\[
R_{\text{lock}}^{-6} \chi_0^{(1)} T_{11} \chi_0^{(2)} T_{11} \approx 1,
\]

i.e.

\[
R_{\text{lock}} \approx (T_{11} \chi_0)^{1/3} \approx \left( \frac{10^{-7} (n \mu_B)^2}{k_B T} \right)^{1/3} \approx 10^{-2} \left( \frac{300}{T} \right)^{1/3} (n^{2/3} \text{nm}).
\]

For the present case with \( n = 1000 \) and \( T = 300K, \) the crossover occurs at about \( R_{\text{lock}} = 1 \ \text{nm}, \) which is consistent with the above finding that the perturbative calculation of the attraction at this separation was unphysical.

To give another example, suppose that \( n = 100, \ R = 10 \text{nm}, \ T = 300K, \) and \( \hbar \tau^{-1} << k_B T . \) Then \( A_{\text{residual}} \approx -2 \times 10^{-6} (100)^4/(300)^2 (1/10)^6 k_B T = 2 \times 10^{-10} k_B T, \) whereas the direct interaction between permanent moments under the same conditions from \([26]\) is \( E_{\text{direct}} = 8.1 \times 10^{-27} 100^2 (1/10)^3 / (300(1.24 \times 10^{-23})) k_B T = 2 \times 10^{-5} k_B T. \) So for this example, neither the direct nor the residual interaction would tend to lock the SPNs into an antiferromagnetically aligned pair. The mechanical forces on the SPNs due to the spin-spin interaction in either the direct or the thermally smeared residual case would be negligible in the context of normal Brownian motion.

6 Clumping considerations in fluid suspension of SPNs

(i) Consider SPNs with \( n = 1000 \) and with a bocking temperature satisfying \( T_b > 300K . \) From the numbers shown above, at \( T = 300K, \) if they are able to approach one another within about a nanometer, these particles will form pairs or larger clusters (“clumping”) that are due to the direct (not thermally suppressed) magnetic dipolar interaction, and that are not readily broken by
thermal processes. Furthermore under these same conditions the demagnetization field inside a single SPN might be significant, so that the SPN would no longer contain a single domain as assumed so far. At larger separations $R$ the binding energy falls off as $R^{-3}$, and so the direct magnetic energy, as $R$ is increased, will soon be less than the thermal energy $k_B T$. The interaction at these larger separations will not immediately cause binding, but may well determine the kinetics of closer approach between nanoparticles, resulting ultimately in clumping when shorter separations are attained. This process is complicated by the strong orientational dependence of the direct interaction \((3)\). SPNs will tend to rotate mechanically within the fluid, in order to minimize the free energy in the "antiferromagnetic" relative orientation, after which their mutual force is attractive. Thus the kinetics of clumping will be far from straightforward.

If clumping is undesirable, the $n^2 R^{-3}$ dependence of the direct SPN-SPN magnetic binding energy suggests that smaller SPNs (e.g. $n = 100$) will be desirable because they are less susceptible to clumping, i.e. they can approach to smaller distances (e.g. $R = \sqrt{10^{-2}}$ nm = 0.2 nm) before clumping occurs. In fact, at such small separations $R$, the point dipole approximation used here may break down, softening the interaction and possibly leading to the conclusion that the binding energy even at contact is less than the thermal energy. This would imply minimal clumping.

(ii) Consider SPNs in suspension at $T = 300 K$, with $n = 1000$, but now with $T_b < 300 K$. Here, despite the thermal suppression of the net individual moments, there is a uniformly attractive residual magnetic SPN-SPN free energy $A^{\text{residual}}$. This varies as $n^4 R^{-6}$ within the perturbative approximation (see (29)), and so becomes much weaker than the direct interaction at large separations $R$. However at shorter separations, the stronger $n$ and $R$ dependence of the perturbative residual energy expression (29) suggests that $E^{\text{resid}}$ could exceed $E^{\text{direct}}$. This is of course unphysical: the correlations between the orientations of giant moments that give rise to $E^{\text{resid}}$ cannot be greater than perfect correlation, corresponding to the direct interaction in the antiferromagnetic configuration of the two giant moments. Thus in general $|E^{\text{resid}}| \leq |E^{\text{direct,max}}|$. In fact the perturbative approximation breaks down in small-$R$ regime, and the full RPA expression (15) will be needed instead of (29). We do not yet have analytic energy and force expressions in this regime. However it is clear that this approach can yield a residual interaction $|E^{\text{resid}}|$ of a strength approaching $|E^{\text{direct,max}}|$. It seems likely,
therefore, that because of the residual interaction, there will not always be
a discontinuous cessation of clumping as the temperature is raised above
the blocking temperature $T_b$. However the direct interaction can be repulsive
whereas the residual interaction is always attractive, so there is scope for
some quite rich behaviour.

7 Prospects for experimental verification of
the theory

7.1 Direct measurement of the force between two in-
dividual SPNs

In Section 5.1 above, the direct interaction between permanently magne-
tized SPNs with $n = 1000$ at separation $R = 1 \text{ nm}$ was estimated to exceed
$k_B T_{\text{room}}$, and the force was estimated as $20 \text{ pN}$. A force of this magnitude is
likely to be observable, with some care, via atomic Force Microscopy. The
simplest configuration might involve one SPN attached to a non-magnetic
substrate, and another SPN attached to the AFM tip. One could then
measure the force as a function of temperature. One might expect a reduc-
tion in the measured force as $T$ is increased above $T_b$. As discussed above, the
force could even change from repulsive to attractive, depending on the initial
orientation of the giant moments prior to heating and subsequent destruction
of the net moments. The need for a measurably large force puts us out of
the perturbative regime for the residual interaction, so more straightforward
but messy theoretical work will be required in order to predict the way in
which $F$ varies with distance and temperature near $(R, T) = (1 \text{ nm}, T_b)$. It
is not clear whether the force will be large enough for AFM detection in the
regime of larger separations where the perturbative analysis (29) is valid.

7.2 Indirect measurement via observation of structure
factors in fluid suspension

Here we propose (e.g.) small-angle xray diffraction measurements on SPNs
in suspension in a viscous fluid such as glycerine. The metallic SPNs should
provide good Xray contrast. The measured structure factor of the array of
SPNs should reveal evidence of positional correlations between the SPNs,
which in turn is related to the forces between the SPNs as predicted here. Again, one hopes to see some changes as the temperature is raised through the blocking temperature $T_b$.

### 7.3 Magnetic resonance experiments

Although the present theory did not predict any lightly damped magnons (combined oscillations of the magnetic moments) for a pair of adjacent SPNs, there might be the possibility of such modes if a strong DC magnetic field is applied. Magnetic resonance experiments might then be able to detect shifts in the single-SPN resonance frequency due to the proximity of a pair of SPNs. Even without the external DC field, an analysis of the linewidth of the zero-frequency "resonance" might reveal information about SPN-SPN coupling.

### 8 Summary and future directions

We have predicted a residual force between superparamagnetic nanoparticles that persists above the blocking temperature. The force is the magnetic analogue of the electrically-driven van der Waals interaction between electrically neutral molecules. Our theory also deals with the dynamic spin response of coupled SPNs to small ac external magnetic fields. Our results may be experimentally testable, and may have implications for ferro-fluids, for nanoparticle-based medical therapies, and for magnetic recording technology. The new force is most likely to be significant for nanoparticles that approach one another quite closely, at separations of $O$(nm). At these separations the point-magnetic-dipole approximation used here will need to be replaced by a theory that attributes a finite spatial size and definite physical shape to the nanoparticles. A good starting model will be an ellipsoidal shape, and fortunately the full electrodynamic theory of Casimir interactions is quite well developed for this geometry. A theory along these lines will be the next step.
9 Appendix A: How to deal with the entropic part (classical angle-distribution approach)

The joint state of two interacting superparamagnets is specified by a classical distribution $f^{(2)}(\Omega_1, \Omega_2)$ in the two solid angles $\Omega_1, \Omega_2$ defining spatial directions where the 2 giant spins point:

The reduced-strength interaction $\lambda E$ between the superparamagnets is given by (6). Then from general thermodynamic principles, at a given temperature $T$, coupling strength $\lambda$ and separation $R$, the correct distribution $f^{(2)}_\lambda(T, R)$ is that which minimizes the trial free energy:

$$A(\lambda, T, R) = \min_{f^{(2)}(\Omega_1, \Omega_2)} A(\lambda, T, R : [f^{(2)}])$$

so that the following functional derivative is zero

$$0 = \frac{\delta A}{\delta f^{(2)}}, \text{ where}$$

$$A(\lambda, T, R : [f^{(2)}]) = \lambda E - TS$$

$$= \lambda R^{-3} \sum_{ij=1}^{3} T_{ij}(\hat{R}) \sum_{\Omega_1, \Omega_2} d_i^{(1)}(\Omega_1) d_j^{(2)}(\Omega_2) f^{(2)}(\Omega_1, \Omega_2)$$

$$+ k_B T \sum_{\Omega_1, \Omega_2} f^{(2)}(\Omega_1, \Omega_2) \ln f^{(2)}(\Omega_1, \Omega_2)$$

Consider an infinitesimal increase in the coupling strength from $\lambda$ to $\lambda + \Delta \lambda$. As a result, $f^{(2)}$ changes by an amount $\Delta f^{(2)}$ and noting that $E = \langle H \rangle_\lambda = E_\lambda/\lambda$ we have a resulting change in $A$:

$$\Delta A = \Delta \lambda E + \sum_{\Omega_1, \Omega_2} \frac{\delta A}{\delta f^{(2)}} \Delta f^{(2)} = \Delta \lambda \frac{E_\lambda}{\lambda} + 0$$

where the zero comes from (30).

Notice that we only have to know the interaction $E$ and not the entropic part, to find the change in $A$.

Then the change in $A$ in switching on the interaction adiabatically is

$$A_{\lambda=1} - A_{\lambda=0} = \int_0^1 \Delta A = \int_0^1 E_\lambda \frac{d\lambda}{\lambda}$$

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We have already shown how to calculate $E_\lambda$ by using the fluctuation-dissipation theorem and the mean-field (RPA) assumption. Also note that the $\lambda = 0$ value of the free energy is independent of separation $R$:

$$f^{(2)}_{\lambda=0}(\Omega_1, \Omega_2) = f^{(a)}_0(\Omega_1) f^{(b)}_0(\Omega_2),$$

$$A(\lambda = 0, T, R) = k_B T \sum_{\Omega_1, \Omega_2} f^{(2)}_{\lambda=0}(\Omega_1, \Omega_2) \ln f^{(2)}_{\lambda=0}(\Omega_1, \Omega_2)$$

Thus the entire $R$ dependence of $A(\lambda = 1, R, T)$ is captured by the integral $\int_0^1 E_\lambda d\lambda$.

10 Appendix B: How to deal with the entropic part (fully quantal approach)

Our quantum mechanical basis (NOT the eigenstates) for the combined magnetic state of the two systems together consists of the factorised states

$$|ij\rangle = |i\rangle |j\rangle,$$

where the first ket refers to quantum state of SPN1 and the second ket to SPN2.

The thermal density matrix operator of a pair of magnetically interacting nanoparticles has matrix elements in this basis denoted by

$$\rho^{(2)}_{ij:kl}$$

and traces can be taken over this or any other basis with the same result.

We consider starting from the thermal equilibrium of two isolated nanoparticles, and consider the effect on the free energy of turning on the interaction by replacing the inter-nanoparticle interaction Hamiltonian $\hat{H}^{(12)}(R)$ by $\lambda \hat{H}^{(12)}(R)$, and then increasing $\lambda$ from 0 to 1 while holding the inter-particle separation $R$ fixed.

For coupling strength $\lambda$ the Helmholtz free energy is a trace:

$$A(\lambda, T, R, [\hat{\rho}^{(2)}]) = E - TS = Tr \left( \left( \hat{H}_0 + \lambda \hat{H}^{(12)}(R) \right) \hat{\rho}^{(2)} \right) - k_B Tr \left( \hat{\rho}^{(2)} \ln \hat{\rho}^{(2)} \right)$$
For fixed Hamiltonian, at thermal equilibrium $A$ is stationary with respect to arbitrary variations in density matrix that preserve $Tr\hat{\rho}^{(2)}$ (see e.g. []):

$$A(\lambda, T, R) = \min_{\rho, Tr\rho^{(2)} = 1} A(\lambda, T, R : [\rho^{(2)}])$$

so that

$$0 = \frac{\delta A}{\delta \hat{\rho}^{(2)}}. \tag{31}$$

Then the first-order change in the equilibrium free energy, when the coupling is increased from $\lambda$ to $\Delta \lambda$, is

$$\Delta A = \Delta \lambda Tr\left(\hat{H}^{(12)}(R)\hat{\rho}_\lambda\right) + \lambda Tr\left(\frac{\delta A}{\delta \hat{\rho}^{(2)}} \Delta \hat{\rho}^{(2)}\right) = \Delta \lambda \frac{E^{(12)}_\lambda}{\lambda} + 0$$

Then the change in free energy in switching on the interaction between the two systems is

$$A(\lambda = 1, T, R) - A(\lambda = 0, T, R) = \int_0^1 E^{(12)}_\lambda \frac{d\lambda}{\lambda} \tag{32}$$

The same formula can be derived for the classical case, by considering a pair distribution $f(\Omega_1, \Omega_2)$ of angular orientations $\Omega$ of the two giant moments. (See Appendix A).

11 Appendix C: simple superparamagnetic model for $\bar{\chi}_{\alpha\mu}(\omega)$

Assume that the individual giant moment has its easy axis along $\hat{e}$. Then the response to a field $\vec{h}$ is only via $\vec{h} \cdot \hat{e}$, and the response is along $\hat{e}$ i.e.

$$\vec{d} = \bar{\chi}(\omega)(\vec{h} \cdot \hat{e})\hat{e} \quad \bar{\chi}_{\alpha\mu}(\omega) = \hat{e}_\alpha \hat{e}_\mu \bar{\chi}(\omega)$$

Here we assume a widely-used model [3] for the frequency-dependent magnetic susceptibility of an individual SPN in the absence of a d.c. external magnetic field:

$$\bar{\chi}(\omega) = \frac{\bar{\chi}_0}{1 - i\omega \tau}, \quad \tau = \tau_0 \exp(E_0/(k_B T))$$
where $\tau$ is the thermal flipping time of the giant moment, assumed to arise from an intrinsic attempt time $\tau_0$ and a thermally-activated Boltzmann success rate in surmounting the anisotropy energy barrier $E_0$. Then

$$
Im \left[ \tilde{\chi}^{(1)}(\omega + i0)\tilde{\chi}^{(2)}(\omega + i0) \right] = Im \left[ \frac{\chi_0^{(1)}}{1 - i\omega\tau^{(1)}} \frac{\chi_0^{(2)}}{1 - i\omega\tau^{(2)}} \right] = 
$$

$$
= Im \left[ \frac{\chi_0^{(1)}(1 + i\omega\tau^{(1)})}{1 + \omega^2\tau^{(1)^2}} \frac{\chi_0^{(2)}(1 + i\omega\tau^{(2)})}{1 + \omega^2\tau^{(2)^2}} \right] = \frac{\chi_0^{(1)}\chi_0^{(2)}\omega(\tau^{(1)} + \tau^{(2)})}{(1 + \omega^2\tau^{(1)^2})(1 + \omega^2\tau^{(2)^2})}
$$

If the two superparamagnetic nanoparticles have the same parameters, we get

$$
Im \left[ \tilde{\chi}^{(1)}(\omega + i0)\tilde{\chi}^{(2)}(\omega + i0) \right] = \frac{2\chi_0^2\omega\tau}{(1 + \omega^2\tau^2)^2}
$$

(33)

Then the second order energy (20) between two nanoparticles with easy axes $\hat{e}^{(1)}$, $\hat{e}^{(2)}$ becomes

$$
< E^{12}_\lambda >= \lambda^2 R^{-3} \sum_{i,j=1}^{3} T_{ij}(\hat{R}) \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta\hbar\omega) - 1)}
$$

$$
\times Im \tilde{\chi}_{\mu}^{(1)}(\omega + i0)R^{-3}T_{\mu\nu}(\hat{R})\tilde{\chi}_{\nu}^{(2)}(\omega + i0)d\omega = \lambda^2 R^{-6} \sum_{i,j=1}^{3} T_{ij}(\hat{R})\tilde{e}_i^{(1)}(\omega + i0)R^{-3}T_{\mu\nu}(\hat{R})\tilde{e}_\nu(\omega + i0)d\omega
$$

$$
\times \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta\hbar\omega) - 1)}\tilde{\chi}^{(1)}(\omega + i0)\tilde{\chi}^{(2)}(\omega + i0)d\omega
$$

For two similar SPNs the frequency integral is

$$
I = \int_{-\infty}^{\infty} \frac{\hbar}{\pi(\exp(\beta\hbar\omega) - 1)} \frac{2\chi_0^2\omega\tau}{(1 + \omega^2\tau^2)^2}d\omega
$$

(34)

If $\beta\hbar/\tau << 1$ then the $Im\tilde{\chi}^2$ factor cuts the integral off for $|\omega| > \tau^{-1}$, i.e. for $\beta\hbar\omega > 1$ and we can Taylor-expand the denominator to 1st order giving

$$
I = \int_{-\infty}^{\infty} \frac{\hbar}{\pi\beta\hbar\omega(1 + \omega^2\tau^2)} 2\chi_0^2\omega\tau d\omega = k_BT\frac{2\chi_0^2}{\pi\tau} \left( \int_{-\infty}^{\infty} \frac{1}{(1 + \omega^2|\tau|^2)^2} d\omega \right)
$$

$$
= k_BT\frac{2\chi_0^2}{\pi\tau} \left( \frac{1}{2\pi|\tau|^2} \right) = \chi_0^2 k_BT
$$

(35)
On the other hand if $\beta \hbar / \tau >> 1$ then

\[ I \approx \frac{\hbar}{\pi} \int_{-\infty}^{0} \frac{-2 \chi_0^2 \omega \tau}{(1 + \omega^2 \tau^2)} d\omega = -\frac{2 \hbar \chi_0^2 \tau}{\pi} \int_{-\infty}^{0} \frac{\omega}{(1 + \omega^2 |\tau|^2)^2} d\omega \]

\[ = -\frac{2 \hbar \chi_0^2 \tau}{\pi} \left( -\frac{1}{2\tau^2} \right) = \chi_0^2 \frac{\hbar}{\pi} \tau^{-1} \]  \hspace{1cm} (36)

References

[1] J. Mahanty and B. W. Ninham, *Dispersion forces* (Academic Press, London, 1976).

[2] V. A. Parsegian, *Van der Waals Forces* (Cambridge University Press, Cambridge, 2006).

[3] W. F. Brown, Phys. Rev. 130, 1677 (1963).

[4] S. C. McBain, H. Yiu, and J. Dobson, Int. J. Nanomedicine 3, 169 (2008).

[5] J. F. Dobson et al., Int. J. Quantum Chem. 101, 579 (2005).

[6] L. D. Landau and E. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Massachusetts, 1969).