

On a Statistical Interrelation Between Boiling Point and Transition to Superconductivity¹

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Abstract

A generally accepted microscopic explanation of the phenomenon of superconductivity is based on the notion of Cooper pairs which can be viewed as a kind of configurational association of electrons. We consider a simple model for such an association enabling us to quantify the depth of a minimum of potential energy w.r.t. an appropriate semiclassical class of configurations of ions and electrons. The computation of the potential depth for a particular substance can be performed based on the boiling point data. We explore the quality of the potential depth as a regressor for predicting the temperature of the transition to superconductivity. Statistical considerations reveal a moderate correlation between regressor and transition temperature for 20 super-conducting chemical elements, which can be interpreted as a bridge between Fluid and Solid State Theories.

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1 Introduction

H. Kamerlingh discovered 1911 the super-conducting state of matter in which there is no measurable electric resistance (cf. Kopitzki (1989)). Typical for this phenomenon is the fact that the electric resistance of a substance X vanishes if an appropriate probe is cooled below a characteristic temperature $T_{\text{sup}}(X)$ which is also called transition temperature. In context of applications one is in particular interested in substances with high transition temperatures.

The qualitative understanding of the phenomenon of superconductivity is based on the microscopic notion of the so-called Cooper pairs of electrons. The prediction of the material specific transition temperature from a microscopic model remains, however, a challenging task.

In the present contribution we point out a semiclassical possibility of determination of the potential energy of a Cooper configuration and explore statistically the predictive power of the obtained depth of the potential minimum w.r.t. the transition to superconductivity.

The paper is organized as follows. In Section 2 we present a possibility of assessment of the Lennard-Jones interaction potential for molecules of substances whose boiling point is available. In Section 3 we motivate and introduce the semiclassical notion of Cooper configuration of electrons and point out a computer based method for the determination of the corresponding potential energy. In Section 4 the regression analysis of transition data for 20 super-conducting chemical elements is reported.

2 Fitting Lennard-Jones Potential to the Boiling Point

Let $T_c(X)$ and $\varrho_c(X)$ denote the critical temperature and the critical density of substance X , respectively. Motivated by the fact that critical data are

sometimes not available, the approximation

$$(2.1) \quad T_c(X) = \alpha \cdot T_B(X)$$

is proposed in Grycko (2006); $T_B(X)$ denotes the standard boiling point of substance X and $\alpha = 1.7759$ is an universal constant.

In Grycko (2005) the general formula

$$(2.2) \quad \frac{1}{5^{1/2}} \cdot \left(\frac{3}{4\pi\rho_c(X)} \right)^{1/3} \cdot \left(\frac{k_B T_c(X)}{m_r(X) N_A} \right)^{1/2} = \frac{\hbar}{2}$$

is motivated and statistically confirmed where $k_B = 1.38 \cdot 10^{-23} \text{J/K}$ and $\hbar = 1.05 \cdot 10^{-34} \text{Js}$ denote the Boltzmann and Planck constant, respectively, $N_A = 6.02 \cdot 10^{26} \text{kg}^{-1}$ is the modified Avogadro number and $m_r(X)$ denotes the relative molecular mass of substance X . Equation (2.2) interrelates critical temperature with critical density.

Combining (2.1) and (2.2) yields an approximation of critical data $T_c(X)$ and $\rho_c(X)$ for every substance X whose boiling point $T_B(X)$ and relative molecular mass $m_r(X)$ are available.

The interaction between atoms of the noble gas Ar is modelled by the Lennard-Jones interaction potential Φ_{Ar} (cf. Bergmann, Schaefer (1992))

$$(2.3) \quad \Phi_{\text{Ar}}(r) = 4U_{\text{Ar}} \cdot \left(\left(\frac{r_{\text{Ar}}}{r} \right)^{12} - \left(\frac{r_{\text{Ar}}}{r} \right)^6 \right)$$

with parameter values

$$(2.4) \quad U_{\text{Ar}} = 120.0 \text{K} \cdot k_B \quad \text{and} \quad r_{\text{Ar}} = 3.4 \cdot 10^{-10} \text{m}.$$

According to the principle of corresponding states the quantities

$$(2.5) \quad \lambda_U := \frac{U_X}{k_B T_c(X)} \quad \text{and} \quad \lambda_\rho := r_X \cdot \rho_c(X)^{1/3}$$

are universal where U_X and r_X denote the parameters of Lennard-Jones potential

$$(2.6) \quad \Phi_X(r) = 4U_X \cdot \left(\left(\frac{r_X}{r} \right)^{12} - \left(\frac{r_X}{r} \right)^6 \right)$$

describing the interaction between molecules of substance X . From the critical data for Ar and from (2.4) we obtain

$$(2.7) \quad \lambda_U = 0.7740 \quad \text{and} \quad \lambda_\varrho = 0.9459.$$

Therefore we are able to fit parameters U_X and r_X of Lennard-Jones potential Φ_X for every substance X whose boiling point $T_B(X)$ and relative molecular mass $m_r(X)$ are known.

3 The Depth of the Potential of the Cooper Configuration

Let us consider a crystallographic cell which is modelled as a cube

$$C := [-r_X/2, r_X/2]^3 \subset \mathbb{R}^3$$

where r_X denotes a parameter of the Lennard-Jones potential Φ_X modelling the interaction between molecules of substance X .

Let us suppose that two ions and two electrons are confined to cube C . The position vectors of the ions are

$$X_1(\gamma) := (-\gamma \cdot r_X/2, 0, 0) \quad \text{and} \quad X_2(\gamma) := (\gamma \cdot r_X/2, 0, 0)$$

for a $\gamma \in [0, 1]$. The positions of the two electrons are modelled stochastically by two independent random vectors Y_1 and Y_2 that are distributed uniformly over C .

The potential energy of this configuration is

$$(3.1) \quad U_\gamma = \Phi_X(\gamma \cdot r_X) + \frac{e^2}{4\pi\epsilon_0} \cdot \left(\frac{1}{d(Y_1, Y_2)} - \sum_{i,j=1}^2 \frac{1}{d(X_i(\gamma), Y_j)} \right)$$

where e, ϵ_0, d denote the charge of an electron, the permittivity of vacuum and the Euclidean distance, respectively. U_γ can be viewed as a superposition of Lennard-Jones and Coulomb potentials. The value $\bar{\gamma}$ of parameter γ for which the expectation $\mathbb{E}(U_\gamma)$ is minimal corresponds to a particular configuration of two ions and two electrons within C ; this configuration is called Cooper configuration. The expected depth of the potential of the Cooper configuration is given by

$$U(X) := \mathbb{E}(U_{\bar{\gamma}}) = \min_{\gamma \in [0,1]} \mathbb{E}(U_\gamma).$$

The value $U(X)$ for a particular substance X whose boiling point is known can be estimated by the Monte Carlo method.

Note that based on the boiling point $T_B(X)$ and relative molecular mass $m_r(X)$ we are able to fit the Lennard-Jones potential Φ_X and, moreover, to estimate the depth $U(X)$ for substance X . Typically we have

$$U(X) < 0$$

which means that the Cooper configuration is energetically favorable.

4 The Statistical Evaluation

For 20 super-conducting chemical elements X the data $T_B(X)$ and $m_r(X)$ are utilized for the computer based determination of the depth $|U(X)|$ of the potential associated with the Cooper configuration (cf. Section 3). In the

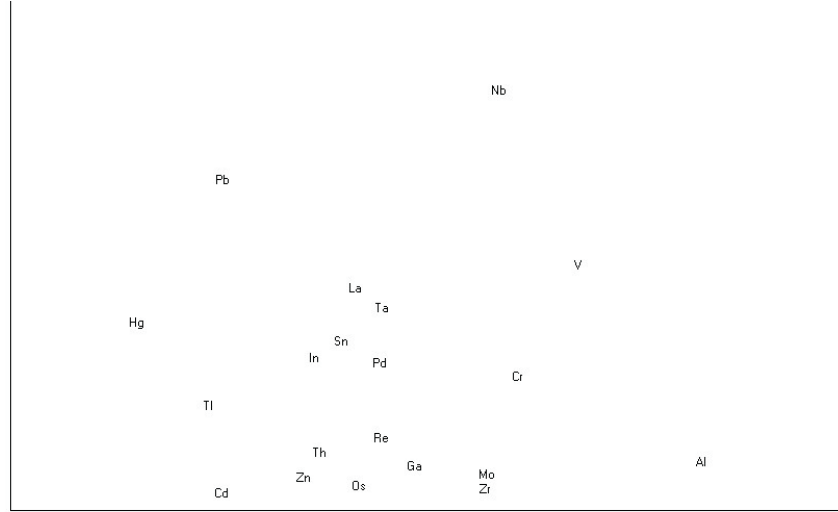


Figure 1: Potential depth versus transition temperature

diagram in Figure 1 the horizontal axis corresponds to the value $|U(X)|$ and the vertical axis to the transition temperature $T_{sup}(X)$. After removal of the outliers Al, Hg, Mo, Pb, Zr, the empirical correlation coefficient between $|U(X)|$ and $T_{sup}(X)$ attains the value 0.56785 which indicates a moderate correlation between the considered quantities. The linear ansatz

$$(4.1) \quad k_B T_{sup}(X) = \gamma_0 + \gamma_1 \cdot |U(X)|$$

yields the least-squares estimates

$$\hat{\gamma}_0 = -2.065 \cdot 10^{-23} \text{J} \quad \text{and} \quad \hat{\gamma}_1 = 3.321 \cdot 10^{-6}.$$

The deeper the potential minimum the higher the temperature at which the likelihood for the formation of Cooper pairs is sufficient for superconductivity; in this sense ansatz (4.1) is microscopically justified and physically plausible. Since $U(X)$ can be computed for substances X whose boiling point is known, the reported statistical results can be viewed as a bridge between Fluid and Solid State Theories.

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